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1999

| | |
|---|---|
| 28.01. - 29.01. | Internal meeting in Munich, for organisation and planning of the work in 1999. Participants: Members of the project from the MPA Bremen, the University of Oldenburg and the Bayerisches Landesamt für Denkmalpflege |
| 22. - 28. 03. | International Symposium in the Shaanxi History Museum, Xi'an: "The Polychromy of the Terracotta Army of the First Chinese Emperor Qin Shihuang - Studies on the Polychromy of Antique Sculptures; Materials, Painting Techniques and Conservation" (Organised by the Museum of the Terracotta Army, Bayerisches Landesamt für Denkmalpflege München and ICOMOS Germany) |
| 03. 05. - 13. 06. | Work Stay of Mr. Rogner, Mr. Utz, Mrs. Blaensdorf in Lintong; Work Visit of Mr. Guelker, Mr. Juling and Mr. Micoulitsch |
| 12. 09. - 24. 09. | Visit of the Chinese Delegation in Germany |
| 20. 09. | 7th Steering Committee Meeting in Munich |
| 09. 10.- 09. 12. | Work Stay of Mr. Guo Baofa, Mr. Lan Desheng and Mr. Xia Yin in Munich |
| 19. - 21. 10. | Travel to Oldenburg and Bremen |

2000

| | |
|---|---|
| 04. -15. 03. | Travel of Prof. Emmerling and Mrs. Blaensdorf to Lintong / Xi'an, Excursion to Henan |
| 26. 06.- 20. 08. | Work Stay of Mr. Zhang Zhijun, Mr. Rong Bo and Mr. Ma Yu in Munich |
| 20. 07. | Travel to Nürnberg (GNM) |
| 24. - 27. 07. | Travel to the Rhineland (Cologne, Aachen, Mainz) |
| 08. - 29. 09. 2000 | Exhibition in the Bavarian State Conservation Office: "Japan und China - Reparatur und Konservierung" |
| 18. 10.- 20. 11. | Work Stay of Mr. Rogner, Mr. Utz, Mr. Scheder, Mrs. Blaensdorf and Mr. Warscheid in Lintong |
| 19. 10. - 31. 12. | Exhibition for the opening of the Centre for Chinese-German Co-operation in Science and Research in Beijing: "Begegnungen - Chinesisch-Deutsche Zusammenarbeit in der Wissenschaft" (Organised by NSFC and DFG) |

## Conservation Treatments on Polychrome Fragments of the Terracotta Army Working Visit in Lintong, May 3 to June 5, 1999

Zhang Zhijun, Zhou Tie, Rong Bo, Ingo Rogner, Catharina Blaensdorf

In 1999 the tests for the conservation of the polychromy of the terracotta figures focussed on the method using the HEMA formulation Plex 6803-1, polymerised by electron beam (EB) irradiation. The method was developed since 1997. In December 1998 it was tested on original fragments for the first time. The treatment showed good results.

Eight fragments were selected for the tests. They were excavated in pit no. 2, T8G11, test area 9, for the purpose of these conservation tests, directly before the test series started. The fragments treated in 1998 fragments had been excavated at the same area. Partly the fragments treated in 1998 and those treated in 1999 can be attached to each other.

The aim of the tests was if and how this facility could be used for the conservation treatment of polychrome fragments. Furthermore, the fragments treated with Plex / EB in 1998 were observed again. On the base of this evaluation the parameters were set for the new test series.

The electron beam facility used for the polymerisation belongs to the Xi'an Radiation Research Center which is located in a village in the vicinity of Lintong (between Lintong and Xi'an). The facility is slightly different from the one in the "Institut für Polymerforschung" at Dresden.[1]

For each fragment a detailed documentation (text, sketches, photographs) is laid out. The following text gives a summary of the problems, methods and result of the consolidation treatment.

### 1 Technological description

The fragments F-001 to F-008/99 come from a reddish brown robe or from a suit of armour. They are comparable to the fragments treated in 1998 (photographs of all fragments in the annex of this text).
F-001 and 002/99 are adjoining pieces of a reddish brown robe (see: fig. 1).
F-004/99 and F-008/99 can be attached to each other. On F-008/99 a small piece of a round border of an armour with one red ribbon is visible, so the pieces can be located to the lower part of the robe below the armour, called "skirt" by the Chinese experts (see: fig. 2).
F-003, 005 and 007/99 are adjoining pieces of a similar part of a figure. The pieces also can be attached to the fragments F-002 and 003/98, so that their position can be located: They come from the front of a soldier and all of them together form the part of the belly and the middle part of the "skirt". As one side of the armour is preserved on F-003/98 and the last plate of the middle row on F-007/99 the armour can be partially reconstructed as a suit of armour with only five vertical rows of plates. It has orange-red "buttons" and bright red "ribbons" as connection stitches of the plates (s. fig. 3 and 4).
F-006/99 is a part of a shoulder piece[2] with red buttons and red ribbons. It could not be attached to other fragments.
Additionally the fragment F-005/98, a part of a hand, consisting of the four bent fingers, was treated. The fragment was examined in 1998, but the polychromy was not consolidated.

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1 Description of the facility in the Xi'an Radiation Research Center, see: Rogner, *Electron beam Treatment in Lintong 1999*, in the Work Report 1999/2000.

2 Part of armour to protect the upper arm and the shoulder, called "epaulette" in the Work Report of 1998.

Fig. 1. F-001 and 002/99

Fig. 2. F-004 and 008/99

direction of brush strokes

Fig. 3. F-003, 005 and 007/99 joined,
together with F-002 and 003/98

Fig. 4. Reconstruction of the armour and robe of a warrior from fragments treated in 1998 and 1999: 002 and 003/98, 003, 005 and 007/99 (see: preceding page)
The figure comes from pit no. 2, T8G11, test area 9. G11 belongs to the rows with war chariots and infantrymen.
The standing warrior wears a suit of armour with bright red straps ("ribbons") and orange button-like stitches. The robe is red with a brownish tint.

In 1999 no technological examination was carried out on the treated fragments. The light grey terracotta is comparable to the fragments examined in 1998. On all fragments, the lacquer is applied in a double layer.
The paint layer of the robe is applied in a single, thick layer. The brush strokes are still clearly visible. They run very straight for more than 20 cm. The size of the paint brushes could not be reconstructed, or a beginning of a stroke could not be found.
On F-008/99 the colour of the robe looked brighter and more red than on other fragments. Maybe the original colour was red rather than reddish brown, i. e. the brownish tinge could be caused by the soil. However it is obvious that the robe is always darker and more brownish than the bright red ribbons.
On F-005/98 ("hand") the lacquer layers clearly differ in colour and structure: The first layer on the terracotta is brownish and porous with recognisable holes, the second layer is almost black and more tight (no holes visible). The pigments are applied in two layers. The first layer is pink, the second almost white. Both layers appear opaque and showed brush strokes (fig. 5).

Fig. 5 F-005/98, four bent fingers of a hand, detail of the ring finger. The missing parts of the pigment layers and the upper lacquer layer reveal the structure of the polychromy.

## 2 State of preservation

The fragments F-001 to 008/99 had been taken from the excavation site on April 28, 1999 and had been packed in plastic bags. On May 6, 1999, they were transferred into the laboratory and stored in a climate chamber with installed hygrometer above a dish with water (RH according to hair hygrometer: c. 95 %). On May 7 they were taken out of the plastic bags for the photographic documentation. The problem of condensation in the plastic bags was already visible. A repeated taking out of the plastic bags endangered the polychromy, so the fragments were stored in the climate chamber without plastic bags.

On May 10, a glove box was set up for the cleaning of the fragments. The humidity was regulated with two big glass dishes full of water. A hygrometer put inside showed 97 % rh.[3] During work the temperature inside the glove box was c. 30 °C, due to the outside temperature of about 24 °C (mornings and evenings) to 31 °C (around noon)[4] and the warmth produced by the light of the lamps and the hands of the person working on the fragments.
On May 24 the weight control showed that the fragments lost weight (i.e. humidity) inside the climate chamber although the hygrometer still showed 97 % rh. Fragment F-005/99 lost 1 %

[3] Measurement with hair hygrometer; principally hair hygrometers should not be used, because they are not calibrated for a humidity higher than 80 %rh, but other types of hygrometers are not available in Lintong.
[4] see: climate measurements, table 3 in the annex of this text

of weight during one week. On several fragments the lacquer started to detach and deformed in some areas (e. g. F-005/99, especially F-006/99).

Mostly the polychromy was preserved very well, especially the fragments 001, 002, 003 and 005/99. The lacquer layer was coherent without cracks. There were only few damages in form of bigger losses of the polychromy or scratches in the terracotta (F-003/99: scratches maybe from excavation tools).
The fragments F-004 and 006/99 showed bigger losses and problems of detaching lacquer layers. The lacquer layers are very thin and proved to be extremely sensitive against changes of humidity and mechanical stress. On fragment F-007/99, the damaged lacquer layer was partly missing (about 50 %) in the area of the armour plate (no pigment layer on the lacquer layer), while the areas with pigment layer (robe and ribbon) are in a much better condition. The pigment layer obviously serves as protection for the lacquer.
The fragment of the hand, 005/98, was very well preserved. The lacquer layers were still in a perfect state, the pigment layers show only some bigger losses. The brush strokes were still visible very clearly, the original surface was still existing.

The reaction of the lacquer against drying out could be examined on a small sample taken from F-005/98: First, the lacquer layers separated from each other, the bottom layer rolled up in a convex shape while the top layer remained flat and stable and still adhered to the pigment layer. After a total dry out also the top layer separated from the pigment layer, but stayed flat.

## 3 Conservation treatment

### 3.1 Removal of the soil (“cleaning”)

The removal of the soil was performed before the consolidation treatment (F-001, 003, 005, 006, 007 and 008/99 as well as 005/98) or as a intermediate step between the steps of soaking (F-002 and 004/99).
If the removal of the soil is conducted before the soaking with consolidants, it has to be done inside the glove box. The soil can be softened and the lacquer is “stabilised” temporarily by adding water during the cleaning process. The result of the cleaning can be improved in that way, but if too much water is used, the pigment layer becomes muddy and looses its structure (as has happened on F-005/99).
F-002/99 and 004/99 were cleaned during the soaking with consolidants. The advantage is that the fragment can be cleaned outside of the climate chamber, what is much more comfortable. F-004/99 was treated with two steps of PEG 200 and cleaned afterwards. F-002/99 was cleaned after the second step of soaking with Plex. A thin layer of the pigment layer remained on the soil, but the pigment layer did not look damaged.

On all fragments the pigment layer was damaged slightly by the cleaning. The use of scalpel blades leads to cuts and holes, especially if the lacquer layer is very thin. On F-006/99 the cleaning was difficult and led to losses because the lacquer layer was very thin and was already detaching and deforming.

### 3.2 Mould growth and disinfection

During storage at a humidity of 97 % rh, the growth of mould on the fragments becomes visible after c. one week. In 1999 mould occurred on the fragments F-001, 003, 006, 007 and 008/99 after six or seven days. The mould covered the surface totally, but did not increase much between the $7^{th}$ and the $12^{th}$ day after cleaning (F-008/99). No mould was observed on F-005/99 which was treated for the consolidation of the polychromy after 4 days.

The fragment F-005/98 had been stored in a climate chamber or the refrigerator since December 1998. Problems with mould had not occurred. On some fragments the mould does not grow while it is growing extremely on others. It is not possible to predict that.

In the previous years, tests were made to disinfect the fragments during the duration of the storage, using biocides (until 1996) or 70% ethanol (1998). In 1999 no disinfection was performed to investigate the effect of Plex on the mould (and vice versa). The electron beam irradiation destroys the mould, so that an infestation after the consolidation treatment could be excluded.

## 3.3 Consolidation treatment

The basis for the consolidation method was the treatment used on the fragments treated in December 1998 in Germany. It comprised a three-step soaking with rising concentration up to 100% and a duration of one day for each step. For the irradiation different parameter had been treated and the ones with the best results were used as points of reference.
In 1999 variations of the methods were tested, concerning the following parameters:
- application method
- duration of soaking steps
- concentration of Plex in the third step
- combination of the method with the soaking with PEG 200
- dose and times of irradiation.

As consolidant the same material (Plex 6803-1) was used as in 1998. The material for the tests was imported to China in two bottles. Some cans with 50 kg Plex were sent to Xi'an by the company Röhm during the time of the work stay.

### *3.3.1 Application method - compresses, spraying and dripping*

Like in the year before, cotton wool compresses were used for the application of the consolidant (Plex 6803-1). Strips of thin Japanese paper served as separation layer. They were cut according to the shape of the surface of the fragment, because Japanese paper is not elastic or smooth. Larger pieces tend to form wrinkles and do not spread well on uneven surfaces. Nevertheless very thin Japanese paper gave satisfying results. Sometimes it is difficult to remove because it tears apart very easily when it is wet.
The Japanese paper was moistened with Plex-solution before applying it to the surface, so it stuck on the polychromy. The cotton wool was applied dry; afterwards the Plex-solution was dripped on top with a pipette.

On the fragment F-005/98, the thick pigment layers proved to be very sensitive against contact with liquids. They became very soft when they were wet. Touching, immersing and application of compresses were impossible, because the pigment layers lost their structure and were flowing down on the sides of the fragment. Also spraying caused a softening of the pigment layer, the wet particles tended to "float" away.
A regular and continuous moistening of the surface (Plex 33 % and 66 %) was performed by dripping the consolidant solution onto a net which distributed the drops. When the fragment was placed on one of the sides, the pigment layers got lost in the zones of contact to the support. The third step of treatment (100 %) was done by spraying.

### *3.3.2 Duration and concentrations - shrinkage cracks*

The concentration of the Plex was raised in three steps. For the first and second step the concentrations of 33 and 66 % were used.
Problems of detaching and the formation of blisters were observed on some of the fragments (especially F-001 and 007/99) during the first and second step of treatment. On fragment

007/99 blisters formed in the red of the robe during the first step of the treatment. The bigger ones were pierced with a needle after the second step and then flattened down.

The application of 100 % Plex in the third step, immediately led to the formation of shrinkage cracks. This could be tested by the application of only one drop onto the polychromy: within seconds cracks formed, the border of the lacquer flakes detached and deformed.
To avoid the formation of cracks, the concentration for the third step was reduced from 100% to 90 %, later on to 80 %. With a concentration of 90 % the formation of cracks could be slightly reduced, but not suppressed (F-005/99). Even the use of 80 % could not prevent the cracking (F-003 and 006/99), but a visible reduction of the dehydration shrinkage of the lacquer could be achieved.[5]
During the soaking process, the deformation and development of cracks could be temporarily stopped by adding 50 % Plex (F-002/99) again: The lacquer layer flattened and the cracks closed, but as soon as a high concentration was applied again, the damage came back and got worse. After irradiation all the cracks were opened widely and the borders of the lacquer flakes had detached and deformed.
The formation of cracks could not be avoided by prolonging the duration of the second step (60 %; tested on F-004 and 008/99).

Besides the three-step treatment a two-step-treatment was tested (002/99). No problems occurred when starting with 50 %; the second step with 100% produced the same problems of cracks forming as on the other fragments treated with 100 % Plex.

### *3.3.3 PEG 200 combined with Plex 6803-1*

On two fragments the polychromy was treated with PEG 200 in relatively low concentrations in one or two steps before the consolidation with Plex was conducted (F-004 and 005/99). This kind of combined treatment should show if it is possible,
a) to treat fragments with Plex which already have been consolidated with PEG during previous conservation campaigns;
b) to treat larger fragments or whole figures, that cannot be taken out of the pit immediately. They could be treated with PEG 200 as an intermediate measurement for the duration of the excavation and later on with Plex / EB irradiation for a long-term stabilisation.
For the tests PEG 200 was used without an adhesive (which it is necessarily added to the PEG to achieve a fixation of the lacquer to the terracotta). As PEG is also an additive to HEMA in the product “Plex”, no major problems were expected for this combined method.

For F-004/99 the consolidation comprised a pre-treatment with 2 steps of PEG 200 (30/60 %) and a three-step-treatment with Plex 6803-1 (33/60/100). The visual impression after the treatment was similar to the adjoining fragment 008/99, which had been treated with a three-step treatment with Plex (same method as in 1998, 33/60/100). Both fragments show a system of fine cracks (no big cracks), which are more distinct and prominent on F-008/99.
Fragment 005/99 was treated with 30 % PEG 200 as first step of the treatment, followed by 50 and 90 % Plex. The visual appearance after treatment is not satisfying, but mainly because of the larger number and size of the cracks caused by 90 % Plex (problem of shrinkage cracks: see above).

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[5] F-003 and 005/99, fragments from the reddish-brown robe with a comparable state of preservation, show that there are much more and bigger cracks on the fragment treated with 90 % (F-005/99) than on the one treated with 80 % in the third step (F-003/99). The fragment 006/99 cannot be compared to them because it is a piece of armour without pigment layer and it was overheated and damaged during the electron beam irradiation.

### *3.3.4 EB irradiation*

The electron beam treatment was conducted on May 28 (F-001, 004, 007, 008/99) and June 4 (F-002, 003, 005/99 and F-005/98). Variations of the irradiation parameters concerned
- times of irradiation (F-001, 003, 004, 006, 008/99: 1x, F-002, 005, 007/99: 2x, F-005/98: 4x)
- dose of the electron beam(kGy: 45, 50, 60; mA: 2.0 or 4.2).

Fragment F-005/98 had to be irradiated four times to reach all parts of the polychromy, because this fragment of a hand is painted on four sides (back and palm as well as the sides of the fingers). Several times of irradiation and changes of the dose did not produce visible problems or changes of the conservation result.

The transport mechanism of the facility has a cooling air jet with the strong stream of air. The stream of air also reaches the fragments in the transport box and causes a drying out of the surface in the last minutes before the irradiation. This leads to an increase of cracks and detached areas. If Plex is dripped or sprayed on the surface directly before the irradiation to prevent the drying-out, the risk of the formation of shiny spots and borders rises.
To exclude the stream of air, the transport box was covered with “Hostaphan” (PETP) foil for the irradiation of F-006/99, a fragment with very sensitive lacquer layers. They already had detached before and during the storage, cleaning and soaking with Plex. The stream of air would have caused a major damage to the lacquer. During irradiation the fragment heated up too much and the lacquer layer showed damages from overheating. The condensation of drops on the underside of the foil was observed.

Directly after the irradiation the Plex film is still soft and flexible. It becomes harder during the following days (evaporation of water). Observations on F-002/99 showed that the mechanical stability of the treated paint layer was much better one weak after than directly after the treatment.

## 3.4 Results

### *3.4.1 Cleaning and storage*

The removal of soil can be done before or in-between the soaking steps. The pigment layer adheres well to the soil, the lacquer layer is soft, flexible and very sensitive when moist. The polychromy was damaged on all fragments by the cleaning procedure. The damage can be reduced by a very careful and slow pace of work.
Cleaning the fragments after the first step(s) of consolidation treatment is has the advantage that the work does not have to be carried out inside the glove box. The disadvantage is that the soil and the polychromy become very soft by the soaking; the pigment layer tends to get muddy.

During the storage of the cleaned fragments in the climate chamber at 97 % rh a loss of weight was observed. It could be caused by the evaporation of the water added during cleaning. Sensitive lacquer layers start to detach and curl in during the storage after cleaning. Obviously, the soil on the surface works as a compress (weight and water content) and prevents the rolling up.

The mould problems are restricted to the time of storage at a very high humidity. At ca. 97% rh, after six or seven days the growth of fungi becomes visible. If a consolidation treatment (PEG or Plex) is conducted during the following days, a disinfection is not necessary. After the consolidation treatment no mould problems occurred again.
On some fragments no mould growth occurred also after a long time of storage. The reasons for this are not known.

### *3.4.2 Application method*

The application with compresses and the use of strips of Japanese paper as separation layer between pigment layer and cotton wool is practicable and gives satisfying results on fragments with a single pigment layer.
Problems occurred with the thick and double-layered pigment layer of F-005/98 (incarnation). The sprinkling system with a net was the best of the possibilities which were available at that time, but did not give satisfying results. For the application of the low-viscose Plex on these types of pigment layers another method has to be developed.

### *3.4.2 Duration of steps*

A duration of one day for each step seems sufficient for a consolidation of the lacquer layer. A longer duration of the second step maybe could reduce the formation of cracks during the third step (F-004/99 compared to 008/99).

### *3.4.3 Concentrations - cracks by dehydration*

The fragments 001, 007, 008/99 and 005/98 were treated with the same concentrations and duration of steps as the fragments treated in 1998 (33/66/100; one day each step). All fragments except F-005/98[6] showed extreme problems of dehydration during the third step of treatment, resulting in the shrinkage, cracking, detaching and deformation of the lacquer. The phenomena are similar to the begin of drying of the lacquer without consolidation. Obviously the Plex extracts water from the lacquer layer, i. e. the exchange of water against Plex is not taking place with the same speed.

The use of lower concentrations of Plex (90 and 80 %) in the third step can reduce the dehydration damages. This becomes visible, when the adjoining fragments 003/99 (80 % in the third step), 005/99 (90 %) and 007/99 (100 %) are compared: While the size and amount of cracks and the degree of deformation are similar on 005/99 and 007/99, the fragment 003/99 shows less and smaller cracks. Still, the formation of cracks by dehydration during the consolidation treatment remains a problem. As the concentrations used in the second step did not cause cracks, the critical concentration seems to be between 66 and 80 %.

The amount and size of the cracks does not only depend on the concentration of Plex, but also of the state of preservation of the lacquer layer. When the polychromy was continuous and showed only a few missing parts, the tension caused by the shrinkage resulted in big cracks and relatively big flakes in-between. When the polychromy already had a considerable amount of losses or did not form a continuous film in larger areas anymore, small cracks have formed. For example, the fragment 008/99 shows a less big cracks as F-001/99 that was treated with the same method and parameters. On F-008/99 the polychromy had a lot of missing parts and damages already before the consolidation treatment, while F-001/99 had an almost undamaged polychromy before the treatment.

The fragment 002/99 was the first one to be treated and the first one on which the formation of cracks was observed. Although different attempts were made to avoid the formation of cracks during the later treatments, F-002/99 shows the best result compared to the other fragments of robes and armours treated in 1999.
This could mean that the method used actually is good for already quite damaged or on exceptionally stable lacquer layers.

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[6] F-005/98 might be different because of very thick pigment layer (incarnation) and long excavation and storage period before treatment (?).

### *3.4.4 Stability of the consolidated pigment layer*

The polychromy of all treated fragment was stable against changes of humidity after the irradiation. Deformations and edges that are curled in or upwards reduce the stability of the polychromy, because they are brittle and tend to brake off.
The pigment layer stays sensitive against touching and is only slightly more stable as if PEG had been used.
On fragment 002/99 small cracks accompany the big cracks formed during soaking with Plex. The borders are rolled in and tend to brake off, because there is no Plex underneath. The shrinkage of Plex during irradiation and the evaporation of the water directly afterwards could be the reason for this phenomenon.

### *3.4.5 Shiny spots*

The amount of Plex on the surface directly before the irradiation is responsible for the formation of shiny borders and spots. The fragments can be dabbed off directly before treatment, but some Plex has to remain on the surface to prevent a drying-out by the cooling air stream during irradiation (the surface should look glossy-wet).

Shiny spots tend to form in depressions of the surface, caused either by the shape and design of the terracotta surface or by missing parts (holes) and remnants of soil (elevations) on top of the polychromy. Flat fragments show less problems with shiny spots than fragments with convex shape; fragments of the robe without structuring of the surface show less shiny borders than fragments of the armour. The fragments 001, 002, 003, 004 and 008/99 (flat fragments of the robe) do not show any shiny spots or borders.
Fragments 005/99 shows a shiny film inside the wide open cracks. F-007/99 has shiny spots, although the surface is flat. F-006/99 shows shiny spots along the borders of the armour plats and buttons and the margins of the lacquer flakes. On F-005/98 shiny spots and borders also formed along differences of the surface level caused by the thick pigment layers.

The fragments can be dabbed off directly after irradiation; this maybe reduces the amount of shiny spots slightly, because the Plex is still very soft directly after irradiation.

### *3.4.6 PEG 200 combined with Plex*

The tests performed on the fragments 004/99 (2 steps with PEG 200, 30/60 %, 3-steps with Plex) and 005 /99 (30 % PEG 200 instead of 33 % Plex 6803-1 in the first) showed that a combination of these two consolidants is possible and does not have a negative effect on the consolidation result. A definite positive effect or advantage of using PEG 200 before the soaking with Plex could not be observed either.
It would be interesting to know if a pre-treatment with PEG reduces the formation of micro-cracks during ageing.

## 3.5 Observations on the fragments in 2000 and 2001

A first evaluation was done directly after treatment. Afterwards the fragments were observed again during the work stays in Lintong in March 2000, October 2000 and March 2001.

Fragment 001/99 is in Germany since December 1999 for measurements with Cryo-SEM and videohology in Bremen or Oldenburg. In July 2000 additionally the fragments 003/99, 006/99 and 005/98 have been brought to Germany. The fragments were checked in Oldenburg in August 2001.

### *3.5.1 Plex coming out of the fragments and polymerising on the surface*

In March 2000 the fragments still had a strong smell of Plex 6803-1. Damages of „flowing out“ of consolidation material as observed on the fragments treated in 1998 could not be observed in March 2000, but have been detected in October 2000 (F-002, 004; 005, 007, 008/99). The shiny Plex does not come out on the painted front side as on F-009/98 and 011/98, but on the sides and the back of the fragments, obviously following the gravity. Partly the material is very soft and sticky (i.e. 004/99). In this state it can be removed with acetone. If hardened, it can not be removed with solvents, but only mechanically. Partly the terracotta looked “clean” after the removal of soil with Plex. Where the material had come out of the terracotta directly (i.e. without soil in between), the material could only be reduced superficially; the darkened spots on the terracotta remain.
Samples of the material were taken from the back of F-008/99 for analysis of the composition.

The damage did not increase until March 2001, but became more between March and October 2001. It seems that the formation of these shiny, sticky spots is favoured by the climate conditions of the summertime (high temperatures, high humidity).

It is remarkable, that the damage did not occur on the fragments stored in Oldenburg or Bremen (001/99, 003/99, 006/99, 005/98: no shiny spots). The climate is much more stable there, comparable to museum conditions. There seems to be a relation between the hot and humid summers in Lintong and the formation of the shiny Plex spots on the surfaces of the fragments.

### *3.5.2 Loss of weight*

Since the day after the irradiation in June 1999 until March 2001 the fragments have lost between 6.5 and 8 % of weight, three of them (003, 005 and 008/99) even 10 to 12.9 %. A dependence on the treatment method cannot be detected. The decrease of weight is taking place most rapidly during the first time after irradiation. It continues during the following years, but only in a very small range. During the year 2001, there was no weight loss or only a minimal one.

### *3.5.3 Development of cracks*

In March 2001, at a RH of c. 30 % inside the room, the system of micro-cracks appeared more distinct and prominent than in October 2000 (RH c. 63 %). In October 2001 there were less visible again (RH c. 65 %). Because the cracks clearly open up and close in dependence of the humidity, it is not possible to decide by microscopic investigation if the cracks get more or wider.
The opening up and closing of the cracks depending on the humidity was observed and recorded with videoholography. The extent of the movements was much bigger than on the fragments treated in 1998 and the fragments treated with PEG; on F-001/99 it was too extreme to be monitored in the microscopic range of the experimental set-up.
On several fragments the two lacquer layers develop a crack system independent from each other. The crack system of the lower layer appears much finer than the one of the top lacquer layer (visible for example on F-007/99).
The crack system was clearly visible in August 2001. Maybe the extent and number of micro-cracks has slightly increased.

## Table 1: List of fragments treated in 1999- identification

| fragment no. | approx. max. size (cm) | location of excavation | | | date of excavation | description |
|---|---|---|---|---|---|---|
| | | pit | T G* | TA** | | |
| F-001/99 | 12 x 7.5 | 2 | T8G11 | 9 | April 28, 1999 | Part of a reddish brown robe. Adjoining to F-002/99 |
| F-002/99 | 23.5 x 9.5 | 2 | T8G11 | 9 | April 28, 1999 | Part of a reddish brown robe. Adjoining to F-001/99 |
| F-003/99 | 17 x 12 | 2 | T8G11 | 9 | April 28, 1999 | Part of the reddish brown robe with a small area of an armour (red ribbons and red buttons). Adjoining to the fragments F-002 and F-003/98, F-005 and007/99 |
| F-004/99 | 12.5 x 13 | 2 | T8G11 | 9 | April 28, 1999 | Part of a reddish brown robe. Adjoining to F-008/99 |
| F-005/99 | 21.5 x 12 | 2 | T8G11 | 9 | April 28, 1999 | Part of a reddish brown robe. Adjoining to to the fragments F-002 and F-003/98, F-003 and007/99 |
| F-006/99 | 14.5 x 7.5 | 2 | T8G11 | 9 | April 28, 1999 | Part of an epaulette with a red ribbon and red buttons with small area of the shoulder part. Adjoining to F-001/98, F-004/98 and F-007/98 |
| F-007/99 | 19 x 11.5 | 2 | T8G11 | 9 | April 28, 1999 | Part of a reddish brown robe with a small part of the bent border of the armour with a red ribbon and (red) buttons. Adjoining to F-002 and 003/98, F-003 and 005/99 |
| F-008/99 | 17.5 x 8.5 | 2 | T8G11 | 9 | April 28, 1999 | Part of a reddish brown robe with a small part of the bent border of the armour with one red ribbon. Adjoining to F-004/99 |
| F-005/98 | 7.5 x 7.5 | 2 | T8G11 | 9 | July 30, 1998 | Part of a hand, consisting the four bent fingers |

* T sector of excavation (areas of 20 x 20 m)
G corridor (pit no. 2: counted from south to north, 1 to 14)

** TA test area. In pit no. 2, there are 18 areas from preliminary excavations carried out in 1994

## Table 2: Fragments treated in Lintong in May 1999- methods of treatment

| frag-ment no. | cleaning | soaking | | | EB treatment | | | | remarks/*evaluation* |
|---|---|---|---|---|---|---|---|---|---|
| | | steps | conc. w% | dura-tion in days | times | kG | MeV | mA | |
| 001/99 | before soaking (climate chamber) | 1 Plex<br>2 Plex<br>3 Plex | 33<br>66<br>100 | 1<br>1<br>1 | 1 | 60 | 1 | 2.0 | method and parameters as in 1998; *lacquer layer stable, no shiny spots; many cracks from shrinkage during the third step of soaking* |
| 002/99 | after the second step of treatment | 1 Plex<br>2 Plex | 50<br>100 | 1<br>5 + 2 | 2 | 45 | 1 | 4.2 | *lacquer layer mainly stable; pigment layer rather stable against wiping; not shiny many big cracks* |
| 003/99 | before treatment (climate chamber) | 1 Plex<br>2 Plex<br>3 Plex | 33<br>66<br>80 | 1<br>1<br>1 | 1 | 60 | 1 | 2.0 | *similar to 005 and 007/99 (adjoining fragments); compared to them less deformations lower Plex concentration in the third step (80 instead of 100 %) reduces the amount of shrinkage cracks* |
| 004/99 | after first step of treatment with Plex (4th step of treatment) | 1 PEG 200<br>2 PEG 200<br>3 Plex<br>4 Plex<br>5 Plex | 30<br>60<br>50<br>66<br>100 | 1<br>5<br>6<br>2<br>2 | 1 | 60 | 1 | 2.0 | PEG 200 + Plex long duration of steps; *relatively good; similar to F-008/99; PEG 200 as first treatment does not have negative effects on Plex treatment 90 % Plex as third step reduced cracks, but still a lot of small cracks* |
| 005/99 | before treatment | 1 PEG 200<br>2 Plex<br>3 Plex | 30<br>66<br>90 | 1<br>1<br>1 | 2 | 60 | 1 | 2.0 | *not so good; many big cracks, shiny inside the cracks and along the borders of the paint layer; no advantage of 30 % PEG 200 instead of 33 % Plex ; formation of cracks reduced by using 90 % instead of 100 % Plex* |
| 006/99 | before treatment (climate chamber) | 1 Plex<br>2 Plex<br>3 Plex | 33<br>66<br>80 | 1<br>1<br>1 | 1 | 60 | 1 | 2.0 | same method and parameters as 003/99 *not satisfying; overheated during irradiation because box was covered with Hostaphan: many cracks, borders of flakes deformed (bent upwards), many shiny borders and spots* |
| 007/99 | before treatment (climate chamber) | 1 Plex<br>2 Plex<br>3 Plex | 33<br>66<br>100 | 1<br>1<br>1 | 2 | 50 | 1 | 4.2 | comparison of irradiation parameters with 001/99 *100 %Plex as third step was too high: big cracks by dehydration borders of flake bent up; shiny spots* |
| 008/99 | before soaking (climate chamber) | 1 Plex<br>2 Plex<br>3 Plex | 33<br>66<br>100 | 1<br>1<br>1 | 1 | 60 | 1 | 2.0 | same method and parameters as 003/99 *mainly small cracks caused by dehydration; not shiny similar to F-004/99* |
| 005/98 | before soaking (climate chamber) | 1 Plex<br>2 Plex<br>3 Plex | 33<br>66<br>100 | 1<br>1<br>1 | 4 | 60 | 1 | 2.0 | method and parameters as in 1998 and F-001/99, but 4 x of irradiation to reach all sides; thick pigment layers; *loss of the surface structure by soaking almost no cracks shiny spots* |

## Table 3: Climatic conditions in the laboratory of the Museum of the Terracotta Warriors and Horses

**1999***

| *date* | *time* | *temp [°C]* | *rh [%]* | *remarks* |
|---|---|---|---|---|
| May 07 | 16:00 | 23 | 52 | |
| May 13 | 11:00 | 29.1 | 47.7 | sunshine, sultry |
| | 13:00 | 31.0 | 45.7 | |
| May 14 | 10:15 | 26.0 | 62.6 | raining since the night |
| May 17 | 12:00 | 24.9 | 63.8 | still raining, windows closed |
| May 20 | 12:00 | 24.1 | 53.5 | cloudy, one window open |
| May 21 | 10:05 | 24 | 57.1 | |
| | 12:20 | 26.3 | 51.2 | |
| May 24 | | | | |
| May 25 | 09:30 | 24.7 | 57.7 | |
| May 25 | 18:30 | 24.5 | 50.9 | fine weather after rain |
| May 26 | 09:30 | 24.2 | 37.7 | ** |
| May 27 | 09:30 | 24.3 | 43.8 | ** |
| May 28 | 08:30 | 24.7 | 47.0 | |
| May 29 | 10:30 | 26.1 | 57.6 | |
| May 31 | 11:10 | 26 | 58.6 | |
| June 1 | 11:00 | 26 | 52.7 | |
| June 2 | 11:15 | 27 | 50.8 | |
| June 3 | 14:15 | 26 | 60.2 | rainy weather |
| June 4 | 14:45 | 26 | 60.3 | |
| June 5 | 08:30 | 25.7 | 64.4 | |
| June 5 | 09:25 | 25.2 | 62.0 | |

* Room without air condition, windows to the south, no direct sun light; measurement with electronic hygro-thermometer (“testo 600”)
** apparatus for distilled water inside the room working

## Fragments treated in 1999- before and after the consolidation of the polychromy

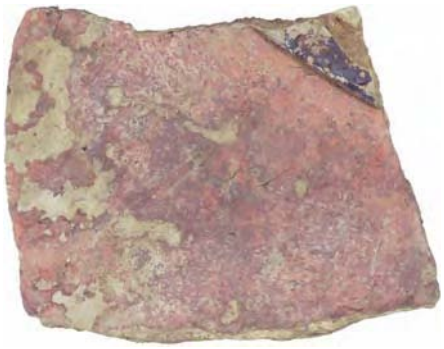
F-001/99 before conservation (May 7, 1999)

F-001/99 after consolidation treatment (May 29, 1999)

F-002/99 before conservation (May 7, 1999)

F-002/99 after consolidation treatment (May 21, 1999)

F-003/99 before conservation (May 7, 1999)



F-003/99 after consolidation treatment (June 5, 1999)

F-004/99 before conservation (May 7, 1999)

F-004/99 after consolidation treatment (May 29, 1999)

F-005/99 before conservation (May 7, 1999)

F-005/99 after consolidation treatment (June 6, 1999)

F-006/99 before conservation (May 7, 1999)

F-006/99 after consolidation treatment (June 6, 1999)

F-007/99 before conservation (May 7, 1999)

F-007/99 after consolidation treatment (May 29, 1999)

F-008/99 before conservation (May 7, 1999)

F-008/99 after consolidation treatment (May 29, 1999)

F-005/98 before conservation (November 13, 1998)

F-008/99 after consolidation treatment (May 29, 1999) - back and inside of the hand

# Electron Beam Treatment in Lintong 1999
# Consolidation of polychrome Fragments from the Terracotta Army of Qin Shihuang

(Report by Ingo Rogner)

Xi'an Radiation Research Center, Electron Accelerator Application Laboratory

Visit on 07.05.1999.
Experimental days on
14.05.1999, 9:30 – 12:00, 14:30 – 18:30
20.05.1999, 14:30 – 22:00
28.05.1999, 13:30 – 15:30
04.06.1999, 14:30 – 19:00

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## Abstract

The aim of the experiments carried out was to develop a standard method for consolidating qi-lacquer coated polychrome fragments from the Museum of the Terracotta Army at the Xi'an Radiation Research Center in Lintong, China.. In 1998 a consolidation method was developed with the electron beam accelerator ELV-2 in Dresden, Germany. This method included three step soaking with the consolidant Plex 6803-1 before the fragments were consolidated by electron beam curing (1 MeV, 4.2 mA, 3 x 20 kGy). The aim was to adapt the existing method for the electron accelerator ELV-8 in Lintong. Furthermore we wanted to facilitate the consolidation to reduce the number of steps involved in the treatment. The consolidation of non flat surfaces (where two or more irradiation steps are needed) was to be investigated.

## General information

The application of an electron beam (beta-radiation) for the polymerisation of methacrylate monomers produced encouragingly positive results. The polymerisation is initiated on the surface of the terracotta where the electrons are strongly decelerated. The polymerisation propagates from the terracotta towards the outside through the monomer impregnated qi-lacquer to the surrounding air. After the electron radiation is switched off there is no radioactivity left within the sample. During the treatment the deceleration of electrons produces a very intense X-ray radiation (bremsstrahlung) which must be thoroughly shielded.

A number of advantages distinguish this consolidation method:
The consolidant is miscible with water in any ratio and can thus penetrate into the qi-lacquer which has to be solidified. It is similar to water in viscosity, colour and density. The consolidant is a commercial monomer formulation and can be bought at a low price. Therefore there is no need to produce it oneself. Pre-treated fragments and the consolidant can be stored under normal

conditions without difficulties. Auto-polymerisation is prevented by a stabiliser, the polymerisation will not start until the fragment is irradiated with electrons. Bacteria, micro-organisms and also mould are destroyed by the electron beam. The polymerised consolidant provides an excellent light transmission ratio and it does not form a shiny film on the surface. It is non-toxic, environmentally tolerable and bonds to hydrophilic terracotta as well as it bonds to organic qi-lacquer. The long-term stability of the polymer is ensured by its original use as a sealing agent for the repair of leaking sewage pipes.

**Description of the Electron Beam Apparatus in Lintong**

The Xi'an Radiation Research Center, Lintong, Electron Accelerator Application Laboratory uses an ELV-8 Apparatus from the Budker Institute of Nuclear Physics SB RAS, 630090 Novo-sibirsk, Russia. The system is usually used to produce shrinking pipes to seal communication wire joints. Furthermore crude oil pipes are coated by plastic which is grafted onto the metal pipes. The machine was especially configured for the Xi'an Nuclear Research Institute (NINT). The electron beam is fanned out to a beam width of 1.60 m instead of the usual of 1.00 m.
The head engineer is Mr. Zhang. The engineer Xing Dong Jian is responsible for the Electron Beam Apparatus. He has five years experience in working with this apparatus. He was working with us during every experimental day.
*Working hours of the institute: Monday – Friday 8:00 to 12:00 and 14:30 to 18:30.*

In the beginning it was considered that the Museum of the Terracotta Army has to pay the amount of 500 Yuan (DM 117.-) for every switch on of the electron accelerator. However this method of payment was changed to a payment on an hourly basis (one working hour = 750 Yuan (DM 167.-)).

The following figures shows the distribution of the sectional density (figure 1) and the linear density (figure 2) of the beam current.
From the right graph [1] it can be seen that the outer 15 cm on each side of the scanner do not form an even beam intensity. Therefore these areas should be excluded for electron beam curing of monomers. This prerequisite is fulfilled, because the sample box is only 120.5 cm in length.

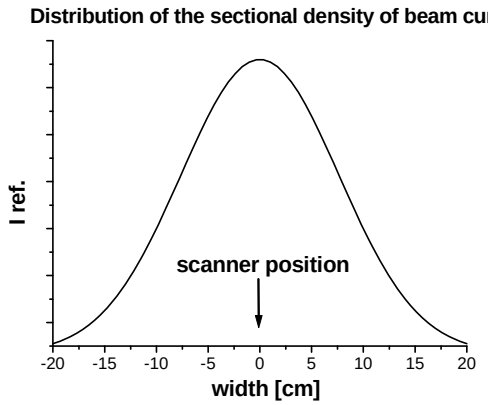


**Figure 1 sectional density of the beam current**

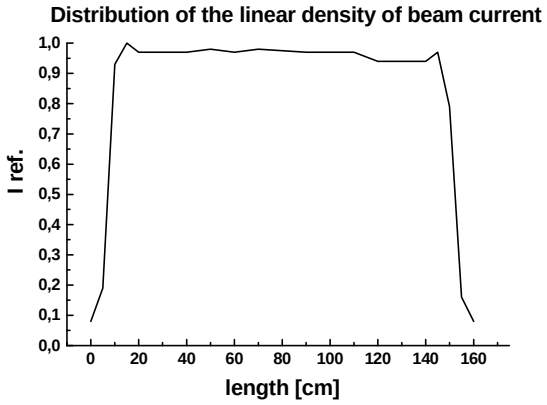


**Figure 2 linear density of the beam current**

The maximum wattage is 20 kW. The beam current can be varied between 2 - 40 mA, the voltage can be varied between 0.8 to 2.5 MeV (2500000 V).
The permissible deviation of voltage and current is 5 % for both values.

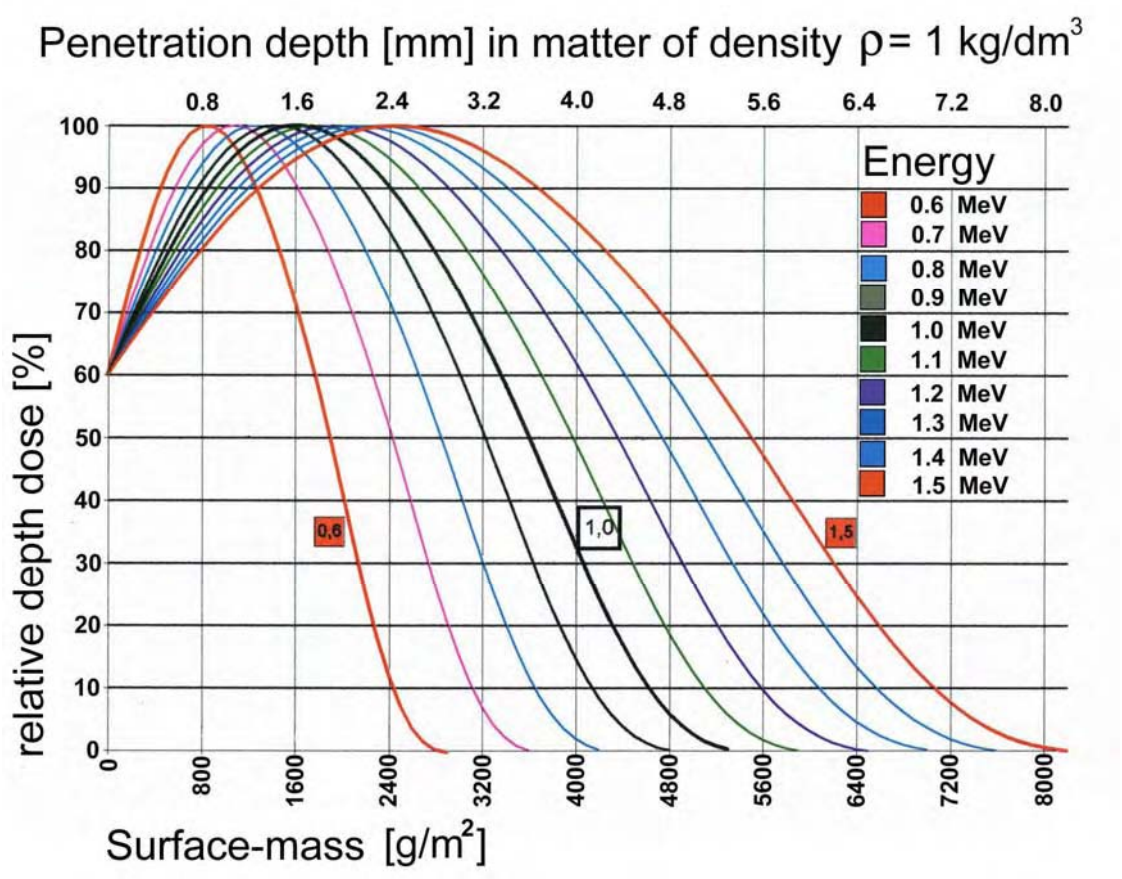


**Figure 3 penetration depth distribution at electron energies from 0.6 to 1.5 MeV**

Figure 3 depicts how deep electrons penetrate into matter of a certain density. For example:
At an electron energy of 1 MeV the maximum penetration depth of the electrons into matter of density $\rho = 1$ kg/dm$^3$ (e.g. water) will be 5.3 mm. However most of the electrons (100% relative depth dose) will only penetrate 1.6 mm into the matter. If matter of higher density like terracotta (~2.5 kg/dm$^3$) is to be investigated, the depth of penetration can be calculated by dividing the value for the penetration depth (1.6 mm) by the density. Thus for terracotta the maximum penetration depth is calculated to be 2.1 mm, most of the electrons will penetrate 0.6 mm into the terracotta.

When the electron accelerator ELV-8 is started, an initial period of about 1 min is necessary to increase the electron gun voltage. The transport mechanism is started and the beam current increases slowly until the required value is reached. After starting the apparatus given values cannot be adjusted online.

The line speed which can be entered into the computer is further called computer value CV and can have values between 0.01 to 4.00 m / min. For the computer controlled motor (202 V, 28 A, 22 Nm, 2000 rpm) is moving the transport system via a chain and a gearwheel with different diameter the line-speed can be found by the following equation (1):

$$\text{Line speed} = 0.9 * CV / 2.0 = 0.45 * CV \qquad (1)$$

The value of CV is measured online and can be displayed on the computer screen. There is a noticeable difference between the value entered (e.g. 0.56) for the line speed and the measured value (e.g. 0.52) which is always found to be lower. According to the protocol the instability which is permitted for the tape moving transport system is ± 5%. There are two transport systems

installed, a tape moving system and a double chain moving system which is used for the experiments. Both systems are moved by the same speed controlled motor which transmits the power.

The dose can be measured at different irradiation conditions. A piece of specially coated plastic (dosimeter) is subjected to the radiation under the conditions to be evaluated. The plastic film will change its colour to blue if irradiated with electrons. The extinction of the colour is measured by an absorbance meter and is proportional to the dose. No information could be obtained on the accuracy of the system. One attempt of the responsible engineer to determine the dose was unsuccessful.

Additionally the dose can be calculated via a special formula (provided by the Russian supplier) which contains all the necessary data from the set-up:

Dose $D = U * I * C / (v)$ (2)

D = dose [kGy]
U = accelerating voltage [V]
I = beam current [mA]
C = apparatus specific constant
v = velocity or line-speed [m / s]

For U = 1 MeV and v = 1.5 m /min the following relation was found experimentally:

$$D = -4.23 + 5.53 * I \quad (3)$$

The line-speed for a given dose (e.g. 80 kGy) and beam current (e.g. 4.2 mA) is calculated as follows:

$$I_1 / v_1 = I_2 / v_2 \quad (4)$$

The dose is inserted into equation (3), a resulting I ( 15.23 mA) is obtained.
With this equation it is possible to calculate the requested line-speed $v_2$ (0.41 m / min) for $I_1$ = 15.23 mA, $v_1$ = 1.5 m / min and $I_2$ = 4.2 mA.

The apparatus has a transport system which can be modified to allow consolidation experiments with PLEX 6803-1. A sketch of the double chain transport mechanism is depicted in figure 3. After removing several cross struts and a water-cooled metal electron beam trap, a special metal box will be inserted into the transport line. This allows to use the existing transport system. Fragments with a height of up to 15 cm can be treated by electron beam radiation. The engineers of the institute made a construction sketch of the box before it was built from tinplate. High-grade steel is not recommended as box material, because it cannot be deformed easily. In case of a manual operational error the box rather than the apparatus will be damaged.

In the beginning of the experiments there were problems controlling the transport mechanism. It is not possible to operate the transport mechanism independent of the electron beam apparatus. This resulted in a very short warm-up time for the electron accelerator. Thus the sample box approached the electron beam outlet before the necessary beam current was reached.

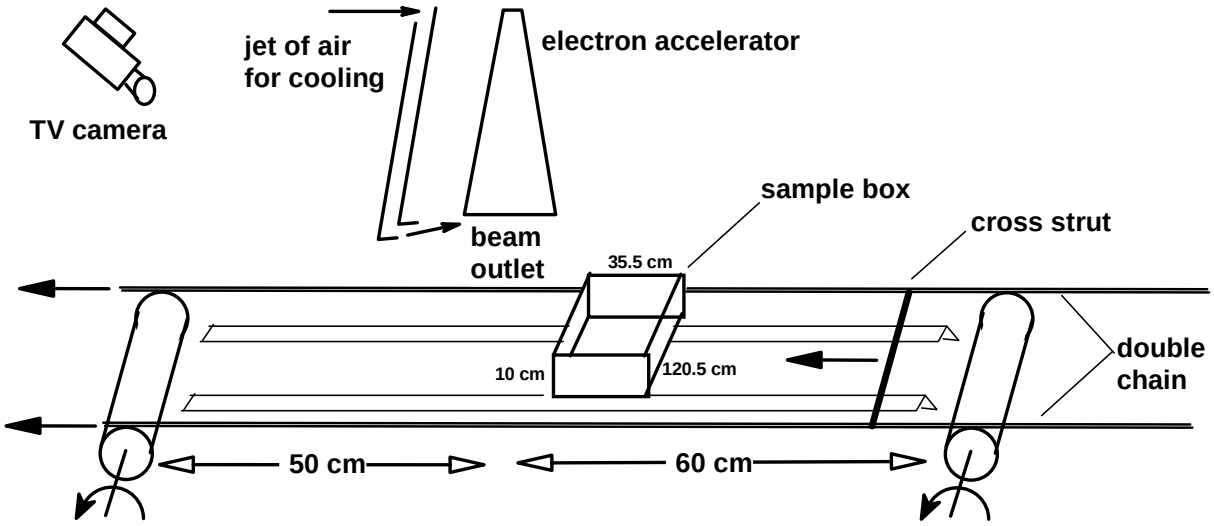


**Figure 3 Double chain transport mechanism**

An enhanced transport mechanism was developed. Now the sample box is not hooked to the cross-struts of the double chain moving system. It is pushed by one cross-strut over two steel V profile bars which act as rails for the sample box. The box will be carried by the transport mechanism for about 1.1 m, during this time it will pass under the beam outlet window. This allows to use the velocity control mechanism of the existing transport mechanism. Furthermore it is possible to move the start position of the pushing cross-strut far enough away from the sample box, so that the warm-up time of the apparatus has passed before the sample box is moved. The samples could then be irradiated with stable electron beam parameters. The conversion of the production facility to an irradiation facility for consolidating samples from the terracotta museum with Plex 6803-1 takes about 40 minutes. The adapted transport mechanism works impeccably and is simple to assemble. However for the treatment of a larger number of fragments it will be necessary to improve the transport mechanism. The improvement has to allow manual operation of the transport mechanism independent of the electron beam apparatus switch on and off.

The pre-treated fragments will be put into the sample box. After the researchers have left the irradiation chamber, the electron beam is turned on. It is necessary to adjust the height of the fragments, so that the upper surface of the fragment to be treated is close to the titanium beam outlet window. If the sample is to far away from the outlet window irradiation conditions will change because the electrons ejected from the apparatus are decelerated by air. The transport mechanism can be supervised by a video camera and has to be operated manually for the experiments. Three minutes after the apparatus was switched off the ventilation had exhausted the ozone formed by the radiation. It was now save to enter the irradiation chamber.

In experiments we found the dose necessary to sufficiently consolidate Plex 6803-1 to be higher (100 kGy) than the dose of 60 kGy which was used in Dresden. There are two possible explanations for this result:
1) The electron beam of the ELV-8 apparatus in Lintong is fanned out to a beam width of 1.6 m instead of the usual 1.0 m. If the data and formulas of the supplying company (BINP) do not reflect this the output energy and therefore the dose is distributed over a length of 1.6 m instead of 1.0 m. If we correct the higher dose value from Lintong we obtain the 60 kGy which were used in Dresden (100 kGy / 1.6 = 62.5 kGy). The validity of this explanation can be proven by measuring the dose with a dosimeter.
2) The titanium outlet window of the ELV-8 apparatus in Lintong is cooled by a strong cooling fan which blows air over the outlet window surface. The same method of cooling is used in

Dresden, but nitrogen is used instead of air. Air mainly consists of nitrogen, but it also contains about 21% Oxygen which is a strong inhibitor of polymerisation. Therefore a higher dose is necessary to achieve polymerisation. The advantage of using air cooling is that a transparent film cannot form, but instead a slimy coating on a solidified Plex sample is obtained. This coating can be removed easily with an adsorbent cloth.

In reality the applied dose D is a complex function of several parameters which influence each other: $D = \frac{dE}{dm} = f(\ldots)$. The parameters which influence the dose are compiled in table 1.

<table>
<tr><td rowspan="3">process parameter</td><td>high voltage</td><td>penetration depth,<br>energy distribution</td><td rowspan="9">product<br>temperature</td></tr>
<tr><td>beam current</td><td>number of electrons per time</td></tr>
<tr><td>line speed</td><td rowspan="2">exposure time</td></tr>
<tr><td rowspan="4">process layout</td><td>number of passes</td></tr>
<tr><td>scan length</td><td rowspan="3">lateral dimensions<br>of radiation field<br>in product plane</td></tr>
<tr><td>distance scanner - product plane</td></tr>
<tr><td>direction of product to scanner</td></tr>
<tr><td rowspan="4">product parameter</td><td>compound density</td><td rowspan="3">high voltage and<br>beam efficiency<br>in product plane</td></tr>
<tr><td>product geometry</td></tr>
<tr><td>construction</td></tr>
<tr><td>dose requirement</td><td>radiation impact to product</td></tr>
</table>

Table 1. Dependency of the dose on several parameters [2]

## Conclusion and Outlook

In co-operation with our Chinese colleagues we succeeded in developing and improving a method of consolidation with electron beam radiation. We proved that this method can also be applied in Lintong, China. For the electron beam treatment the following standard values were derived in several experiments:
accelerating voltage: 1 MeV, electron beam current: 2.0 mA, dose: 1 x 60 kGy.
If there will be problems in future with samples consolidated with these standard values, it will be necessary to reduce the stress on the fragment by energy deposited as heat (the dose of 60 kGy leads to a heat up of the fragment). Then it will be necessary to apply the dose in two (2 x 30 kGy) or three (3 x 20 kGy, like in Dresden) steps. However the number of steps is limited by the transport mechanism. For every irradiation step it is necessary to switch the electron accelerator on and off. The lifetime of the accelerator and its service intervals will reflect this.

The experiments clearly show that the original fragments behave very differently. Thus a standard method for the pre-treatment which is valid and successful for all fragments cannot be derived. For different kinds of fragments the following general advice can be given:
- *Pieces with thick lacquer and pigment layer (e. g. incarnation)*
Pre-treatment: Mechanical cleaning of the fragment. Spraying consolidant onto surfaces if pigment layer is easily lost, otherwise multi-step soaking with cotton wool compress on Japanese paper: 1) Plex 33 %, 1 day; 2) Plex 66 %, 1 day; 3) Plex 100 %, 1 day.

- *Pieces with already damaged or cracked lacquer layer, less sensitive to changes in humidity (e. g. paint layer of armour (without pigment layer))*
Pre-treatment: Mechanical cleaning of the fragment. Multi-step soaking with cotton wool compress on Japanese paper: 1) Plex 33 %, 1 day; 2) Plex 66 %, 1 day; 3) Plex 100 %, 1 day.

*- Pieces with continuous lacquer layer without damages or cracks, very sensitive to changes in humidity (e. g. paint layer of robe (with thin pigment layer))*
Pre-treatment: Mechanical cleaning of the fragment. Multi-step soaking with cotton wool compress on Japanese paper: 1) Plex 33 %, 1 day; 2) Plex 66 %, 1 day; 3) Plex 80 %, 1 day. Before the last step of the pre-treatment it should be tried to use Plex 100 % on one spot of the fragment. If no adverse effects are observed it is recommended to use Plex 100 % instead of Plex 80 %. If this Plex / electron beam method does not lead to satisfying results it is recommended to use the PU / PEG consolidation method for this kind of fragments.

On Thursday 03.06.1999 Mr. Wu Yongqi, the director of the Museum of the Terracotta Army, told us that it is planned to build an electron beam facility workshop at the museum site. This would include a building with an electron accelerator and a suitable transport mechanism. It is assumed that this facility will be used as cost effective and profitable means to treat archaeological objects. The Shaanxi province can be seen as a cultural treasure house of many Chinese dynasties with many finds to be expected in future. Before this workshop will be built, it will be necessary to conduct further experiments with the electron accelerator at the Xi'an Radiation Research Center. The electron beam consolidation method with the consolidant Plex 6803-1 was specifically developed, tested and improved for consolidating the polychrome layer on aged qi-lacquer on the terracotta of the terracotta warriors at the museum of the terracotta warriors and horses in Lintong, China. Any other application of the electron beam apparatus apart from its intended use and apart from using the emitted X-radiation for disinfecting non paper objects from mould and insects needs to be thoroughly tested for viability. If a workshop is to be set up it will be necessary to build a compound which ensures radiation protection. An adaptable, continuous transport system with trays and at least one well trained engineer will be needed. For the short and middle term I would like to suggest to form a co-operation or joint venture with the Xi'an Radiation Research Center to evaluate all risks entailed with setting up an electron beam facility at the Museum site. After this it will be a pleasure for me to see the building of the electron beam facility workshop at the museum of the terracotta warriors and horses thanks to the long term thinking of the director of the museum Mr. Wu Yongqi.
The investigation of the stability of the solidified lacquer and polychromy of nine fragments demonstrates the value and the benefit of this consolidation method. The electron beam polymerisation is therefore a promising method for the conservation of qi-lacquer and in particular for the preservation of the polychromy of the terracotta army of the First Chinese Emperor, Qin Shihuangdi.

## EXPERIMENTAL

Experiments were carried out with Plex 6803-1 produced by the German company Röhm. On 31.05.1999 we obtained 2 x 50 kg of the product from Xi’an airport stored in opaque blue plastic canisters. The product was sent to China free of charge by the company to help consolidating the polychrome layer of the terracotta soldiers.

### 1) Experiments on the polymerisation of Plex 6803-1 (hydroxyethyl-methacrylate formulation)

### 1.1) Variation of the dose to find an optimal degree of hardness

In order to find the best conditions to consolidate the monomer several preliminary experiments were carried out. Glass beakers with ground stopper (inner diameter of 32 mm, height 25 mm)

were filled with equal amounts (3 ml) of the consolidant and were exposed to a specific dose of electron beam radiation to evaluate differences in the effect of the irradiation.
First it was necessary to determine at constant 1 MeV, 4.2 mA (values determined at the ELV-2 accelerator in Dresden) the dose necessary to obtain the required hardness of the consolidant. In order to reduce this dose we chose to repeat these experiments with constant 1 MeV, 2.0 mA. The beam current of 2.0 mA is the lowest possible a the ELV-8 accelerator. It will result in longer polymer chains and will cause the Plex to harden at a lower dose.
The optimal dose values for both beam current values were then to be administered in one, two or three steps to see whether changes in the hardening process are apparent. The accelerating voltage of 1 MeV was not changed, because at lower values the electrons will not have enough kinetic energy to penetrate both the pigment and the lacquer layer. A higher value is not required and would only lead to a stronger heat up the fragment.
A synopsis of the experiments is presented in the following table:

| Treatment | Line-speed | Computer Value CV | Real measured CV | Plex 6803-1 LINTONG | Plex 6803-1 DRESDEN (REFERENCE) |
|---|---|---|---|---|---|
| | [m /min] | [m /min] | [m /min] | sample is: | sample is: |
| 60 kGy, 4.2 mA | 0.54 | 1.20 | 1.21 | very viscous | solid |
| 70 kGy, 4.2 mA | 0.47 | 1.04 | | more solid, but not hard | solid |
| 80 kGy, 4.2 mA | 0.41 | 0.92 | 0.94 | hard slimy film on surface | solid |
| 90 kGy, 4.2 mA | 0.37 | 0.82 | 0.79 | hard slimy film on surface | |
| 100 kGy, 4.2 mA | 0.33 | 0.74 | 0.73 | harder slimy film on surface | |
| 110 kGy, 4.2 mA | 0.30 | 0.65 | | harder, no film | |
| 120 kGy, 4.2 mA | 0.28 | 0.56 | 0.52 | harder, no film | |
| 130 kGy, 4.2 mA | 0.26 | 0.48 | | harder, no film, warm ! | |
| 2 x 20 kGy, 4.2 mA | | | | | liquid |
| 3 x 20 kGy, 4.2 mA | | | | | solid |
| 4 x 20 kGy, 4.2 mA | | | | | solid |
| 20 kGy + 40 kGy, 4.2 mA | | | | | solid |
| 2 x 45 kGy, 4.2 mA | 0.71 | 1.57 | 1.56 | hard slimy film on surface | |
| 3 x 30 kGy, 4.2 mA | 1.02 | 2.26 | 2.29 | hard slimy film on surface | |

**Table 2. Consolidation experiments with Plex 6803-1 at 1 MeV and 4.2 mA beam current.**

| Treatment | Line-speed | Computer Value CV | Real measured CV | Plex 6803-1 LINTONG | Plex 6803-1 DRESDEN (REFERENCE) |
|---|---|---|---|---|---|
| | [m /min] | [m /min] | [m /min] | sample is: | sample is: |
| 30 kGy, 2.0 mA | 0.49 | 1.08 | 1.07 | liquid | |
| 40 kGy, 2.0 mA | 0.37 | 0.83 | 0.79 | semisolid | |
| 50 kGy, 2.0 mA | 0.31 | 0.68 | 0.67 | solid, slimy film on surface | |
| 60 kGy, 2.0 mA | 0.26 | 0.57 | 0.52 | solid, slimy film on surface | |
| 60 kGy, 2.4 mA | | | | | solid, evaporation of Plex monomer |
| 2 x 25 kGy, 2.0 mA | 0.57 | 1.26 | 1.22 | solid, slimy film on surface | |
| 3 x 17 kGy, 2.0 mA | 0.78 | 1.74 | 1.70 | solid, slimy film on surface | |
| 260 kGy, 2.0 mA | 0.06 | 0.14 | 0.099 | very hard, very hot | |

**Table 3. Consolidation experiments with Plex 6803-1 at 1 MeV and 2.0 mA beam current.**

One sample was irradiated with the glass lid closing the sample beaker. This sample was as liquid as before, because electrons cannot penetrate through the glass stopper. The samples were placed on top of a wooden box (10 cm height) to bring them closer to the beam outlet. The beam intensity is thus increased. It is necessary to fix the lightweight glass sample beakers (16.5 g)

with an adhesive tape, otherwise the samples will be blown away by the strong air jet of the cooling fan.

The hardness of the cured samples was determined by brushing a spatula over the surface of the solidified Plex. For further evaluation the hardness was measured by infra-red spectroscopy (see chapter 2). The combination of the simple and rapid comparative technique (brushing with the spatula) with the quantitative IR technique is useful and necessary. The IR technique only records changes of the number of C=C double bonds. At higher doses all double bonds have undergone polymerisation and cross-linking of polymer chains occurs. The changes in hardness due to cross-linking will only be noticed by the spatula brushing method. Other methods to determine the hardness of cured film comprise: finger-tip test, solvent rub test, pencil hardness and the Sutherland rub test [3].

In all experiments the accelerating voltage was kept constant at 1 MeV. In two series of tests the dose was varied at 4.2 mA and 2.0 mA beam current. For optimal consolidation we chose a dose of 90 kGy at 4.2 mA and a dose of 50 kGy at 2.0 mA. The optimal dose was applied in one, two and three steps at both evaluated beam currents (2.0 mA and 4.2 mA). The results of the different irradiation conditions were comparable (see table 2 and table 3). This is explained in detail in chapter 2.
After treating the first fragment (F002/99) with 1 MeV, 4.2 mA and 2 x 45 mA it was found that the consolidation was not sufficient enough. The Plex was too soft, the dose of the treatment was considered too low. It was chosen to use 1 MeV, 4.2 mA and 2 x 50 kGy or 1 MeV, 2.0 mA and 1 x 60 kGy for improved hardness. A further increase of the dose was considered to be inadequate. At higher doses the formation of a slimy film on the surface was inhibited in preliminary experiments. This results in a shining surface coating.

**1.2) Variation of the concentration of the consolidant Plex in water**

During the pre-treatment of some original samples cracks were observed in the lacquer layer and the polychrome layer when the consolidant concentration was increased from 66% in aqueous solution to 100%.
Most likely the following effect is observed: The water which is contained in the fragment diffuses through the lacquer and the overlying polychrome layer towards the compress containing 100 % Plex. The Plex monomers diffuse in the opposite direction. Both liquids are miscible in every ratio, however the dynamic viscosity of Plex ($\eta_{Plex}$ at 23°C < 15 mPa*s, rotating viscometer, density ($\rho$ = 1.07 g/cm$^3$) is somewhat larger than the dynamic viscosity of water ($\eta_{H_2O}$ at 23°C = 0.93 mPa*s, density ($\rho$ = 1 g/cm$^3$).
In porous material like aged qi-lacquer the mobility of molecules in the pores is defined by the quotient (permeability / viscosity). No information was gathered on the permeability of Plex in lacquer - however dry and wet lacquer is able to absorb the liquid Plex. The larger Plex monomers are supposed to diffuse more slowly into the lacquer than the smaller water molecules diffuse out. This leads to a dehydration (dry up) of the lacquer and results in shrinkage cracks in humidity sensitive fragments. This effect can be prevented by the use of lower Plex concentrations in which the water content is higher. After the electron beam treatment the lacquer flakes are consolidated and the surplus water can evaporate without causing any harm to the fragment.

To suppress the formation of cracks we performed additional experiments in which 80%, 90%, 95% and 100% Plex 6803-1 were electron beam cured. Water added to the consolidant acts like a softening agent. With increased water content the hardness of the consolidated Plex is decreased.

At a concentration of 80% Plex the irradiated samples were considerably more soft than at 100% Plex. The usage of Plex in concentrations lower than 80% in water is thus not recommended. An IR spectroscopic evaluation of these samples was undertaken to show that the degree of polymerisation was the same for the 80%, 90%, 95% and 100% Plex samples. The results are compiled in chapter 2.

Fragment F007/99 was cured at 1 MeV, 4.2 mA with 2 x 50 kGy. For comparison fragment F001/99 was cured at 1 MeV, 2.0 mA with a dose of 1 x 60 kGy. Together with the fragments samples containing 80%, 90%, 95% and 100% Plex 6803-1 were also consolidated. Under both conditions the degree of hardness of the Plex samples was identical for respective Plex concentrations.
The results from this series of experiments were used to treat fragments which were very sensitive to changes in humidity. Fragment F003/99 and F006/99 were pre-treated with 80% Plex. Fragment F005/99 was pre-treated with 90% Plex.

### 1.3) Variation of the concentration of the consolidant (Plex) in polyethylene-glycol (PEG 200)

PEG 200 added to the Plex consolidant is assumed to have a softening effect as described above for water. The aim in this series of experiments was also to reduce the formation of cracks. Samples with 100 % PEG 200, 70% Plex in PEG 200, 80% Plex in PEG 200, 90% Plex in PEG 200 and 100% Plex were treated with the electron beam radiation at 1 MeV, 2.0 mA, 60 kGy.

Half a year after the treatment, stored in a sealed container the samples have the following properties:

| 100% PEG 200 | 70% Plex<br>in 30% PEG 200 | 80% Plex<br>in 20% PEG 200 | 90% Plex<br>in 10% PEG 200 | 100% Plex |
|---|---|---|---|---|
| viscous liquid,<br>properties not<br>changed by EB<br>treatment | highly viscous,<br>not solid | highly viscous,<br>gel like consistency | solid,<br>gum like<br>consistency | solid,<br>gum like |

**Table 4. Properties of Plex / PEG 200 mixtures six months after curing**

For a more quantitative investigation of the properties of these samples (which are shown in table 4) IR spectra were recorded. The results are described in the following chapter.
It is not possible to prevent the formation of cracks by impregnation with PEG 200 30% in the first step of the pre-treatment (see fragment F004/99). Fragments (F004/99, F005/99) which had already been treated with PEG 200 could nevertheless be consolidated using Plex and electron irradiation.

### 1.4) The relationship between dose and temperature

The dose corresponds to a certain amount of energy that is transferred to the material where it is converted into heat. Thus in order to avoid negative effects due to heating, it is considered to apply the amount necessary to consolidate the monomer in more than one step. Between the irradiation steps the treated fragment now has the possibility to distribute and loose the heat it has taken up. If water is administered a dose of 10 kGy it will heat up by 2.39 °C (specific heat capacity: 4.19 J $g^{-1}$ $K^{-1}$ ; 1 Gray = 1 Gy = 1 J $kg^{-1}$). The expected increase of temperature per dose is given in table 5. The specific heat capacities of qi-lacquer, Plex 6803-1 and the terracotta

are not known until now. Therefore values for similar matter was chosen. Rupert Utz found that the terracotta has a porosity of about 25-30%. If water or Plex is inside these pores the terracotta has a higher specific heat capacity and will thus not heat up as much as shown in table 5. Further investigation of this subject is necessary.

| Material (similar to ...) | Specific heat capacity [J $g^{-1}$ $K^{-1}$] | Heat up in °C at | | |
|---|---|---|---|---|
| | | 10 kGy | 20 kGy | 60 kGy |
| | | | | |
| Water | 4.19 | 2.4 | 4.8 | 14.4 |
| | | | | |
| Rubber | 1.1 | 9.1 | 18.2 | 54.6 |
| (Qi-lacquer) | | | | |
| | | | | |
| Granite | 0.82 | 12.2 | 24.4 | 73.2 |
| (terracotta) | | | | |

Specific heat capacities: Physical Chemistry, P. W. Atkins, 4. ed, Oxford University Press, Oxford, 1990.
**Table 5. Increase of temperature per dose for different components of the original samples**

## 2) Infra-red spectroscopic evaluation of irradiated Plex samples

On 25. May 1999 Plex samples (irradiated on 20. May 1999) were investigated by IR spectroscopy together with Mrs Fan Juan at the technical centre for archaeology in Xi'an. Apart from ordinary substance identification IR spectroscopy can be used for time resolved spectra of reactions and quantitative measurements. Under optimum conditions quantitative measurements with a relative standard deviation of $s \geq 0.1\%$ can be achieved. However the relative standard deviation for samples prepared with the KBr pellet method is in the range of a few percent.
Infrared spectroscopy allows to determine the degree of polymerisation by performing a quantitative measurement. During electron beam curing the C=C bond of the monomer is broken when the polymer is formed. The fall of the absorbance at the C=C stretching vibration (1637 $cm^{-1}$) or the C=C twisting vibration (816 $cm^{-1}$) is supposed to be a measure for the polymerisation [3].

The samples investigated had very different consistencies: liquid, viscous, rubber like and rock hard. Instead of the disappearance of a peak to be related to the degree of polymerisation it was preferred to monitor a peak that was linearly proportional to the degree of polymerisation. If the C=C peak became smaller we could only conclude that the monomer was consumed, this could be due to the addition of water to the double bond, due to polymerisation or due to other side reactions.

The polymerisation of Plex 6803-1 affords the formation of linear chains like:
-[-$CH_2$-$CR_2$-$CH_2$-$CR_2$-]-.
The newly formed methylene group ($CH_2$) is found at 748.5 $cm^{-1}$ and its peak is proportional to the degree of polymerisation. The longer the chain the more methylene groups are formed the higher the absorbance at this wavenumber.

The IR-spectra of the Reference spectra were normalised for the -$CH_2$-H valence vibration at 2957 $cm^{-1}$ (methyl group is not affected in the reaction). The baseline was corrected and the wavenumber 780 $cm^{-1}$ was set to zero. The peak at 748.5 $cm^{-1}$ is asymmetric because of the Christiansen effect. This effect occurs if the refractive index between sample (Plex) and Matrix (KBr) is very large and it can be minimised by thorough grinding of the sample substance.

IR-spectra recorded in Xi'an were more difficult to interpret quantitatively. In general the scattering of the IR radiation is not well reproducible. This is because the sample particles have a large particle size distribution and the mixture of the sample with the KBr matrix will not be an ideal solution. When Rayleigh scattering occurs the intensity of scattered radiation depends on $1/\lambda^4$ therefore the influence of scattering is reduced at long wavelengths (lower wavenumbers). Thus it is better to use the absorption peak at 748.5 $cm^{-1}$ than to use the C=C stretching vibration (1637 $cm^{-1}$) for the determination of the degree of polymerisation.

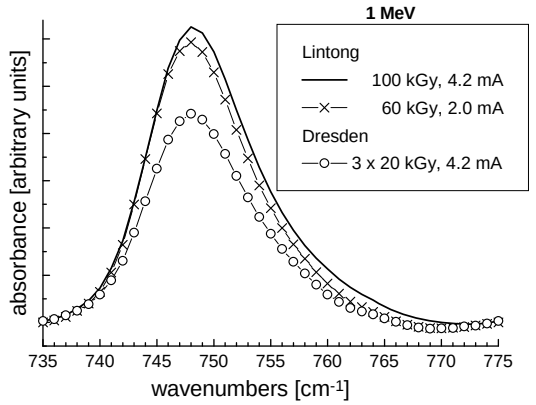


**Figure 4 electron beam curing of Plex 6803-1, comparison of the curing conditions in Lintong and Dresden**

Experiments in Lintong proved the samples treated with 4.2 mA, 1 MeV, 100 kGy to be as hard as samples irradiated with 2.0 mA, 1 MeV, 60 kGy. This allows for a single step treatment with a dose of 60 kGy. Which in turn facilitates the handling during the consolidation process. If we compare the results of curing Plex in Dresden and in Lintong, we can conclude that the samples from Dresden have a lower degree of polymerisation. As can be seen in figure 4 the two different curing conditions which were used in Lintong provide similar hardness. This was already confirmed by brushing a spatula over the solidified Plex samples. The simple and quick spatula brushing method for determining the hardness of the samples is very useful for on site evaluation of the curing results.

*Figure 5a presents IR spectra focusing on the peak at 748.5 $cm^{-1}$ which were taken after a single step electron beam curing with doses from 0 to 80 kGy. The proportional relationship between dose and absorbance was monitored at an electron energy of 1 MeV and 4.2 mA beam current.*

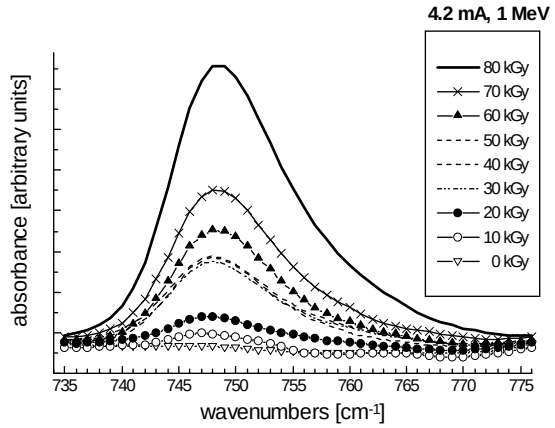


***Figure 5a Reference: electron beam curing of Plex 6803-1 in Dresden 1 MeV, 4.2 mA at different doses (one step treatment)***

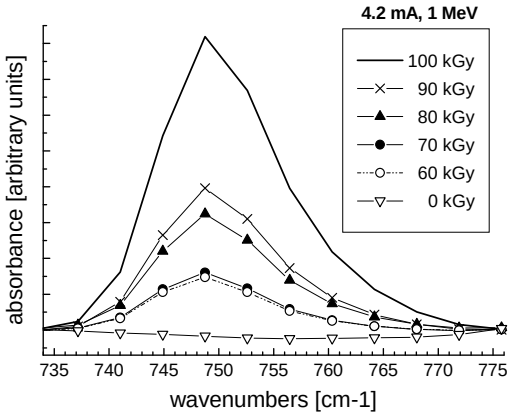


**Figure 5b: electron beam curing of Plex 6803-1 in Lintong 1 MeV, 4.2 mA at different doses (one step treatment)**

The experiment was repeated in Lintong with the same parameters for the electron beam curing. Apart from the fact that a higher dose of 90 kGy was necessary for consolidation the proportional relationship between dose and absorbance was also found in the Lintong experiments. Figure 5b shows the results with a reduced number of data points. Therefore the absorbance peaks are not as smooth as those from figure 5a.

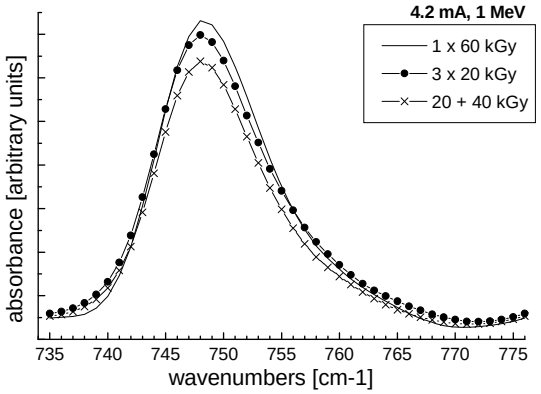


**Figure 6a. Reference: electron beam curing of Plex 6803-1 in Dresden, 1 MeV, 4.2 mA with 60 kGy dose**

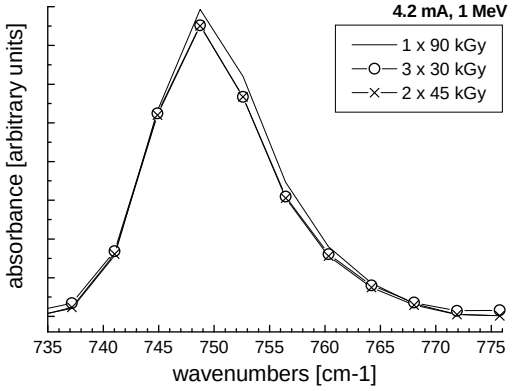


**Figure 6b. electron beam curing of Plex 6803-1 in Lintong 1 MeV, 4.2 mA with 90 kGy dose**

*In Dresden the lowest dose necessary to obtain solid Plex 6803-1 was found to be 60 kGy. The dose was applied in a single step, in two steps (20 kGy + 40 kGy) and in three steps (3 x 20 kGy). The resulting spectra are shown in figure 6a. All three curing methods afford about the same degree of polymerisation. This dose was to be used for one of the original polychrome fragments (Fragment F011-98).*

At constant beam current the hardness of the irradiated samples is dependent on the total dose, irrelevant of the number of steps it is accumulated in. This was shown for two different irradiation conditions (4.2 mA, 1 MeV (figure 6b) and 2.0 mA, 1 MeV (figure 7b)). The single step treated sample had the same degree of polymerisation, was as hard as a sample which was treated in three consecutive steps. In this respect a single-step treatment has no disadvantage in comparison with a three-step treatment. Like the hardness the heat-up of the fragments depends on the total dose. A dose of 100 kGy results in a higher stress on the fragment than a dose of only 60 kGy. If it is necessary to choose a single-step treatment in Lintong then it is preferred to use 2.0 mA, 1 MeV at 60 kGy.

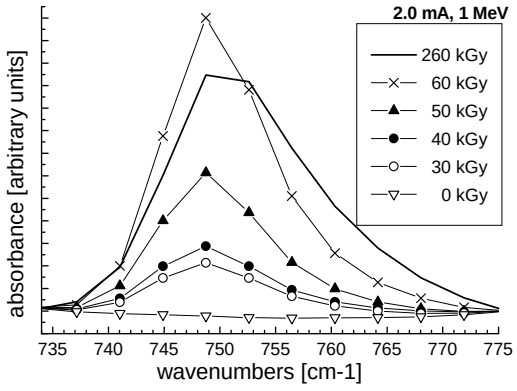


**Figure 7a. electron beam curing of Plex 6803-1 in Lintong 1 MeV, 2.0 mA at different doses (one step treatment)**

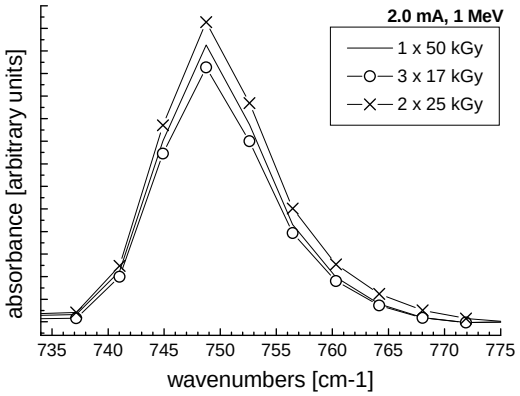


**Figure 7b. electron beam curing of Plex 6803-1 in Lintong 1 MeV, 2.0 mA with 50 kGy dose**

As pointed out before it is possible to reduce the thermal stress for the fragment by administering the dose in two or more steps. Thus the dose given in a single step is lower. Another way of reducing the thermal stress and the dose is to lower the beam current. The reason for this is explained in the next paragraph. When we reduced the beam current to 2.0 mA at 1 MeV we obtained a solidified sample at a dose of only 50 kGy. The degree of hardness for different doses at 1 MeV and 2.0 MeV is shown in figure 7a. It compares well to figure 5a and figure 5b. The dependence of the Plex sample hardness on the administered total dose can be seen in all these figures. The degree of polymerisation increases with the dose value until it reaches a limiting value when all monomers are consumed. Prolonged electron beam irradiation can cause a further increase in hardness by cross-linking separate polymer chains. This process cannot be monitored by IR spectroscopy and leads to the liberation of gaseous hydrogen. As can be seen in figure 7a the extremely high dose of 260 kGy does not show a higher absorbance peak than the dose of 60 kGy.

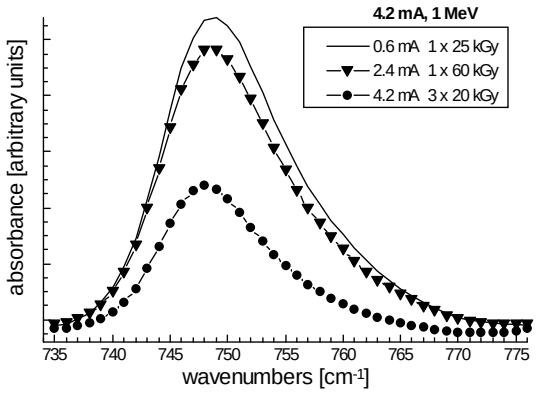


***Figure 8 Reference: electron beam curing of Plex 6803-1 in Dresden 1 MeV, 4.2 mA with a beam current of 0.6, 2.4 and 4.2 mA.***

*In another set of experiments in Dresden the electron beam current was varied. The lower the beam current, the longer the polymer chains, the higher the absorbance at the $CH_2$ rocking vibration (748.5 $cm^{-1}$). Fig. 8 shows the spectra taken from samples irradiated with an electron beam with a beam current of 0.6, 2.4 and 4.2 mA. The highest degree of polymerisation was obtained at 0.6 mA. The solidified Plex 6803-1 was rock hard. The fragment F006-98 was treated in this way. Single step irradiation with a beam current of 2.4 mA (60 kGy) resulted in the evaporation of the consolidant. Although longer polymers are formed the detrimental effect of the heat-up of the polychrome lacquer and the fragment has to be taken into consideration.*

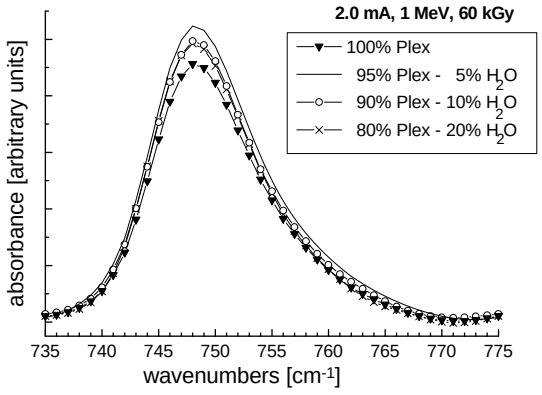


**Figure 9 electron beam curing of Plex 6803-1 in Lintong 1 MeV, 2.0 mA with different water concentration**

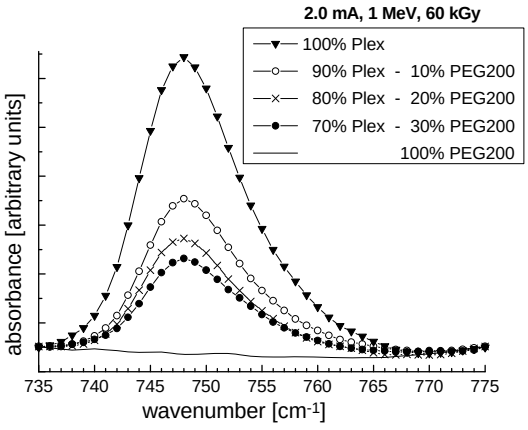


**Figure 10 electron beam curing of Plex 6803-1 in Lintong 1 MeV, 2.0 mA with different PEG 200 concentration**

The concentration of the consolidant Plex in water was varied in order to reduce the formation of cracks in the qi-lacquer of the original fragments during the pre-treatment and the curing process. Plex samples containing 5%, 10% and 20% water were consolidated at 60 kGy, 1 MeV and 2.0 mA. When the solidified Plex samples were tested by brushing a spatula over the surface, it was found that a higher water content leads to a softer polymer. IR spectroscopy reveals that this softening is only due to the water content, the degree of polymerisation of the Plex monomers is the same for all samples investigated. This can be clearly seen in Figure 9.

Chapter 1.2) describes the addition of PEG 200 to the Plex formulation to achieve a softening effect and to reduce the formation of cracks in consolidated qi-lacquer. Samples with 100 % PEG 200, 70% Plex in PEG 200, 80% Plex in PEG 200, 90% Plex in PEG 200 and 100% Plex were treated with electron beam radiation at 1 MeV, 2.0 mA, 60 kGy. In contrast to the Plex / water mixtures the samples with cured Plex / PEG 200 did not have the same degree of polymerisation. The higher the percentage of PEG 200 the more liquid the electron beam cured samples became. If more than 10% PEG 200 are added the Plex does not solidify any more. Reasons for this behaviour can be as follows:
Reduced mobility of the monomers in the viscous PEG 200 during the electron beam curing. Thus monomer radicals have problems adding to monomer molecules.
Due to radical reactions the PEG 200 is inserted into the polymer chain or the monomer radicals are deactivated by abstracting a hydrogen atom from the PEG 200.

### 3) Original polychrome fragments treated by electron beam radiation

Detachment of lacquer flakes can be observed on very humidity sensitive fragments, if the Plex concentration is increased from 50% or 66% to 100% in one step. If Plex 50% is applied again the flakes move back to their original position. A single step pre-treatment is not possible. A three step process (33%, 66%, 100% Plex) is favoured.
On some fragments parts of the lacquer layer remain unaffected by Plex 100% while other parts exhibit curled up lacquer flakes. Plex 90% reduces this effect, Plex 80% can even reverse the reaction of very humidity sensitive samples.
Samples must be stored in a sealed container with a thick compress. A thin compress leads to a dehydration effect. To obtain good results the compress: „tuo zhi yao mian“ (degreased medical cotton wool) from the company: „jiao zuo di er wei sheng cai liao chang“ (Second factory for hygienic articles in the city of Jiaozuo) was used.
After electron beam treatment fragments were freed from surplus consolidant by an absorbent, fluff-free cloth: “han xing gao ji wei sheng zhi“ (Hanxing quality toilet paper) from the company: „han xing shi ye you xian gong si“ (Hanxing company Ltd.).

The mechanical firmness of the lacquer layer and its overlying pigment layer on the terracotta is achieved for all treated samples. Some Fragments (F004/99, F008/99, F005/98 do not show cracks because of pre-treatment with Plex 100%. Other fragments exhibit profound cracks because of shrinking after Plex 100% treatment. Samples treated with lower concentrations of Plex (90% and 80%) exhibit less cracks. The best results for the consolidation of fragments which are very sensitive to changes in humidity were obtained with a concentration of 80% Plex in water.

The pre-treated fragments dry too quickly after the compress is taken off, because of the strong jet of cooling air for the beam outlet window. If necessary the fragments have be sprayed with consolidant to avoid drying out. Covering the fragments with Hostaphan film to keep away the strong jet of air avoids the drying out, but it leads to a stronger heat up and thus damage of the fragment.

After the electron beam treatment the samples are stored under ambient conditions. The exclusion of dust is further on necessary. It is suggested to store the consolidated samples in closed containers after they have dried completely. If possible the treated samples should not be subjected to strong changes in humidity.

Detailed description of the fragments and their treatment: see: *Conservation Treatment on Polychrome Fragments of the Terracotta Army, Working Visit in Lintong, May 13 to June 5, 1999,* p. 4 of this Annual Report

## Conclusion

The conditions under which the original fragments were treated in Lintong and the assessment whether the consolidation was successful are compiled in detail in table 6. Further research comprised the following results: A comparison between the treatment (1 MeV, 2.0 mA, 1 x 60 kGy) with the alternative two step treatment (1 MeV, 4.2 mA, 2 x 50 kGy) yielded identical results however the one step treatment is preferred. It was shown that after impregnation with a certain concentration of a non-volatile consolidant (Plex, boiling point 250 °C) it was possible to mechanically clean the original fragments outside a climatic chamber. The formation of shrinkage cracks could be reduced by lowering the Plex concentration in the third step of the impregnation from 100% to 80%. With this method the formation of cracks was almost entirely prevented in one experiment. Whereas it is not possible to prevent the formation of cracks by impregnation with PEG 200 30% in the first step of the pre-treatment. Fragments which had already been treated with PEG 200 could nevertheless be consolidated using Plex and electron irradiation. An electron beam treatment can consolidate fragments with incarnate layer on top of a thick qi-lacquer layer. Even fragments with more than one polychrome face show good results after consolidation. The multiple irradiation of different faces (sides) of the fragment can be done without any difficulties.

Further research and necessary improvements include that the transport mechanism of the ELV-8 accelerator can be controlled independent of the accelerator apparatus. This seems to be an electric problem which needs to be solved by specialists from NINT (Xing Dong Jian). If necessary advice from an engineer of the manufacturing company NINT should be requested.
The pre-treatment of thick incarnate covered fragments needs to be improved to avoid loss of pigment layer. The effect of the strong air jet of the beam outlet cooling onto fragment cooling and evaporation of the consolidant will have to be discussed. After the evaluation of the latest Kryo-REM and TV-holography experiments the results of the fragments treated with 80% Plex and 20% water will have to be discussed. One question will be if the evaporation of the 20% water after the electron beam polymerisation of the Plex will cause undesired effects or affect the ageing process.

[1] Protocol of acceptance test for ELV-8 (buyer NINT Xi'an, seller BINP Novosibirsk) performed on 10.06.1995
[2] Huber & Suhner AG, Pfäffikon, Switzerland: Possibilities and limits of electron beam cross-linking of wire, cable and tubing, at Electron Beam Workshop at RadTech Europe 99 conference, 8. - 10. November 1999, Berlin.
[3] A. K. Davies, Experimental Techniques to Monitor the Degree of Cure in Radiation-cured Coatings in Radiation Curing of Polymers II, ed. D. R. Randell, The Royal Society of Chemistry, 1991 p. 379-399

# Conservation Treatment on Polychrome Fragments of the Terracotta Army, Work Stay in Lintong, Oct. 23 to Nov. 20, 2000

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## 1 Introduction

During the work stay in Lintong a series of conservation tests was performed focussing on the use of Plex / electron beam irradiation. Starting from the results obtained in 1999, new methods for application of the consolidant, different concentrations and parameter of irradiation were tested. The aim of the tests was to avoid problems which had appeared in 1999 and thus optimising the method.

The seven fragments treated in 2000 had been excavated specially for the purpose of the conservation experiments between Oct. 24 and 27, 2000 (the first week of the work stay). The consolidation of the polychromy started the following week (performed between Oct. 30 and Nov. 17).
The fragments were taken from two different places pit no. 2: Five fragments (001, 004, 005, 006, 007/2000) were excavated in T5G1, border of test area 1. This test area had been excavated in 1976 and now is uncovered for at least seven years. The fragments belong to one figure of to the unit of the war chariots. The warrior wears an armour of the type usually worn by infantry men and probably is one of the adjutants of the charioteer. The fragments comprise parts of the green collar, the pink robe and the armour with red ribbons and pink buttons. The fragments 004 and 007 can be joined as well as 005 and 006. They belong to the back of the figure, coming from the level of the waist (connection zone of the back to the front part of the armour, at the left side, F-004 and 007), the right upper arm and the collar (F-005 and 006). The fragment 001/2000, a part of the robe, cannot be attached to the other fragments. The reddish pink as colour of the robe and the ‘buttons’ on the armour was detected for the first time.
The fragments 002 and 003/2000 come from T21G20 (exact position not clear). G20 is the last corridor to the north of the unit of the archers, containing standing archers. They do not wear suits of armour. The corridor G20 was excavated in 1999 and 2000. Fragment 003/2000, from a soldier without armour, shows a robe with a green stripe round the neckline followed by a light pink of which only a very small part is preserved. The light pink could be the colour of the robe. As F-002/2000 is part of a reddish brown robe, it does not seem likely that the two fragments belong to the same figure.

Fig. 1. Pit no. 2. Place of excavation of the fragments treated in 2000.

F-002 and 003/2000
T21G20

F-001, 004, 005, 006, 007/2000
T5G1

## 2 Technological description

The technique of production of the terracotta and the structure of the polychromy do not differ from the fragments treated in the previous years: The terracotta is light grey. All fragments show a double layer of lacquer as ground layer. The colours are bright, the brush stroke is still visible. Investigations concerning the painting technique could be only performed in a small range. Samples were taken from the pigment layers.

Fragment 004/2000 reveals some details concerning the production of the terracotta figures including an ancient repair. Two elements of the ribbon (indicating long stitches) on the second row of armour plates, had been fallen off after the firing of the figure. The upper stitch element, the one next to the button-shaped end of the ribbon, was not replaced The following stitch element was stuck onto the armour again after firing using a grey clay material which is preserved on the terracotta (fig. 2, (1)). It has the colour of the terracotta, but it is soft (i. e. it is not fired).[1] When the figure was painted, the space of the upper stitch element was overpainted with lacquer. The button-shaped end of the ribbon which stood isolated because of the missing stitch (fig. 2, (2)), was painted pink like the small 'buttons' instead of red as the 'ribbons' had to be.
On the same fragment incised (fig. 2, (3)) and impressed (fig. 2, (4)) lines along the sides of the ribbon elements and the 'buttons' are visible. They either are marks to determine the position of the applied elements or come from the pressing on of these elements (softer lines and small depressions) or the clearing of their borders. On the upper stitch element of the missing ribbon, the step between the two overlapping armour plates was levelled out by a small clay ball pressed in the depression. It still shows the fingerprint of the craftsman (fig. 2, (5)).
Fragment 005/2000, a part of a collar, shows a system to fit the head into the body. The back of the fragment (i. e. the inside of the collar) shows a bulge of terracotta which forms a base for the head. This base is shaped like flat "bottom" with a hole cut in the centre for the ventilation during firing.

Fig. 2. F-004/2000

(2) button-shaped end of the stitch

(5) clay ball with fingerprint

(3) incised line

(4) impressed line

(1) grey clay to stick on the stitch element again

[1] Repairs like this are described in the excavation report (*Qin Shihuang ling bing ma yong keng* 1988).

Fig. 3. Reconstruction of the polychromy of the adjutant of a charioteer or adjutant from pit no. 2, T5G1, TA 1 from fragments treated in 2000.
The fragments 004 and 007/2000 come from the left side of his back, height of waist; the fragments 005 and 006/2000 form his right shoulder piece and an adjoining part of the neck.

The lacquer is applied in two layers. The first lacquer layer is rather brown and has visible pores. The top layer is more dense and darker.
On the fragments of robes and collars (F-001, 002 and 005/2000) the brush strokes are still visible. The width of the brushes or an end of a brush stroke could not be found. On fragment 003/2000 similar strokes are also visible in the lacquer layer, which could indicate that the lacquer was applied with paint brushes and not wooden spatulas.
The ribbons show that the red was applied with a single brush stroke, just covering the heights (top) and leaving out sides and smaller irregularities.
Some of the pink buttons on the adjoining fragments 005 and 006/2000 show a light green underneath the pink. Probably the first layer had been applied with a "dirty" paint brush, still containing some green. This was corrected by retouching the heights of the buttons with pure pink again.

## 3 State after excavation

Pit no. 2 has dried out considerably since 1999. So it was difficult to obtain fragments with a quite well preserved paint layer from the borders of the actual excavation areas. Recently excavated fragments from the eastern end of T8G11, test area 9 (i. e. the area from which the fragments treated in 1998 and 1999 had been taken) only showed no or only little polychromy which was heavily cracked and was flaking off because of dryness. So the fragments used for the conservation experiments had to be taken from other areas.

Several of the treated fragments showed detaching lacquer layers (blisters), shrinkage cracks and detaching borders of the polychromy already before treatment.[2] They reacted extremely sensitive to changes of the humidity: The lacquer started to deform as soon as the fragments were taken out of the climate chamber. The fragments seemed to have dried out more than the fragments treated in 1998 and 1999. However, the water content was about 8.75-9.75 weight %, i. e. comparable to the fragments taken from pit no. 2 in 1998.[3] It also has to be considered that after excavation and before weight measurement, the fragments were stored inside climate chambers at about 97 % RH; maybe they had already taken up water at the time of the first weight measurement.
The lacquer layer showed small cracks caused by shrinkage on all fragments already. The areas without pigment layer (armour plates) show a poor state of preservation: Only in parts which had been covered with a thick layer of soil the lacquer layer is still preserved. On armour plates more than 50 % of the lacquer layer was lost. The adhesion to the terracotta partly is very poor; the lacquer tends to stick to the soil. When soil particles are removed, the lacquer layer tends to stick to the soil and flakes off, while the pigment layers often separate inside in the layer. Part of the pigment layer stick to the soil, the rest remains on the fragment. Some of the losses therefore might be caused by the first rough cleaning during excavation.
The paint layer of the red ribbons is mainly preserved on all fragments, but always showed a fine system of cracks, partly following the surface structure. As the fragments treated in the previous years do not show these problems on the ribbons, this seems to be a damage of drying out before treatment. The ribbons show much more cracks than other areas with pigment layers. There might be a connection with the shape of the ribbons: The wavy structure cause a very inhomogenous thickness of the lacquer layer. The lacquer layer tends to get cracks in all areas where there are thick spots next to thin layers, i.e. depressions of the surface.
The damages on the pink buttons seem to be due to their shape (sometimes the whole paint layer broke off when a button was touched). Flat areas as the parts of the robe are well preserved.
On the fragment 003/2000 the polychromy of the collar had already been lost almost totally. There are only small remnants of lacquer preserved in depressions of the surface. It was impossible to determine if there had been a pigment layer originally. The reason for this complete loss could not be explained.

Photographs of all fragments were taken before starting the treatment (Oct. 30th).

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[2] blisters: F-002/2000; shrinkage cracks: F-001/2000; detaching and bending up borders of the polychromy or lacquer flakes: F-002/2000, F-005/2000, 006/2000

[3] Calculated for F-002/2000: The fragment was soaked with water by putting it into a dish with water. It absorbed about 5.5 weight % of water. As the maximum water content of the terracotta is about 13-15 weight %, the water content after excavation can be estimated (8-10 %).

## 4 Conservation treatment

The method of application of Plex and hardening in general was the same in the experiments of 1999 and 1999: The fragments were cleaned before treatment, the liquid Plex was applied with compresses in three steps with rising concentrations. The hardening was performed by electron beam irradiation.
The aim of the experiments was to avoid damages occurring during the treatment and to develop the base for a standard method. Improvements could be made concerning the cleaning of the fragments and the application of Plex.
As consolidant, as before, Plex 6803-1 was used. The material used was a rest of the amount sent to China in May 1999, still stored in the original bulks and also small rests in the bottles used for the experiments in 1999. The material did not seem to have changed during the time of storage, there was no visible increase of viscosity.

### *4.1 Pre-treatment before application of Plex*

The fragments were stored in climate chambers before and during the time of the treatment to avoid drying.
Before the soil was removed from the paint layer (‘cleaning’) the fragments were soaked with tap water from the back (without contact to the paint layer). The soaking was controlled by measures of the weight. After c. one to two hours the increase of weight stopped; the surface of the terracotta below the paint layer looked wet. The maximum of water take up seemed to be reached.
The soaking fulfilled several purposes:

a. It was easier to clean the fragments when they were soaked with water: The soil get smooth and soft and is easier to remove. The lacquer flakes detaching from the terracotta flatten down again when touched with water and ‘stick’ to the terracotta, so the danger of loose lacquer flakes adhering to the soil instead of the terracotta is minimised.
b. The Fragment could be brought into room ambience for a while without damages by drying out, e. g. for taking photographs, cleaning the glove box and beginning the conservation treatment.
c. One the aims is to reduce the amount of Plex taken up by the terracotta. So it should be tested if the amount of Plex could be reduced by filling the pores of the terracotta with water before treatment. A parallel test had been performed with PEG 200 in 1998. The success of this method could be controlled by the weight measurements.

### *4.2 Improvement of the application system of Plex*

Two new ideas were tested with positive results:

a. Spraying

The Plex was sprayed on the surface instead of dripping it on with a pipette. This procedure avoided damages of the pigment layer by drops, i. e. changes of the surface structure of the pigment layer. Especially the thick pigment layers are highly endangered to loose their surface structure if liquid water is added (particles are ‘swimming’ away or ‘floating’ down). The spraying can be performed quickly when necessary (e. g. a last time directly before irradiation); it can be finely dosed. The surface structure could be preserved on all fragments except for very small areas (e. g.. F-001/2000).

b. Japanese paper and compresses in stripes

Like in the years before cotton wool was used as material for the compresses; Japanese paper served as separation layer below the compress. The Japanese paper is not elastic, i.e. it is not following the shape of the surface very well, but tends to form little tents over elevated parts (especially the buttons) and fold in wrinkles on other areas. To provide a good contact to the surface of the fragments several narrow strips of paper were used instead of a big one in the size of the whole fragment. These narrow strips could also be removed easier after the soaking.
Another problem of Japanese paper is that pigment and lacquer particles tend to adhere to the fibres of the Japanese paper and get lost when the Japanese paper is removed.[4] On more stable areas, the pigment layer is not torn off, but fibres stick on the polychromy. To minimise these problems, after the first tests, the Japanese paper strips were left on the fragments for the whole soaking treatment.

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[4] F-003/2000: When the compress was removed after the first step of treatment, lacquer flakes and colour particles stuck to the Japanese paper. So the Japanese paper was left in its place for the third step. The same happened on F-007/2000 after the second step of treatment. Therefore the Japanese paper was not exchanged anymore on the fragments treated later on (after Nov. 6).

From these ideas a system was developed that gave good results: Before the compress was applied, the fragment was sprayed with Plex several times. The dry Japanese paper was applied in overlapping stripes with a width of ca. 3 cm. Afterwards the fragment was sprayed again. The cotton wool compress was applied in several pieces which were already soaked with Plex. This system was used on the fragments 002, 004, 005 and 006/2000.
Very sensitive pigment layers as the green part on the fragments 003/2000 and 005/2000 still suffered from the contact with water and got very soft and sensitive. The original structure partly got lost, the surface looked rough and "muddy".
The red of the ribbon could be well protected during the compress treatment, but loose particles have spread over the surrounding lacquer areas ("flown down" or "washed off"). The fixation of these loose pigment particles on the wrong positions could be reduced by removing them with a paint brush directly before the electron beam irradiation (F004, 005 and 006/2000).

*4.3 Duration of steps*
After a discussion with the Chinese colleagues it was decided that the steps should last 2 days at least. Deviations from this plan were caused by week ends (longer periods) and lack of time (duration shortened to 1.5 days).

*4.4 Concentrations*
Based on the results of 1999 the decision was made to lower the concentration for the third step to reduce cracks. The effect of 100 % Plex as third step was tested on small spots under the microscope on the fragments 001, 003, 004, 006 and 007/2000. It immediately led to the formation of cracks and deformation of lacquer flakes. The application of Plex 100 % after the third step (80 %) was tested on F-005/2000. A formation of cracks was not observed. But, as the lacquer layer was cracked already before, maybe the reaction was not so obvious (tensions in the lacquer layer already reduced).
On all fragments concentrations of 33, 60 and 80 % were used.

*4.5 Amount of Plex used*
The amount of Plex taken up by the fragments during the treatment could not be calculated yet. As first problems of shiny material developing out of the Plex after irradiation and forming sticky, shiny spots on the surfaces had been observed on the fragments treated in 1998 and 1999, the amount of Plex added to fragments was reduced as far as possible:
a. The compresses did not overlap the fragments.
b. No Plex was allowed to flow down on the edges of the fragments. The fragments were stored inside climate chambers during the soaking treatment, so they could not dry out.
On F-005/2000, a fragment of an upper arm Plex had to be added during the 3$^{rd}$ step after one day of treatment. The liquid had flown down because of the height of the fragment, so the top of the fragment started to dry.

*4.6 Electron beam treatment*
The electron beam treatment was performed on two days (Nov. 8 and Nov. 15). On the first term the fragments 001 and 007/2000 were treated; on the second the fragments 002, 004, 005 and 006/2000. The fragment 003/2000 was treated once on Nov. 8, but the lacquer showed a poor adhesion afterwards. Because the electron machine had already been switched off, the second treatment was done on Nov. 15, 2000. The fragment was kept in a damp-proof plastic box in the meantime. This method did not show any negative effect on the conservation treatment.

Before and directly after the electron beam irradiation the surfaces of the fragments were dabbed off with soft tissues. The amount of material on the surface could be reduced by this, avoiding the formation of shiny spots. The fragments dried quicker afterwards.
Nevertheless it was necessary to spray the fragments with Plex again directly before the irradiation, because the strong cooling air jet. It seems difficult to avoid the formation of a shiny film totally as long as it is necessary to spray the fragments again.

The stability of the polychromy was checked directly after irradiation. If the lacquer was not perfectly consolidated or the fragment could not be irradiated in all areas in one time, the fragment was irradiated again.

## 5 Results

*5.1 Stability*
The lacquer layer could be stabilised and fixed to the terracotta on all fragments. Also buckled and detached borders of lacquer flakes show a good adhesion.
The pigment layers are still sensitive against touching and wiping. They appear very matt except for the few areas which became shiny by a surplus of Plex. If necessary, a further fixation of the pigment layer with another adhesive could be done.

*5.2 Cracks and shiny spots*
The cracks in the lacquer layer that were observed directly after the treatment are systems of micro-cracks and some bigger shrinkage cracks. Some of the bigger cracks had been there already before treatment, e. g. one bigger shrinkage crack on F-001/2000 and the cracks on the red ribbons. A microscopic examination to detect micro-cracks was not possible before the end of the consolidation treatment.
Some cracks opened up or developed during the cleaning or the soaking, but the formation of big shrinkage could be totally avoided. The tests with 100 % Plex after the second step of treatment (60 %) showed that the same problem with shrinkage cracks would have appeared on these fragments if 100 or 90 % Plex had been used. The reduction onto 80 % Plex for the third step did not show negative effects on the stability of the Plex film and the lacquer layers.

Although the surfaces very dabbed off before the electron beam treatment to avoid a surplus of Plex, shiny borders and spots could not be totally avoided. Because of the strong air blow in the irradiation chamber, it often was necessary to spray some Plex directly before the treatment to avoid a dehydration in the last minute before the electron beam treatment. The dabbing off of the pigment layer has to be performed very carefully because the pigment layers are very sensitive against touching.

*5.3 Evaporation of Plex - Border zones*
The two fragments treated during the first day of radiation (F-001 and 007/2000), showed a dark and wet looking border zone along the edges of the fragment for more than a week. In the centre the paint layer already appeared totally dry, but seemed to dry very slowly in these border zones. The fragments treated during the second time of radiation did not show this phenomenon.

*5.4 Evaluation*
The stability of the lacquer layer after irradiation was satisfying. The visual appearance was very good.
The formation of shrinkage cracks during soaking and larger shiny spots and borders has been successfully reduced. Deformations of the borders of the lacquer, cracks and shiny spots could be further reduced if an electron beam facility with a less strong blower could be used.

## 6 Control checks during following years - changes and long-term stability of the consolidation

The consolidation treatment is controlled in two ways:

a. For the first time continuous weight measurements have been carried out on five of the fragments. The measurements show that there is a rapid weight loss during the first two to four weeks after electron beam treatment of 9 to 11 weight %. Afterwards the velocity of weight loss decreases: the fragments lost about another 1.5 to 3 % during the following 10 months.

b. During every work stay in China the fragments are controlled by visual and microscopic examination (until now: March 2001 and October 2001).

| *fragment no.* | *rapid weight loss* | | *weight loss during 11.5 months* | |
|---|---|---|---|---|
| | time after EB | weight loss in % | additional weight loss | total weight loss |
| 001/2000 | 1 month | 10.29 | 2.8 | 13.1 |
| 002/2000 | 2 weeks | 8.83 | 2.81 | 11.64 |
| 003/2000 | 1 month | 10.06 | 2.0 | 12.1 |
| 004/2000 | 1 month | 11.2 | 1.58 | 12.78 |
| 005/2000 | 1 month*<br>1 month** | 8.98<br>12.53 | 1.16<br>1.56 | 10.14<br>14.09 |
| 006/2000*** | | | | |
| 007/2000 | 1 month | 9.17 | 3.11 | 12.28 |

* F F-005/2000: calculated from the first weight measurement one week after irradiation; before the fragment was over the maximum limit of the scales (2 kg).
** F-005/2000: calculated with an average weight loss of 5.4 % during the first week
*** 006/2000 could not be controlled because its weight is more than 2 kg.

Tab. 1. Weight loss of the fragments treated in 2000

*6.1 Stability*

Also after one year the stability of the paint layer is still very good. Detached borders of the lacquer layer are very brittle now and tend to break off when touched.

*6.2 Cracks*

The first visual control in March 2001 showed that all the fragments have a fine system of micro-cracks that covers the whole lacquer layer. The two lacquer layers have developed a system of cracks independent from each other: the cracks are smaller and the system of cracks is finer in the first (lower) lacquer layer (F-001, 002, 003, 004, 005/2000), while the top lacquer layer shows less, but wider cracks.

These micro-cracks might have been there before treatment or might have developed during treatment. They obviously opened up in the dry climate of the winter (March 2001: ca. 30 % RH) and became more visible and prominent. In October 2001, at a humidity of about 70 % the cracks were still visible, but less disturbing. It is hard to decide if they got more in the meantime.

*6.3 Shiny spots*

Until October 2001, spots of shiny material coming out of the terracotta and forming out of the Plex, have developed on all fragments except F-007/2000. According to Rong Bo's observation the development of shiny spots started in April and became considerably more within one week (no documentation).

Different stages of development can be distinguished, starting with a slight darkening to small spots, followed by sticky, shiny spots until thick layers in form of "lakes" or drops of shiny, sticky material on the surface. The material comes out on the front (i.e. the polychromy), as well as on fracture edges. Different from the fragments treated in 1999 the shiny spots do *not* come out on the back.

The shiny material does not "flow" out on the lowest points of the fragments (i.e. where they lie on the supports), but obviously are pressed out of the terracotta. The worst damage with very big and thick shiny spots have developed on fragment 005/2000, followed by fragment 003/2000.

There seems to be a correlation between thickness of the terracotta and development of shiny spots: As thicker the terracotta is, as more shiny spots develop. The thick terracotta pieces seem to be a reservoir for the material from which the shiny spots emerge.

Furthermore there seems to be a correlation with some pigment layers: The green areas (malachite) are much more affected by the phenomenon than other areas. On F-003/2000 and 005/2000 the material comes out on the front only where the green is; the pink layer next to the green does not show the damage. However, thick drops of shiny material also form directly on the terracotta. This means that the existence of special pigments can favour the formation of these spots, but they are not necessary for the process.

Tests were made to remove the shiny material. Ethanol gave good results, solving the material completely. A small test was made on F-004/2000. On F-005/2000, the material was removed from the green collar which was totally covered with a thick layer of it. A test on the also thickly covered red ribbon caused a severe loss of pigment and was stopped.

## Tab. 2. Fragments treated in 2000 in Lintong - identification

| fragment no. | approx. max. size (cm) | location of excavation | | | date of excavation | description |
|---|---|---|---|---|---|---|
| | | pit | T G TA* | fig | | |
| F-001/00 | 14 x 7 | 2 | T5G1 TA 1 | a* | Oct. 24-27, 2000 | Part of a pink robe |
| F-002/00 | 15 x 13 | 2 | T21G20 | b* | Oct. 24-27, 2000 | Part of reddish brown robe |
| F-003/00 | 16 x 12 | 2 | T21G20 | b* | Oct. 24-27, 2000 | Part of collar (colour lost) and the neck part of the robe with a green stripe around the neckline and light pink next to it |
| F-004/00 | 24 x 14 | 2 | T5G1 TA 1 | a* | Oct. 24-27, 2000 | Part of armour with red ribbons and pink buttons. Adjoining to F-007/00 |
| F-005/00 | 17 x 23 | 2 | T5G1 TA 1 | a* | Oct. 24-27, 2000 | Part of green collar with neck part of armour with red ribbons and pink buttons, from the back of a soldier. Adjoining to F-006/00 |
| F-006/00 | 28 x 21 | 2 | T5G1 TA 1 | a* | Oct. 24-27, 2000 | Part of an epaulette with red ribbons and pink buttons with an area of the pink robe below the armour Adjoining to F-005/00 |
| F-007/00 | 9 x 6 | 2 | T5G1 TA 1 | a* | Oct. 24-27, 2000 | Part of armour with red ribbons and pink buttons. Adjoining to F-004/00 |

* T sector of excavation (areas of 20 x 20 m)
G corridor, running east to west, counted from south to north (pit no. 2: 1-14 and 15-20 (archers))
TA Test area, excavated in 1976

fig. a: charioteer with armour, F-002 and 003 come from the same or two different figures
b: standing archer without armour, F-001, 004, 005, 006, 007 belong to the same figure

## Tab. 3. Fragments treated in 2000 in Lintong - methods of treatment

| fragment no. | pre-treatment | | application of Plex | | | EB treatment | | | | | remarks/evaluation |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | cleaning | soaking with water | steps | conc. w% | duration (days) | times | kG *** | MeV | mA | CV (m/min) | |
| 001/2000 | before treatment (climate chamber) | before cleaning: 0.5 h<br>before application of Plex: 17 h | 1<br>2<br>3 | 33<br>60<br>80 | 2<br>4.5<br>2 | 1 | xx | 1 | 2.0 | 0.54 | test with 100 % after the 2nd step immediately led to the formation of cracks<br>EB: 08. 11. 00<br>*+ stable*<br>*- fine cracks everywhere*<br>*- shiny spots come out on the front*°° |
| 002/2000 | before treatment (climate chamber) | before cleaning: 3 h after cleaning | 1<br>2<br>3 | 33<br>60<br>80 | 1.5<br>2<br>2 | 2 | xx | 1 | 2.0 | 0.57 | Japanese paper in stripes<br>Plex sprayed on<br>not tested with Plex 100 %<br>EB: 15. 11. 00<br>*+ stable*<br>*- micro-cracks, brittle*<br>*+ only 2 small shiny spots on back*°° |
| 003/2000 | before treatment (climate chamber) | before cleaning: 3 h after cleaning: 17 h | 1<br>2<br>3 | 33<br>66<br>80 | 2<br>4.5<br>2 | 1*<br>1** | xx<br>xx | 1<br>1 | 2.0<br>2.0 | 0.54<br>0.57 | Japanese paper stayed in its place during 2nd and 3rd step of treatment<br>test with 100 % after the 2nd step immediately led to the formation of cracks<br>EB: * 08. 11. 00. ** 15. 11. 00<br>*+ stable, almost no shiny spots*°<br>*- paint layer damaged during cleaning and soaking*<br>*- big shiny spots have come out of terracotta (edges) and the green paint layer*°° |
| 004/2000 | before treatment (climate chamber) | before cleaning: 1 h, after cleaning | 1<br>2<br>3 | 33<br>60<br>80 | 1.5<br>3<br>2 | 2 | xx | 1 | 2.0 | 0.47 | details of treatment as F-002/2000<br>test with Plex 100 % caused separation of the lacquer layers, top layer bent upwards, rolled in<br>EB: 15. 11. 00<br>*+ polychromy stable*<br>*- some shiny spots of Plex*°<br>*- many shiny spots have come out of the terracotta (edges and front)*°° |
| 005/2000 | before treatment (climate chamber) | before cleaning, 18 h, after cleaning | 1<br>2<br>3 | 33<br>60<br>80 | 1.5<br>3<br>2 | 2 | xx | 1 | 2.0 | 0.47 | - details of treatment see F-002/2000<br>- test with Plex 100 % after 3rd (no cracks)<br>- EB: 15. 11. 00<br>*+ polychromy stable; very few and small shiny spots; brush stroke still visible*<br>*- many shiny spots on edges and front, worst of all fragments*°° |
| 006/2000 | before treatment (climate chamber) | before cleaning: 1.5 h | 1<br>2<br>3 | 33<br>60<br>80 | 1.5<br>3<br>2 | 2+1 | (60) | 1 | 2.0 | 0.47 | - not tested with Plex 100 % after 2nd step<br>- EB: 15. 11. 00<br>*+ polychromy stable*<br>*- some shiny spots of Plex*°<br>*- many small shiny spots on edges and front*°° |
| 007/2000 | before treatment (climate chamber) | before cleaning: 1.5 h and before treatment: 18 hours | 1<br>2<br>3 | 33<br>60<br>80 | 2<br>4<br>2 | 2 | (50) | 1 | 1.83 | 0.54 | - test with 100 % after the 2nd step immediately led to the formation of cracks<br>- EB: 08. 11. 00<br>*+ polychromy stable*<br>*- some shiny spots of Plex*°<br>*+ no shiny spots have come out*°° |

***kG the values indicated on the machine were not correct; true values between ca. 50 - 60 kG
° directly after electron beam treatment, November 2000
°° October 2001

## Fragments treated in 2000- before and after the consolidation of the polychromy

F-001/2000 before conservation (Oct. 30, 2000)

F-001/2000 after consolidation (Nov. 17, 2000)

F-002/2000 before conservation (Oct. 30, 2000)

F-002/99 after consolidation (Nov. 17, 2000)

F-003/99 before conservation (Oct. 30, 2000)

F-003/99 after consolidation (Nov. 17, 2000)

F-007/2000 before conservation (Oct. 30, 2000)

F-007/2000 after consolidation (Oct. 26, 2001)

F-004/2000 before conservation (Oct. 30, 2000)

F-004/2000 after consolidation (Nov. 17, 2000)

F-005/2000 before conservation (Oct. 30, 2000)

F-005/99 after consolidation treatment (Nov. 17, 2000)

F-006/2000 before conservation (Oct. 30, 2000)

F-006/2000 after consolidation (October 26, 2001)

# Evaluation of conservation treatments carried out between 1998 and 2000

Catharina Blaensdorf

## 1 Introduction

In 1996 the consolidation of the polychromy with PEG was tested for the first time on original fragments. The treatment with PEG was successful; for the first time, one of the consolidation methods was used on a larger scale: Up to now, several figures have been treated with this method.
In 1997 the treatment with acrylic monomers and hardening by electron beam irradiation was developed. The first tests on original fragments were conducted in 1998. The principles of both methods are described in several reports since 1996 and will not be repeated here[1]. The following text tries to draw preliminary conclusions on successes and problems of these conservation methods from observation of the fragments treated between 1998 and 2000[2] over a period of one to three years.

The fragments treated in the previous years are checked on every working stay in Lintong. Especially the fragments treated since 1998 are controlled regularly. Weight changes, changes of the visual appearance and the state of preservation were documented in May 1998[3], May 1999, March[4], October 2000, March and October 2001. Fragments treated in 1996 are also checked for changes and serve to compare the measurements carried out in 1998. The comparison of the fragments treated between 1998 and 2000 helps to evaluate the long-term effect of different conservation methods and materials. The two different methods already show different ageing problems.
The figures of kneeling archers from pit no. 2, T21G18 and the figures of acrobats from pit no. 9901, T1G3, which have been treated with PEG/ PU after their excavation in July 1999 as well as the figures of the civil servants from pit no. 0006, found and treated in 2000 and 2001. These figures are checked regularly as well. As the conservation treatment is not recorded very well, it is difficult to understand the visible phenomena in detail. Nevertheless, they show the possibilities and problems to treat whole figures with PEG and PU.

## 2 Problems around the conservation treatments

Except for the choice of consolidation treatment, the major problems that always occur are the storage of the fragments before treatment, the removal of the soil from the polychromy (‘cleaning’) and the storage of the fragments after treatment.

### 2.1 Mould growth and disinfection

Before the conservation treatment the fragments have to be stored at a high humidity, generally produced by placing them in a damp-tide box over a dish with water. In this environment of ca. 97 % RH, the growth of mould becomes visible after ca. six or seven days. The mould covers the surface of the fragments totally, but did not increase much between the 7$^{th}$ and 12$^{th}$ day after cleaning.[5]
The fragment F-005/98 had been stored in a climate chamber or the refrigerator between December 1998 and May 1999, but no mould occurred. The reason is not known.
In 1996 and 1998, tests were made to disinfect the fragments during storage, either using biocides

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1 See: Annual reports and work reports 1996/97, 1998 and this report 1999/2000; Arbeitsheft 83; on Plex/EB: dissertation thesis of Ingo Rogner, 2000

2 Between 1996 and 1998 all fragments have been consolidated with PEG (and an adhesive). In 1998 ten of the 13 treated fragments were consolidated with PEG /PU (10 fragments) and three fragments with the HEMA formulation Plex 6803-1 and electron beam (EB) irradiation. In 1999 and 2000 all fragments were treated with Plex / EB (1999: eight fragments; 2000: seven fragments).

3 Only the fragments treated in 1996/97. The first series of treatments during this period of the project was performed in October to December 1998.

4 Because of the limited time, in March 2001 the fragments could be checked only very roughly.

5 Observed on the fragments treated in 1999. No mould had occurred on F-005/99 which was treated with consolidants four days after cleaning the surface.

(1996) or 70 % ethanol (1998). In 1999 the fragments were not disinfected to test the effect of electron beams on the mould. In 2000 the fragments were soaked with consolidants before mould started to grow. If a disinfection seems necessary at all, a spraying with 70 % ethanol gives good results. The mould growth is stopped for 3 days, what mostly is long enough.

### 2.2 Removal of the soil from the polychromy

The fragments that have been used for conservation tests, were still covered with more or less soil when they were taken out of the excavation site. A layer of soil on top of the polychromy obviously serves as a protection for the lacquer layer, keeping the humidity and also giving a mechanical stabilisation to the sensitive paint layer. however, before the consolidation treatment, the soil has to be removed. Up to now, the removal of the soil was carried out in a glove box at a humidity of about 97 % RH with mechanical tools. The addition of water can soften the soil and temporarily enhance the adhesion of the lacquer layer to the terracotta.
To achieve a satisfying result, the removal of the soil has be conducted very carefully, and therefore is very time-consuming. The tools, as scalpel blades, paint brushes, wooden spatulas, bamboo sticks, always damage the surface of the paint layer slightly. Losses of smaller lacquer flakes and a losses of the surface structure of the pigment layer could not be avoided yet. Often remnants of soil or charcoal have to remain on the surface, because they cannot be taken off without loosing the paint layer underneath.
Nevertheless, the polychromy gives a satisfying impression after cleaning, as far as it is carried out very carefully. Variations of the method have been tested without showing major advantages. After all it seems the best to perform the removal of the soil before the consolidation treatment.

### 2.3 Condition of storage of the fragments after treatment

The conditions of storage after treatment have a considerable influence on the long-term stability of the consolidated fragments. The important aspects are the climatic conditions and the dust.
In Lintong, the fragments have been stored in drawers of the laboratory tables or in open dishes on the tables until spring 2000. Since then they are stored in climate chambers made of Plexiglas which either are closed or slightly open, but not air conditioned. The Plexiglas boxes protect them against the dust, but are not thought to produce a special climate. The built-in hygrometers in the boxes are out of function. The climate inside the boxes is almost the same as in the room.[6] Although the room where the fragments are stored now faces north and the curtains are more or less totally closed most of the time, daylight (and artificial) light reach the fragments. Until March 2001 the boxes had been placed near the windows. After the renovation of the laboratories, in October 2001 the boxes were put on the sides of the room. While the humidity inside the room climbed up to 80 % on very foggy days, the RH inside the boxes was much lower (about 60-65 % RH) and relatively stable.
The weather and outside climate has a noticeable influence on the room climate. The climate in the rooms on the south side does not differ much from those on the north side. The climate measurements were carried out in a laboratory room on the south side, which served as working room during the work stays. During these times the fragments treated in the previous years were also stored in the working room. The following table shows the results of climate measurements in the laboratory rooms, carried out during the work stays.

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[6] Measurements of October 24, 2000 (first day of work): The boxes were closed tightly. The RH inside the boxes was c. 60 to 70 %, inside the room it was 62 %.

| *month* | *temperature [°C]* | *RH [%]* | *remarks* |
|---|---|---|---|
| March (2001) | c. 20 | c. 30 | dry weather (room on the north side, heated) |
| May-June (1999) | c. 24<br>c. 31 | c. 62<br>c. 47 | rainy days (room on the south side)<br>sunny days (room on the south side) |
| Oct. (2000) | c. 16-17<br>c. 19.3 | c. 62-65<br>c. 40-42 | fine weather (room on the south side)<br>sunny days |
| Nov. (2000) | c. 16-17 | c. 42-47 | cold, after snow fall, room slightly heated (room on the south side) |
| Oct. (2001) | 17.4-19.2<br>c. 18 | c. 68-80<br>c. 55-62.5 | foggy or raining (room on the north side)<br>dry, sunny (room on the north side, not heated yet) |
| Oct. (2001) | 17.8-18.2 | c. 60-66 | inside the storage boxes (room on the north side, foggy or raining) |

Table 1. Climate conditions in the laboratory in Lintong during the last years

The control of the fragments in March 2001 showed that during the dry winter period the cracks open up, so the damage looks more dramatic. As the cracks partially close and bent up flakes flatten down at higher humidity, in March 2001 (after the last check in October 2000) it was difficult to decide if the damage really had become more. It seems that major changes especially happened during the warm and humid summers.

The storage in the Plexiglas boxes essentially reduced the amount of dust settling down on the surfaces of the treated fragments. The front cover should be kept slightly open to allow air to ventilate in the boxes and the evaporating Plex to escape into the room. The climate inside the boxes and in the room should be measured regularly over a longer period (i. e. one year). This would help to understand the range of climate changes the fragments have to stand and to investigate the influence of special climatic conditions on the formation of damages of the polychromy.

Several fragments were brought to Germany for examination with videoholography and Cryo-SEM. Since October 1999 the fragments 006/98, 007/98, 011/98, 012/98, 001/99 are in Germany for this purpose, since July 2000 additionally the fragments 005/98, 008/98; 003/99 and 006/99. Except for the long-term measurements with climate cycles and videoholography, they are stored in the room climate in Oldenburg or Bremen and are observed from time to time.
The climatic conditions in Bremen and Oldenburg are quite different from those in Lintong. There is no air conditioning, but there is less influence of the seasons in the Laboratory of the Museum. In Bremen the average values are bout 20 °C and 60 % RH, in Oldenburg the average humidity is about 40 % RH. The fragments 006, 007, 011 and 012/98 which have been stored in Oldenburg for a long time, are kept in a dissiccator over a salt solution producing 60 % RH.

The storage conditions for the figures with consolidated polychromy cannot determined easily. The kneeling archers and the civil servants remained inside the pit for a longer period or have been stored in temporary buildings or tents. The acrobats are stored in the storage room of the laboratory which has a large door to the outside which often is open. In 2001 some of the figures were exhibited in show cases or in the entrance hall of the new exhibition building. The climatic conditions are not measured there and can only be guessed roughly. Dust and changes of humidity are a visible problems for the kneeling archers still remaining inside pit no. 2.

## 3 Fragments treated with PEG / PU

After the first big test series in 1996 the aim of further tests was avoid some problems and to develop a standard method which could be used on most of the fragments. Several test series served to find out ideal parameters concerning: application method, duration of steps, concentrations of consolidants and type of adhesive.

### 3.1 Application of consolidants

The application method which gave the best results was using cotton wool compresses. To avoid the compress sticking to the surface, a separation layer is necessary. Firstly, Japanese paper was used. It was replaced by a perforated plastic foil. Both materials have their advantages and problems; both are in use now. The same type of application with cotton wool compresses and Japanese paper as separation layer was adopted for the method using acrylic monomers and electron beam treatment.

### 3.2 Duration of steps

Duration of the treatment and concentrations have to be chosen inbetween two different aims: To *apply enough* consolidant to provide a satisfying consolidation and to *reduce* the amount of consolidant as far as possible. To stabilise the lacquer as good and reliable as possible, the application of higher amounts of consolidants over a longer period is reasonable. On the other hand, a surplus of consolidant gives an unsatisfying visual impression and probably creates problems for the long-term stability.
The method developed since 1996 comprises a treatment in two or three steps with rising concentrations from 30 to 80 or 100 % PEG 200. The adhesive is added in the first step with 2-7.5 weight % of the mixture. Momentarily a polyurethane (PU) dispersion is used (40 % solid content). It gets insoluble in all suited organic solvents; ageing properties are not known. The duration of the steps should be longer than 1 day; 2 days seem sufficient.

### 3.3 Observations on treated fragments

The observation of the treated fragments over a period of at least two and a half years allow to draw some conclusions on the effect of the tested conservation method:

#### *3.3.1 Fragments treated in 1996 and 1997 (F-002, 003, 005a, 008/96)*

Three of the fragments treated in 1996/97 have been controlled since May 1998. No evident changes could be observed on F-002, 003 and 005a/1996. A small part of 002/96 (treated in Lintong in 1997) has broken off during transport; it appears damp and darkened. It is possible that detaching and cracks of the lacquer layer have become more in a microscopic range. As there are only very few microscopic photographs this is difficult to determine. No major changes could be detected since 1998.
According to the observations of Zhang Zhijun in 1998, the crack got wider on F-008/96.

#### *3.3.2 Fragments treated in 1998 (F-001, 002, 003, 004, 007, 008, 010, 012, 013/98)*

After the consolidation treatment the fragments have been checked in the laboratory in Lintong in May 1999, March and October 2000 as well as March and October 2001. In October 1999, the fragments 006/98, 007/98 and 012/98 have been brought to Germany for investigation; in July 2000 additionally the fragment 008/98 was brought to Munich. The observation allows to draw the following conclusions:

1. Fragments treated with *PEG without adhesive* remain extremely sensitive against changes of humidity and mechanical stress. The soft lacquer layer tends to bend and flake off as it is not fixed on the terracotta.

2. On the fragments treated in 1998 there is no visible difference concerning the stability between fragments consolidated with *PEG 400* and those consolidated with *PEG 200*.

3. *Weight measurements* showed a considerable weight loss during the first two months after the consolidation; during this time not bound water evaporates. A small decrease of weight over the last two years could be measured on most fragments. The weight now changes slightly in dependence on the RH inside the room, because of the hygroscopicity of the PEG. Tests with changes of the humidity carried out in 1998 showed that during a slowly performed raising of humidity from 65 to 90 % RH, the weight of the fragments increased between 3.16 to 5.86 w%; a change from 65 to 24 % RH caused a loss of weight of 2.4 %. Furthermore, PEG can move towards the surface and even drip out of the fragments at a high humidity, which would result in a weight loss. Unfortunately, some of the fragments have also broken or slightly damaged during transport.

4. On all fragments the amount of *cracks* and the *detaching* of lacquer flakes has increased since the treatment. The formation of cracks and detaching of flakes normally starts at the margins of the lacquer layer or at missing parts. The only fragment that does not show micro-cracks and detaching areas is F-007/98; it had been treated with PEG 200 for a long period. Even with videoholography no movements could be detected. The fragment does not loose weight anymore. The paint layer seems very stable, but the visual impression is not satisfying: the whole fragments appears damp, darkened, dull and fatty. The similarly treated fragment 010/98 appeared damp even at a very low humidity of c. 30 % RH (March 2001).
A special form of detaching can be observed on the fragment 013/98. The lacquer layer does not show cracks, but forms an increasing number of blisters all over the surface. F-013/98 is the only fragment to show this kind of damage.

5. Areas with thick *shiny adhesive films* on the surface tend to roll in because of their inner tensions and peels off together with the lacquer layer which sticks to it. The adhesive film looks like a rubber skin (“rubber skin effect”). Both tested adhesives, PU- and PA-dispersion, showed this effect. The PA can be reduced by solvents, but only with the danger of damaging the polychromy. The PU cannot be solved at all.

6. The *stability* and *adhesion* of the lacquer layer and *the visual impression* of the treated fragments depend a lot on the details of the method. The fragment tend to look damp and darkened by the PEG penetrated into the terracotta - or the lacquer layer starts to flake off if to little PEG was taken up. Nevertheless, some fragments show a very satisfying impression and a sufficient stabilisation of the lacquer.

7. The lacquer layer remains extremely sensitive to the *contact with liquid water*. A small drop of water on the surface, immediately leads to the flattening of buckling lacquer flakes. After drying, the lacquer flake is much more deformed than it was before.

## 4 Figures treated with PEG 200 / PU in Lintong since 1999

Based on the conservation tests, in 1999 a "standard method" was developed for the treatment of newly excavated figures in Lintong by Zhou Tie. It emerged from the different tests carried out from 1996 to 1998, but modifications also had to be made to use the method during the excavation inside the pits. The method is used since April 22, 1999, for the conservation of the polychromy of the kneeling archers in pit no. 2, T21G18.
The soil is removed before the conservation as far as possible without damaging the surface. Compared to the work in the laboratory the cleaning is rough. When the figures are transported to the laboratory a further cleaning and consolidation was carried out.
Before the consolidation, the surface is sprayed with water twice or three times until no more water is taken up by the lacquer/paint layer. The consolidation is a 3-step-treatment with PEG 200 and PU (1st step: 30 % PEG 200, 2.5 % PU, duration: 2 days; 2nd step: 60 % PEG, 1 day; 3rd step: 100 % PEG, 1 day). The application is performed by compresses, as far as possible, and spraying on the surface in the non-horizontal areas. Small perforated plastic bags with the soaked cotton wool inside are used as compresses. After the treatment the surfaces are dabbed off to reduce superfluous PEG. Compared to the test carried out in 1998, the duration of the step are very short and the concentration of the adhesive is very low.

### 4.1 The kneeling archers in pit no. 2

The six figures from T21G18, section of the kneeling archers, had been treated between April and July 1999 inside the pit. The treated areas are restricted to those which could be excavated and cleaned; the reverse of the figures and/or fragments remained inside the soil. In March 2000 the preserved paint layers appeared stable and aesthetically satisfying. Obviously it had been possible to avoid the damp impression and shiny spots as well as continuous detaching of the lacquer. Cracks could be seen in some parts, but they were rare. The lacquer layer was stable enough to be touched with fingers.
Three of the figures (fig. 1, 2 and 8) had been removed from the pit and transported into the laboratory. Figure 1 and 2 belong to the newly excavated figures, while figure 8 was excavated during an earlier excavation campaign. Remnants of polychromy have only on the back of the figure which was still lying in the soil. On the figures and 8 the polychromy showed problems with micro-cracks, bending up lacquer flakes (bowl-shaped and buckling) and detaching. The figure 2, which was taken from the pit together with figure 8 one week ago(later than figure no. 1), was not consolidated yet, but did not show any cracks, obviously because it was still humid enough. The humidity inside the room was very low. Bowls with water were set up in different corners to raise the moisture to 40 to 50 % RH.
In October 2000, all the figures showed severe problems of micro-cracks and detaching. Shiny spots and running-down drops showed a surplus of PU sprayed onto the surface. The surface of the polychromy is damaged from the cleaning (scratches, cuts and holes). The problems with cracks and detaching have increased during the year 2000 and were confirmed by Rong Bo on July 6, 2001.
One head, the so-called "green face" (head of figure 1), was cleaned and consolidated very carefully. As the conservation result is much better than on the figures, a very careful application of the conservation method obviously enhances the conservation results. In October 2001, small areas with cracks and detaching borders of lacquer flakes could be observed (i. e. on the back of the collar (neck), but the paint layer appears mainly stable. The head is now kept under a dust-tight Plexiglas cover and stored in the storage rooms in the basement of the laboratory.

### 4.2 The acrobats from pit 9901, T1G3

The acrobats had been excavated from a test section of pit no. 9901 in spring and summer 1999. The polychromy is only preserved in rather small areas, but there are also some larger areas where it is almost perfectly preserved (e. g. the skirt of the thick man). The lacquer layers and the pigment layer in all preserved areas, both are very thick layered compared to the terracotta army.
The polychromy had been consolidated with PEG /PU in the "standard method". There are no shiny spots and no damp looking areas. So far, no problems are visible, except for very few cracks which

seem not become more since 1999. This is especially surprising, because the figures are stored in a room which also serves as package room and has a large door to the outside which is open most of time during the day. The surfaces are dusty, they show some superficial scratches of recent origin, but no flaking off of the polychromy.

### 4.3 The civil servants from pit no. 0006

The pit was found in 2000 and excavated in a very short time. The twelve figures, originally standing side by side, now laying face-down in the soil and are broken into pieces. Compared to the terracotta army the polychromy is thinner and not performed as carefully and rich in detail. Lips and beards are not painted separately, but just show the pink incarnation. The cloth are painted less detailed as well. Large areas of the polychromy, especially the incarnations, are preserved rather well.
In November 2000, two of the figures (bodies) had been already glued together and their polychromy was consolidated. On four heads the polychromy was consolidated. The conservation of the polychromy was carried out with PEG 200/PU in three steps: 30 % PEG + 5 % PU; 60 % PEG, 100 % PEG. The duration of each step was two days. Compared to the “standard method” the concentration of the adhesive was higher and the duration of the 2$^{nd}$ ands 3$^{rd}$ step was longer. Over night the figures were covered with plastic bags. No mould occurred. The consolidants were applied by spraying or with compresses which were always applied wet. Where only little polychromy was remaining, the consolidant was applied with a paint brush. Spraying was used mainly for sensitive parts of the pigment layers. The other figures were excavated as far as possible, but the conservation treatment just started in spring 2001, after the winter period.
In March 2001 the two restored figures were standing inside the pit. Cracks and shiny spots could not be detected. The fragments appears unequally darkened by PEG, what disturbed the visual impression. The fragments of four more figures are stored in plastic bags in the shelves of the storage and work room inside the hall of pit no. 0006. Cleaning and treatment are performed without climate chambers by spraying the fragments with water or PEG. According to Rong Bo, also in July 2001, no problems with detaching and cracks have occurred.
In October 2001 two of the figures were exhibited in the “New Exhibition Hall” of the museum. They are standing in the basement of the entrance hall. Most of the colour is lost, except for the faces and the small instruments hanging on their belts.
Four of the figures (without the heads) are standing inside the hall of pit no. 0006. The terracotta partly is darkened from the use of PEG. The grade of darkening is different on the single fragments, so the figures look spotted. Three or four of the figures are still lying inside the pit. It does not look as if there is much polychromy left now.

## 5 Fragments treated with Plex 6803-1 (HEMA) and electron beam (EB) irradiation

The method was tested on original fragments for the first time in 1998. The parameters for the application of the consolidant are similar to the method using PEG. Additionally the suited parameters for the hardening had to be found. All fragments have been treated with an acrylic monomer formulation Plex 6803-1 (hydroxy-ethyl-metacrylate plus additives) and hardened by electron beam irradiation.

### 5.1 Application of the consolidant

The application of the consolidant is performed with cotton wool compresses and Japanese paper as separation layer. The difference between the two materials is that the Plex is not sticky, but less viscose. Using Japanese paper therefore gives less trouble. The loss of pigment particles which are washed away by the consolidant liquid is a bigger problem than when using PEG: The pigment layer gets very soft during treatment, the surface structure (i.e. brush strokes) tends to get lost, pigments are spread over areas where they do not belong.
The application of was enhanced every test series. The method developed is: spraying the surface with Plex solution; applying the dry Japanese paper in narrow strips; spraying again; applying the soaked cotton wool compress in several pieces. The Japanese paper is not exchanged during the steps of treatment.
On a part of a hand with a thick double layer of pink incarnation, was treated by dripping and spraying the Plex onto the surface. The result was not ideal.
There are still problems with fibres sticking to the pigment layer and loss of surface structure during soaking, but they could be reduced to a minimum for the fragments that do not have very thick pigment layers with very low cohesion.

### 5.2 Concentration and duration of steps - cracks forming during soaking

Concentrations and duration of steps in the beginning were chosen analogue to the treatment with PEG: 2 days for each step; rising concentrations from 33 to 100 % in three steps.
The three fragments treated in 1998 with this method did not show any problems, but in 1999 on all fragments the lacquer layer developed severe shrinking cracks when 100 % Plex was used. Tests under the microscope showed that the cracking happens within seconds after a drop of 100 % Plex is applied to the surface. The formation of cracks cannot be avoided by prolonging the duration of the second step (60 %). The concentration therefore was reduced to 90, than to 80 % Plex. One test was made to leave out the first step (F-002/99: 50 and 100 %); it did not show negative results.
The amount and size of the cracks did not only depend on the concentration of Plex, but also of the state of preservation of the lacquer layer. When the polychromy was continuous and showed only a few missing parts, the tension caused by the shrinkage resulted in big cracks and relatively big flakes in-between. When the polychromy already had a considerable amount of losses or did not form a continuous film in larger areas anymore, small cracks formed. This could mean that the actually used method works good on already quite damaged or on exceptionally stable lacquer layers.
Maybe the soaking pre-treatment could be performed in two steps, but the concentration must not be risen over 80 %, because otherwise the lacquer layer develops shrinking cracks. The fact that on some fragments the lacquer did not get shrinking cracks has to be seen as an exception.

### 5.3 Plex in combination with PEG

In 1999 the combination of PEG and Plex was tested: After a pre-treatment with PEG 200 the fragments were consolidated with Plex. This test was made to see if a pre-treatment with PEG, either as an old measurement or as first action inside the excavation site, would still allow a treatment with Plex. The tests did not show any negative, but also no noticeable positive effects for the conservation results. As PEG 200 is one of the additives to the acrylic monomer in the product “Plex 6803-1”, a negative effect was not expected.

## 5.4 Irradiation

The dose of the irradiation can be adapted by changing the energy, the transportation velocity, the voltage and the times of irradiation. Test with different parameters have been performed by Ingo Rogner to find a suitable adjustment of the machine. With different adjustments the polymerisation is controlled, i.e. chain length and cross-linking of the molecules, making the film sticky or hard, elastic-soft or brittle. The depth of penetration the electron beam determines the thickness of the polymerised layer and its level inside the terracotta.
The conservation test were made in two facilities (Xi'an and Dresden) which are of the same type and built by the same company, but are a little different in the design. The power of the machine in Lintong is higher; the transport mechanism is totally different. The transport mechanism of the facility in the Xi'an Radiation Research Center has a cooling air jet with the strong blow. The stream of air also reaches the fragments in the transport box and causes a drying out of the surface in the last minutes before the irradiation. This leads to an increase of cracks and detached areas. If Plex is dripped or sprayed on the surface directly before the irradiation to prevent the drying-out the risk of the formation of shiny spots and borders becomes high.
Shiny spots tend to form in depressions of the surface, caused either by the shape and design of the terracotta surface or by missing parts (holes) and remnants of soil (elevations) of the polychromy. Flat fragments show less problems with shiny spots than fragments with convex shape; fragments of the robe without structuring of the surface show less shiny borders than fragments of the armour.

## 5.5 Appearance directly after consolidation treatment

On all fragments the lacquer layer was stable after the irradiation, on some even the pigment layer is fixed to the fragment. The thickness of the hardened zone could be measured on fragments from which small parts of the terracotta have been broken off afterwards: The fragments 006/98, 011/98 and 001799 show a dark zone below the front surface of the fragment corresponding to the layer of hardened Plex. The thickness is about 0.8mm (F-001/99) to 1 mm (F-011/98).

The visual impression after treatment depends on the extent of cracks formed during soaking with Plex and the amount of shiny spots formed during irradiation. If these problem can be avoided, as it was possible in 2000, the visual impression is very good after treatment. One or two days after irradiation the fragments look dry; the pigment layer is matt. The appearance is better than on the fragments treated with PEG, because these tend to look damp, slightly fatty and dull.
Shiny spots which have formed on the surface cannot be removed with solvents, but just scratched off directly after treatment as long as the material is still containing some water. If there are shiny spots on the polychromy, nothing can be done. As the saturation of the materials and the degree of gloss are very high, shiny spots affect the impression a lot. On the light grey terracotta they appear almost black.

## 5.6 Control of the conservation success

### *5.6.1 Weight control*

Only in a zone of about 1mm the Plex is hardened during the irradiation. The not hardened Plex as well as the water remaining inside the terracotta should evaporate after the treatment. The evaporation from the surfaces is visible as "drying" after irradiation, taking about 24 hours.
The evaporation of remaining consolidant and water was controlled by checking the weight of the fragments. Continuous weight controls during and after treatment could been performed for the first time in the test series of 2000. The results are listed up in table 2.

| *fragment no.* | *rapid weight loss* | | *weight loss during 11.5 months* | |
|---|---|---|---|---|
| | time after EB | weight loss in % | additional weight loss | total weight loss |
| 001/2000 | 1 month | 10.29 | 2.8 | 13.1 |
| 002/2000 | 2 weeks | 8.83 | 2.81 | 11.64 |
| 003/2000 | 1 month | 10.06 | 2.0 | 12.1 |
| 004/2000 | 1 month | 11.2 | 1.58 | 12.78 |
| 005/2000 | 1 month*<br>1 month** | 8.98<br>12.53 | 1.16<br>1.56 | 10.14<br>14.09 |
| 006/2000*** | | | | |
| 007/2000 | 1 month | 9.17 | 3.11 | 12.28 |

* F-005/2000: calculated from the first weight measurement one week after irradiation; before the fragment was over the maximum limit of the scales (2 kg).
** F-005/2000: calculated with an average weight loss of 5.4 % during the first week
*** 006/2000 could not be controlled because its weight is more than 2 kg.

Tab. 2. Weight loss of the fragments treated in 2000

The weight decreases rapidly during two to four weeks after treatment. After the first month the weight loss happens much slower. On the fragments treated in 1999, no continuous weight checks could be performed, but the decrease of weight seems to follow the same principles as on the fragments treated in 2000. Although the weight loss is very slow now, the fragments treated in 1999 still loose weight. This seems to indicate that the evaporation of the Plex is taking place very slowly and that it is still not finished. There also still is a strong smell of Plex on the fragments and inside the storage boxes.

### *5.6.2 Micro-cracks*

On all fragments treated in 1999 and 2000, the lacquer layer shows a fine system of micro-cracks. It is noticeable that the fragments treated with PEG do not show this type of micro-cracks.
Micro-cracks and also bigger shrinkage cracks can develop before or during the consolidation treatment, but can also indicate a process of embrittling of the consolidant and the lacquer layer.

Micro-cracks and shrinkage cracks were observed on the fragments treated in 2000 already before the consolidation treatment[7]: We had the impression that the fragments were more dry than the ones from 1998 and 1999. The shrinkage cracks and detaching lacquer layers indicated that the fragments had slightly dried already. A measurement on the dry-appearing fragment F-002/2000 showed that the water content before treatment was 8.75-9.75 weight %. This corresponds to the value estimated for the fragments treated in 1998, but it has to be considered that the fragments were stored inside climate chambers at about 97 % RH: maybe they had already taken up water at the time of the first weight measurement.

The presence of micro-cracks before treatment could explain why the fragments treated in 1999 and 2000 showed a distinct net of cracks directly after treatment. As long as the lacquer is wet and swollen, micro-cracks are not visible. Furthermore, a microscopic examination was not possible before the consolidation treatment. Especially the red ribbons and the pink robe present on F-001/2000 and F-005/2000 showed a lot of cracks. The red ribbons on fragments treated in the previous years do not show cracks, at least not in this extent.

During treatment shrinkage cracks can develop by dehydration. The fragments treated in 1999 got these cracks when 100 or 90 % Plex was applied during the third step of treatment. In 2000 big shrinkage cracks could be avoided by using 80 %, but all fragments treated in 2000 show much more micro-cracks than the fragments treated in1999.

There is also a relation or the surface structure of the terracotta and maybe to the type of colour. The bent surface of the ribbons with deep incised lines show more cracks than flat surfaces. The pink of

[7] F-001/2000: one long shrinkage crack; F-002/2000: detaching lacquer layers

the robe on F-001 and 005/2000 shows a fine system of micro-cracks which is not present on the reddish brown robes.

The micro-cracks open up at low humidities and close again when the humidity rises. This could be documented very well with a series of micro-photographs. [8] The effect could be also seen on the fragments stored in Lintong: The micro-crack system was very prominent in March 2001 at a RH of about 30 % and much less visible in October 2001 when the RH was about 60 to 75 %. Therefore, it is hard to decide from occasional microscopic examination, if the micro-cracks get more.
The opening up and closing of the cracks depending on the humidity was observed and recorded with videoholography. The extent of the movements was much bigger than on the fragments treated in 1998 and the fragments treated with PEG. The experiment showed that on the fragment 011/98 which did not show any micro-cracks directly after treatment, a distinct net of micro-cracks developed during 50 climate changes. This net is now also well visible under the microscope. The experiment also proved that the extent of the cracks and the movements of the borders of lacquer flakes increase with every climate cycle.[9]

On several fragments the two lacquer layers develop a crack system independent from each other. The crack system of the lower layer appears much finer than the one of the top layer.[10]

These experiments and observations seem to indicate that the cracks get more because the brittleness of the Plex increases during extreme climate changes. The cracks might develop as a result from the stress of the movements of swelling and shrinking of the consolidant and the lacquer in dependence of the humidity. They might also form during longer dry periods, as the Plex and the lacquer cannot stand very low humidities very well.
In this context it would be interesting to know if a pre-treatment with PEG reduces the amount of cracks forming during ageing. This could not be investigated yet.

### *5.6.3 Shiny material coming out of the fragments after treatment*

There is a long-term damage on almost all fragments treated with Plex: Mostly after one summer period in Lintong, shiny spots start to come out of the terracotta. The damage starts with darkened areas without distinct borders, looking damp. Then dark, wet looking spots appear. The next step are shiny spots with a visible layer of material on the surface. The shiny material is soft and sticky in the beginning, but gets hard. If the material comes out on the front (polychromy), the lacquer layer is lifted by the material coming up from below. Little “craters” or “vulcanos” form, in one case the lacquer layer got wrinkles like a film of drying oil, i. e. linseed oil.[11]

On the fragments treated in 1998 (F-009 and 011/98), the Plex came out on the *front side* (i.e. the polychromy). The fragment 009/98 shows this damage in a very dramatic form.
On the fragments treated in 1999 the Plex came out on the *edges and backs* of the fragments, as if following the gravity. Some spots are *soft and sticky* (especially the ones on the back), others are *solid*.
Five of the seven fragments treated in 2000 show shiny, sticky spots on the *front* (polychromy) and *edges*, but not on back (Oct. 2001).[12]
No or only little Plex coming out of the fragments that are stored in Oldenburg or Bremen: 006/98 shows one small sticky spot on the back, but no spots on the surface of the polychromy, as the other fragments treated in 1998. The “craters” on 011/98 are very small compared to 009/98 and probably did not have become more since October 1999.

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8 Taken by Arne Kraft, University of Oldenbrug, Applied Optics Group

9 see: Investigation on fragments with consolidated polychromy with videoholography - detection of deformations of the lacquer layer during climate changes, p. XXX of this report.

10 F-007/99, F-002/2000, 003/2000. F-005/2000

11 F-009/98, violet strip of the collar. The wrinkles in a film of linseed oil develop because of the increase of volume of the oil film during drying.

12 No shiny spots on F-001 and 007/2000; worst damage on F-005/2000.

| date of treatment | position of spots | description of spots | observed for the first time | fragment no. | worst damage | no damage |
|---|---|---|---|---|---|---|
| stored in Lintong | | | | | | |
| Dec. 1998 | front | many, solid | March 2000 | 009/98 | 009/98: violet and green | |
| May 1999 | edges and back | sticky or solid | Nov. 2000 | 002, 004, 005, 007, 008/99 | 008/99: entire back covered | 005/98 |
| Nov. 2000 | front and edges | darkened zones sticky or solid | April (?) 2001 | 002-006/2000 | 005/2000: green and thick part of terracotta | 001/2000, 007/2000 |
| stored in Oldenburg | | | | | | |
| Dec. 1998 | front | small vulcanos | Oct. 1999 | 011/98 | | |
| | back | 1 sticky spot | August 2001 | 006/98 | | |
| May 1999 | none | --- | --- | 001, 003, 006 | | |

Tab. 3. Survey on damage of shiny spots coming out of the terracotta, state: November 2001

The shiny spots develop out of the not or not totally hardened Plex that remains inside the terracotta after irradiation. The mechanisms of the process and the composition of the material are still unknown. Theoretically a further polymerisation after the electron beam irradiation should not be possible. The investigation on this phenomenon will be subject for further research work.
There are some factors that seem to influence the formation of shiny spots:

*a. climate conditions*
Obviously the damage develops during the summer period, i.e. under humid and warm conditions.

*b. thickness of terracotta*
Thick terracotta fragments are much more damaged that thin fragments. This could explain why the fragments treated in 2000 are more affected than the ones treated before. It also explains why the thick fragments treated in 2000 show extreme damages, while the small, thin fragments are not affected.

*c. special pigments in the polychrome layers*
On several fragments the damage is much worse on special parts of the polychrome than on the rest of the fragment. Violet (F-009/98: Han Purple, azurite, malachite, cinnabar) and green (F-009/98, F-003/2000, F-005/2000) areas are specially affected. The shiny, sticky spots are covering these areas entirely while the surrounding is more or less unaffected. Nevertheless, thick shiny spots also formed on terracotta, lacquer or pigment layers of other colour (red, pink). Maybe the copper pigments favour the formation of the shiny spots, but they seem not to be necessary for the development of this damage.

*d. time of storage of Plex as monomer before use*
In 1998 and 1999 freshly delivered Plex has been used. In 2000, the rest of the material from 1999 was used. The damage is worse on the fragments treated in 2000 than on the ones treated in 1999.There is a possibility of a pre-polymerisation during storage. This could mean that it is not favourable to use Plex which had been stored for one year already. The material used in 2000 did not show visible changes, i.e. a higher viscosity. Possible changes during storage will be examined in the future.

*5. concentration and conditions during hardening*
The dose and the penetration depth of the electron beam current influence the thickness, hardness and the exact localisation of the hardened Plex film. The concentration of the Plex in the third step of treatment also influences the polymerisation properties. Thin fragments also heat up more during irradiation than thick fragments. The effect of these factors is still not known. The properties and the exact level of the hardened Plex film inside the terracotta might be responsible for the place where the shiny material comes out (i.e. if it comes out on the front or the back of the fragment).

Tests showed that there is a chance to reduce or even remove the shiny spots as long as they are still soft and sticky. Attempts to remove the spots with ethanol have been quite successful.

## 6 Comparison between the consolidation methods with PEG and with Plex/EB

In the moment the two method for the consolidation of the polychromy are developed and used parallel to each other. The treatment with PEG 200 and PU is used on freshly excavated figures since 1999, while the treatment with Plex / EB is still just tested on single fragments, i. e. in a laboratory scale.
Both methods have advantages and disadvantages; there are still problems to solve on both of them. Maybe they will be alternative methods for the treatment of the polychrome terracotta figures in future.

The situation before the consolidation treatment, i.e. the storage after excavation, the removal of the adhering soil and the microbial contamination are the same; they are not depending on the method going to be used.

The method of the pre-treatment, i. e. the application of the consolidant with compresses, is very similar. The problems that occur during this step of treatment are slightly different, depending on the method: When PEG and an adhesive (PU) is used, the cotton wool compress or the Japanese paper tend to stick on the surface. This does not happen when Plex is used, because it is not sticky. The treatment with Plex can cause shrinkage cracks, which does not occur if PEG is used. The low viscose Plex also tends to “dissolve” the pigment layer, resulting in a loss of surface structure and loose, “washed away” pigments spread over the polychrome surface. Shrinkage cracks and loss of cohesion of the pigment layer during soaking with Plex could be reduced in the tests carried out in 2000.

The stability and adhesion of the lacquer layer as well as the visual impression of the fragments after treatment depend on the treatment method in general, but also on the details of each particular performance.
Principally the treatment with Plex /EB produce a hard and brittle lacquer layer. The fragments always appear totally dry; terracotta and pigment layers are very light in colour. Compared to that, when PEG and PU are used, the lacquer layer gets less hard and less stable against mechanical stress (touching, scratching) and liquid water. The fragments always look slightly darkened, because the PEG and the attracted water produce a higher saturation of the surface as the Plex does. Nevertheless, the visual impression and the stabilisation effect of the method depend a lot on the way the treatment is conducted in detail: If treated too long, the fragments tend to look damp and darkened by the PEG penetrated into the terracotta; if treated too short, the lacquer layer cracks and starts to flake off, because too little PEG has been taken up. Some fragments and parts of figures therefore look disappointing, but there are also very convincing results: Especially the figures of the acrobats and the “Green Face” (head of figure no. 1 from pit no. 2, T21, G18) show a very satisfying impression and a sufficient stabilisation of the lacquer. The acrobats are standing in the storage and packing room under difficult and changing climate conditions, but the polychromy is stable.

Both methods have the problem of shiny spots formed by the consolidant, which are hard to avoid. The shiny PU-film on the surface is a problem during ageing as it tends to roll in and tear the polychromy underneath off from the terracotta. The shiny spots of Plex are very glossy and appear dark by saturation of the material (especially the terracotta). Both consolidants cannot be removed with organic solvents.

Both methods stabilise the lacquer layer, but not the pigment layer. The pigment layer stays sensitive against touching and wiping. Often it is slightly more stable when Plex was used.

One important fact for the performance is that the treatment with PEG can be conducted inside the pit or in the laboratory at any time without further planning, while the treatment with Plex requires the high-technological equipment of the electron beam facility and a well panned schedule, because the fragments have to brought and irradiated there after a certain period of pre-treatment (ca. six days). In the moment, the electron beam facility can be used only with problems, because the transport mechanism has been changed to irradiate plastic foils. Figures like the kneeling archers from pit no. 2, which cannot be removed from the pit after some days, probably could not be treated with Plex / EB, also if a facility was nearby and always ready for use.

The most problematic disadvantage of the treatment with Plex still are the damages forming after treatment, i. e. the formation of micro-cracks and shiny spots coming out of terracotta. The fragments treated with this method are sensitive against climate changes and periods with low humidities. Maybe they have to be kept inside air conditioned rooms or show cases. The micro-cracks and especially the formation of shiny spots have to be avoided.
On the fragments treated with PEG the lacquer layer is less hard and stable and tends to detach from the terracotta in single areas, but there are no major changes during ageing. there are no micro-cracks, maybe because the hygroscopic PEG attracts enough water to keep the lacquer soft and slightly swollen.

A possibility to reduce the problems caused by the consolidants, is to reduce the amount of consolidant as far as possible without reducing the consolidation effect. Tests focussed on suited types of compresses and the duration of soaking. Theoretically the not hardened Plex should evaporate from the fragments; in practice this only happens very slowly (if at all).
To understand how much consolidant remains inside the fragment an estimation was set up for three fragments, two of them being treated with Plex, one with PEG. The calculation shows that the fragment treated with PEG, after three years, still contains 25 weight % of consolidant and water. It is surprising that it not looking as damp as other fragments treated with PEG. One year after treatment the fragments treated with Plex still contain 13 or 18 weight % of consolidant (+ water). It is obvious that this is much more than the zone of 1 mm of hardened Plex film which was planned to remain inside the terracotta.

| | F-002/2000 - Plex** | 004/2000 - Plex** | 012/98<br>PEG 200 / PU*** |
|---|---|---|---|
| before treatment, stored at 97 % RH | 487.0 | 1527.5 | 295.2 |
| after soaking with water, ca. 2-3 h | 514.0 | 1537.5 | 301.71 |
| after 7 months, 52 % RH | | | 279.5 |
| after 11 months, 70 % RH | 450.0 | 1331.0 | |
| at 0 % RH (calculated) | 380.36 | 1137.75 | 223.26 |
| without treatment* at 70 % RH (3 %)<br>at 52 % RH (2 %) | 395.57 | 1171.88 | <br>227.7 |
| true weight, October 2001<br>= content of consolidant + water | 450.0<br>**18 %** | 1331.0<br>**13 %** | 279.5<br>**25 %** |

* method of calculation: calculated for grey fragments without polychromy: saturated with water = water content of terracotta 26 %; water content at 70 % RH: ca. 3 %, water content at 52 % RH: ca. 2 %
** treatment in Nov. 2000: 33/60/80; soaking time: 1.5/3/2 days; 2 x 50-60 kG, 1 MeV, 2 mA, CV 0.57 (002) and 0.47 m/min (005/2000); density of Plex (not polymerised): 1.07 g/cm$^3$
*** treatment in Nov. 1998: PEG 30 % + PU 7.5 % / PEG 60 / PEG 100; soaking time: 3/1/1 or 3 days, density of PEG 200: 1.124 g/cm$^3$

Table 4. Evaporation of consolidants after treatment

# 7 List of fragments treated between 1998 and 2000

## 7.1 Fragments treated with PEG and adhesive in 1998 (F-001, 002, 003, 004, 007, 008, 010, 012 and 013/98)

**001/98** - PEG 400 (1 and 3 steps) / PU
*Evaluation directly after treatment*: stable, but visually not satisfying because of adhesive film on the surface
*Checked*: May 1999, March 2000, October 2000, March 2001, October 2001
*State of preservation and detected damages*: Detaching of the lacquer layer has increased from 1998 to 1999, 1999 to 2000, maybe also from 2000 to 2001. The number and size of the cracks has increased between 1998 and 2000, maybe also in 2001. 'Rubber skin effect': detected in 1999-2000: the adhesive film on top of the surface is too thick, the lacquer rolls up because of the tensions of the adhesive film. October 2001: no visible changes.
*Weight control*: weight stable since Dec. 23, 1998 (6 weeks after treatment)

**002/98** - PEG 400 (2 steps) / PA
*Evaluation directly after treatment*: consolidation effect and visual impression not satisfying
*Checked*: May 1999, March 2000, October 2000, March 2001, October 2001
*State of preservation and detected damages*: Between 1999 and 2001 the state of preservation did not change much. The thick adhesive layer causes a not satisfying visual impression, but the pigment layer is stable against touching and wiping. 'Rubber skin effect': On one of the ribbons the thick adhesive layer is shiny and starts to bend up and roll in. In October 2000 the formation of cracks had increased, starting at losses in the lacquer layer and matt areas. Single flakes have detached totally. October 2001: no visible changes.
*Weight control*: weight stable since May 1999

**003/98** - PEG 200 (3 steps) / PU
*Evaluation directly after treatment*: consolidation and visual impression okay / mediocre
*Checked*: May 1999, March 2000, October 2000, March 2001, October 2001
*State of preservation and detected damages*: Between 1999 and October 2000 the number of detaching areas had increased. In March 2001 no visual changes could be detected. Compared to the other fragments treated in 1998, the state of preservation is relatively good. The lacquer layer does not visible micro-cracks. October 2001: dusty, no visible changes.
*Weight control*: weight probably stable since May 1999. The lower weight measured in March 2001 might have been due to the very low RH at that time (30 %, compared to 65 % in Oct. 2000).

**004/98** - PEG 200 (1 step); (PA)
*Evaluation directly after treatment*: failure
*Checked*: May 1999, March 2000, October 2000, March 2001, October 2001
*State of preservation and detected damages*: The conservation treatment can be regarded as failure. The lacquer layer is deformed, detaches and bends upwards. As this treatment is not of any interest for further treatments, so detailed examination was carried out since May 1999. October 2001: no visible changes.
*Weight control*: weight stable since May 1999 (very slowly decreasing since then).

**007/98** - PEG 200 (3 steps, long time) / PU
*Evaluation directly after treatment*: visually not satisfying, but stable
*Checked*: May 1999, August 2001 (Oldenburg)
*State of preservation and detected damages*: Since 1998 no changes have been detected, the paint layer seems very stable. It does not show any cracks. No movements could be detected with videoholography. The visual impression is poor, because the fragment appears damp and darkened.
*Weight control*: Weight stable since Dec. 23, 1998 (six weeks after treatment)

**008/98** - area A: PU / PEG 400 ($2^{nd}$ step); area B: PEG 200 (2 steps)
*Evaluation directly after treatment*: evaluation directly after treatment: area A: consolidation effect good, shiny spots; area B: not stable enough
*Checked*: May 1999, (March 2000), in Oldenburg until August 2001
*State of preservation and detected damages*: The lacquer layer is not stable in area B. The detaching and buckling of the lacquer flakes increased between Dec. 1998 and May 1999. A consolidation without an adhesive seems not possible. In area B no changes seemed to have taken place. In July 2000 the fragment has broken into two pieces during the transport to Germany. In August 2001, both areas of treatment showed several detaching lacquer flakes. A difference between the treatment zones is hardly visible.
*Weight control*: Weight stable since May 1999

**010/98** - PEG 200 (3 steps, long time) / PU
*Evaluation directly after treatment*: visually not satisfying
*Checked*: May 1999, March 2000, October 2000, March 2001, October 2001
*State of preservation and detected damages*: The paint layer and the terracotta are darkened by a surplus of PEG. After losses on the borders of the lacquer right after the treatment and during the following six months, no changes seem to have occurred (since May1999). The lacquer layer does not show many micro-cracks, but the visual impression is not satisfying. In March 2001 the detached border zones of the polychromy partly flaked off. Even at a RH of 30 % the fragment appears to be damp. In October 2001 a small part of the broken-off area had got lost.
*Weight control*: No weight loss since May 1999.

**012/98** - PEG 200 (3 steps, pre-treatment: soaking with water) / PU
*Evaluation directly after treatment*: good
*Checked*: May 1999 (Lintong), February 2000 (Oldenburg), August 2001 (Oldenburg)
*State of preservation and detected damages*: The amount of cracks and detaching has increased between May 1999 and February 2000. In August 2001 no changes could be observed.
*Weight control*: weight stable since the end of December 1998 (six weeks after treatment)

**013/98** - PEG 200 ($1^{st}$ step), PEG 400 ($2^{nd}$ and $3^{rd}$ step) / PU
*Evaluation directly after treatment*: consolidation and visual impression good
*Checked*: May 1999, March 2000, October 2000, March 2001, October 2001
*State of preservation and detected damages*: In Oct. 2000 blisters had been detected in one area, not much difference in the other areas. In March 2001 a thicker adhesion film on the surface in a depression close to the ribbon started to roll in (rubber skin effect). Along the borders, the lacquer detaches and partially flakes off. It seems to be soft and flexible. A bigger flake fell off, when the fragment turned to the side during examination. The upper lacquer layer seems to detach from the lower one. In Oct. 2000 the lacquer layer showed blisters in some areas without cracks. The amount of the blisters had increased in October 2001.
*Weight control*: weight stable since May 1999

## 7.2 Fragments treated with Plex 6803-1 / EB

### 7.2.1 Fragments treated in 1998 (F-006, 009 and 011/98)

**006/98** - 3-step-treatment, 30/60/100; 1 x 25 kG, 1 MeV, 0.6 mA
*Evaluation directly after treatment*: consolidation good, no shiny spots
*Checked*: May 1999
*State of preservation and detected damages*: The lacquer layer is stable. No changes could be detected since 1998. In August 2001 one spot of sticky Plex was detected on the back, but there is no Plex coming out of on the front side (i.e. the polychromy) as it has been observed on the other fragments treated in 1998.
*Weight control*: The weight was stable in May 1999. Because a sample has been cut off from the fragment the lower weight measured in July 2001 cannot be evaluated.

**009/98** - 3-step-treatment, 30/60/100; 4 x 29 kG, 1 MeV, 4.2 mA
*Evaluation directly after treatment*: consolidation good, no shiny spots
*Checked*: May 1999, March 2000, October 2000, March 2001, October 2001
*State of preservation and detected damages*: No changes could be detected at the first check in May 1999. In March 200o shiny spots had come out on the polychromy, especially the violet strip and the green button. According to Zhou Tie, the damage was first observed in July 1999 and became worse in July 2000.
An increase of this damage could clearly be documented in October 2000 and in March 2001. In October 2000 and 2001 tests were made to remove the shiny film from the surface of the violet strip of the collar.
*Weight control*: The weight did not decrease since November 2000 and nearly not since May 1999. Obviously the Plex is evaporating from the terracotta very slowly, if at all.

**011/98** - 3-step-treatment, 30/60/100; 3 x 20 kG, 1 MeV, 4.2 mA
*Evaluation directly after treatment*: consolidation and visual impression very good, no shiny spots
*Checked*: May 1999 (Lintong), August 2001 (Oldenburg)
*State of preservation and detected damages*: No changes have been detected until October 1999. Little shiny drops coming out of the lacquer have been detected in Oldenburg in October 1999. The damage did not increase during the following two years.
*Weight control*: weight stable since the end off December 1998 (six weeks after treatment)

## 2.2 Fragments treated in 1999 (F-001, 002, 003, 004, 005, 006, 007, 008/99; F-005/98)

**001/99** - 3-step-treatment, 33/66/100; 1 x 60 kG, 1 MeV, 2.0 mA
*Evaluation directly after treatment*: polychromy stable, many shrinkage cracks from soaking, no shiny spots
*Checked*: May 1999 (directly after treatment; in Oldenburg since October 1999), August 2001 (Oldenburg)
*State of preservation and detected damages*: No documentation directly after treatment; August 2001: No shiny spots are coming out of the terracotta after the treatment. Besides the big cracks which had developed during the soaking with Plex, almost the hole polychromy shows a system of micro-cracks. A small part has been cut off (sawn off) superficially for investigations with Cryo-SEM and thin sections in Bremen. The fracture edge reveals that the zone of hardened Plex is about 0.8 mm thick (looks dark grey).
*Weight control*: The weight has decreased about 8% between June 1999 (one week after treatment) and July 2001, but a small sample of the terracotta has been taken for examination in the meantime.

**002/99** - 2-step-treatment, 50/100; 2 x 45 kG, 1 MeV, 4.2 mA
*Evaluation directly after treatment*: polychromy stable, many big shrinkage cracks from soaking, no shiny spots
*Checked*: March 2000, October 2000, March 2001, October 2001
*State of preservation and detected damages*: The polychromy appears mainly stable. On few spots the borders of lacquer flakes tend to break off. Until March 2001 a system of micro-cracks had developed which could not be detected in October 2000. Since October 2000 shiny spots have come out on sides and back of the fragment. On the back they are still sticky. The seize of the spots has increased between March and October 2001. The spot on the back (ca. 1 g of material) was taken off on Oct. 30, 2001, for investigation of the material.
*Weight control*: The weight has decreased about 7% between June 1999 (one week after treatment) and March 2001. Since October 2001 the weight loss seems to continue very slowly (Oct. 2000 to March 2001: 0.35 %).

**003/99** - 3-step-treatment, 33/66/80; 1 x 60 kG, 1 MeV, 2.0 mA
*Evaluation directly after treatment*: polychromy stable, less cracks than fragments treated with 100 % Plex, some deformations of lacquer, no shiny spots
*Checked*: March 2000 (Lintong), July 2000 (Munich), August 2001 (Oldenburg)
*State of preservation and detected damages*: The polychromy appears mainly stable. In March 2000 a system of micro-cracks has been detected especially in the centre of the fragment. August 2001:There is no shiny material coming out of the terracotta. The lacquer layer appears brittle; number and size of cracks seems to have increased, one area shows detaching lacquer flakes. On August 15 the fragment was taken back to Munich and stored in the laboratory.
*Weight control*: The weight loss between June 1999 (one week after treatment) and July 2001 is about 12.9 %.

**004/99** - 2-step-treatment with PEG 200 (30/60) and 3-step-treatment, 33/66/100; 1 x 60 kG, 1 MeV, 2.0 mA
*Evaluation directly after treatment*: polychromy stable, no bigger shrinkage cracks, no deformation, no shiny spots
*Checked*: March 2000, October 2000, March 2001, October 2001
*State of preservation and detected damages*: In March 2000 fine micro-cracks have been detected, extending over the whole polychromy and forming a coherent system in some areas. In October 2000 sticky spots of shiny Plex were observed on two if the edges of the fragment. The situation did not change between October 2000 and March 2001. In October 2001 the shiny spots had become a little bigger, but no new spots had developed. The polychromy did not show any changes; the micro-cracks are less visible because of the higher humidity.
*Weight control*: Between June 1999 (one week after treatment) and March 2001 weight loss of about 7.65 %, between October 2000 and March 2001 only 0.48 %. No weight loss between March and October 2001.

**005/99** - 1st step PEG 200, 30 %, 2-step-treatment with Plex, 66/90; 1 x 60 kG, 1 MeV, 2.0 mA
*Evaluation directly after treatment*: polychromy stable, many shrinkage cracks, but almost no micro-cracks; no deformation, shiny inside cracks; pigment layer damaged by cleaning with too much water.
*Checked*: March 2000, October 2000, March 2001, October 2001
*State of preservation and detected damages*: The situation of the polychromy did not change since June 1999. In October 2000 shiny spots were observed on the edges and the back of the fragment. The situation did not change between October 2000 and March 2001. The spots have become more between March and October 2001, some also coming out on the front (on the fracture edge no. 4). A small green particle on top of the polychromy is surrounded by a “lake”, as if the green had “attracted” the shiny material to come out.
*Weight control*: Total weight loss between June 1999 (one week after treatment) and March 2001: 11.4 %, between October 2000 and March 2001: 0.36 %. No weight loss since March 2001.

**006/99** - 3-step-treatment with Plex, 33/66/80; 1 x 60 kG, 1 MeV, 2.0 mA (same as F-003/99)

*Evaluation directly after treatment*: polychromy stable, many shrinkage cracks, but almost no micro-cracks; no deformation, shiny inside cracks; pigment layer damaged by cleaning with too much water.

*Checked*: March 2000 (brought to Oldenburg in July 2000), August 2001 (Oldenburg)

*State of preservation and detected damages*: The situation of the polychromy did not change since June 1999. In October 2000 spots of shiny Plex were observed on the edges and the back of the fragment. The situation did not change between October 2000 and March 2001. In August 2001 there were no shiny spots or drops of Plex coming out of the terracotta.

*Weight control*: Total weight loss between June 1999 (directly after treatment) and July 2001: 6.3 %. Weight change between situation after cleaning to directly after irradiation: + 2.43 %, to July 2001: - 4 %

**007/99** - 3-step-treatment with Plex, 33/66/100; 2 x 50 kG, 1 MeV, 2.0 mA (same as 1998)

*Evaluation directly after treatment*: polychromy stable, many big shrinkage cracks with deformed borders; shiny inside cracks and in depressions of the terracotta.

*Checked*: March 2000, October 2000; March 2001, Oct. 2001

*State of preservation and detected damages*: The situation of the polychromy did not change since June 1999. In October 2000 shiny and sticky spots were observed on the edges and the back of the fragment. This phenomena maybe increased between October 2000 and March 2001. A system of fine cracks was detected in March 2001, especially in the first lacquer layer. During the summer 2001 (between March and October) the amount and seize of the shiny spots on the edges and the back of the fragment has increased considerably.

*Weight control*: Weight changes compared to weight after cleaning: + 1.4 %; weight loss between June 1999 (one week after treatment) and March 2001: 7.7 %. No weight loss after March 2001 anymore.

**008/99** - 3-step-treatment with Plex, 33/66/100; 1 x 60 kG, 1 MeV, 2.0 mA (same as F-001/99 and fragments 1998)

*Evaluation directly after treatment*: polychromy stable, many shrinkage cracks, but mainly small cracks; no shiny spots and borders, not shiny inside cracks. Compared to F-001799 less big (wide and long) cracks.

*Checked*: March 2000, October 2000; March 2001, October 2001

*State of preservation and detected damages*: The situation of the polychromy did not change since June 1999. In October 2000 a system of micro-cracks has been detected in the area of the robe. Spots of shiny Plex have been observed on the edges and the back of the fragment. The back of the fragment is almost covered with Plex coming out of the terracotta. The situation did not change between October 2000 and March 2001. In October 2000 a test was made to reduce or remove the Plex from the back. The removed material was used for analysis. In October 2001, on the back of the fragment different solvents (ethanol, acetone, ethyl acetate) have been tested to remove the soft,. shiny spots. Ethanol gave the best results.

*Weight control*: Total weight loss between June 1999 (one week after treatment) and March 2001: 7.6 %. Weight change between situation after cleaning to: a. directly after irradiation: + 1.9 %, b. March 2001: - 10.8 % (1.5 g of hardened Plex have been taken off from the back in October 2000).

**005/98** - 3-step-treatment with Plex, 33/66/100; 4 x 60 kG, 1 MeV, 2.0 mA (same as 1998); Plex dripped onto the fragment (no compresses)

*Evaluation directly after treatment*: polychromy stable, only a few cracks, many shiny spots, also inside cracks, especially on the inner side of the hand; structure of pigment layer lost by soaking. The four times of irradiation, necessary because of the shape and the two polychrome sides of the fragment (back and inner side of the fingers), showed no negative side effects.

*Checked*: March 2000, July 2000 (Munich; brought to Oldenburg in July 2000)

*State of preservation and detected damages*: No changes could be detected until July 2000.

*Weight control*: Total weight loss between June 1999 (directly after treatment) and July 2001: 6.3 %. Weight loss between June 1999 (directly after irradiation) and July 2001: 6.4 %

### 7.2.3 Fragments treated in Nov. 2000 (F-001, 002, 003, 004, 005, 006, 007/2000)

**001/2000** - 3-step-treatment with Plex, 33/60/80; 1 x xx? kG, 1 MeV, 2.0 mA; soaking with water before treatment; test with 100% produced severe shrinking and cracking of the lacquer layer

*Evaluation directly after treatment*: one long shrinkage crack had already developed before the treatment. After the treatment the polychromy was stable; one week after the treatment there still was a dark, wet looking zone along the borders of the fragment. A system of fine shrinkage cracks is visible everywhere: from soaking or already before treatment ?, two shiny spots of hardened Plex on two edges of the front.

*Checked*: March 2001, October 2001

*State of preservation and detected damages*: No change could be detected in March 2001. In October 2001 dark areas along the edges indicated that shiny material starts to come out on the front side. No shiny spots on the back and edges. The stability of the polychromy did not change.

*Weight control*: Weight increased about 1 g between the state before treatment and directly after EB irradiation. Biggest weight loss (10%) during the first month after treatment. Further slow weight loss afterwards (additionally 3 % during the following 10 months.)

**002/2000** - 3-step-treatment with Plex, 33/60/80; 1 x xx? kG, 1 MeV, 2.0 mA; soaking with water before treatment; test with 100% produced severe shrinking and cracking of the lacquer layer

*Evaluation directly after treatment*: There were blisters and detached areas already before the treatment; the lacquer layers tended to separate from each other. Remnants of soil had to be left on the surface, because they could not be removed without loosing the polychromy. After the treatment the polychromy is stable. A system of fine cracks is visible everywhere; it is finer than on F-001/2000; the lower, brown lacquer layer shows a finer system of cracks. Two shiny spots of hardened Plex on two edges of the front and shiny inside cracks.

*Checked*: March 2001, October 2001

*State of preservation and detected damages*: The state of preservation of the polychromy did not change. Until October 2001 two small shiny spots came out of the terracotta on the back (on the spots where the fragment lies on).

*Weight control*: Before treatment about 8.75-9.75 weight % of water content; after irradiation ca. 14 weight of liquid content. Rapid weight loss stopped two weeks after treatment (loss of 8.83 % of weight); slower weight loss during the following 10 months (until Oct. 2001: 11.64 %).

**003/2000** - 3-step-treatment with Plex, 33/60/80; xx? kG, 1 MeV, 2.0 mA, 2 times with one week in between; soaking with water before treatment; test with 100% produced severe shrinking and cracking of the lacquer layer

*Evaluation directly after treatment*: The polychromy of the collar had already been lost almost totally. The treatment concentrated on the part of robe (green strip and light pink). After the treatment the polychromy is stable. A system of fine cracks is visible everywhere; the lower, brown lacquer layer shows a finer system of cracks. There are small shiny spots of hardened Plex inside depressions of the front and one of the edges.

*Checked*: March 2001, October 2001

*State of preservation and detected damages*: In March 2001 small dark spots had appeared on the one of the fracture edges (thickest part of the terracotta). October 2001 on this area there were very big shiny spots. The green strip appears darkened by shiny material starting to come out.

*Weight control*: Weight loss during the first month c. 10 %; slower weight loss during the following 10 months (until Oct. 2001: 12.1 %).

**004/2000** - 3-step-treatment with Plex, 33/60/80; 2 x xx? kG, 1 MeV, 2.0 mA; soaking with water before treatment; test with 100% Plex did not produce cracks, but the lacquer flakes bent upwards, separation of the lacquer layers

*Evaluation directly after treatment*: Most of the lacquer layer has been lost; it is only preserved where it still was covered with soil; the parts with pigment layer (ribbon, buttons) are better preserved. The lacquer was very sensitive before treatment. After the treatment the polychromy was stable. Shiny borders had formed in all depressions of the surface, inside cracks and along the borders of the lacquer flakes.

*Checked*: March 2001, October 2001

*State of preservation and detected damages*: In March 2001 no changes had been detected. October 2001 a lot of small and some bigger shiny, sticky spots were detected on the front and on three of the edges. A test was made to reduce the shiny material with ethanol.

*Weight control*: Weight loss during the first month 11,2 %; slower weight loss during the following 10 months (until Oct. 2001: 12.78 %).

**005/2000** - 3-step-treatment with Plex, 33/60/80; 2 x xx? kG, 1 MeV, 2.0 mA; soaking with water before treatment; test with 100% Plex after the third step did not produce cracks

*Evaluation directly after treatment*: Before the treatment the lacquer layer was very sensitive against changes of humidity and started to detach and bend upwards. After the consolidation treatment the polychromy was stable. The brush strokes in the green are still visible.

*Checked*: March 2001, October 2001

*State of preservation and detected damages*: In March 2001 no changes had been detected. In October 2001 a lot of small and some bigger shiny, sticky spots were detected on the front and on the edges - worst damage of all fragments. The material was removed on the green with ethanol. On the red this lead to a loss of the polychromy.

*Weight control*: Weight control started one week after EB, because before the fragment's weight was above the maximum limit of the scale (2 kg).

**006/2000** - 3-step-treatment with Plex, 33/60/80; 2 x one side + 1 x second side, xx kG, 1 MeV, 2.0 mA; soaking with water before treatment; not tested with 100% Plex

*Evaluation directly after treatment*: After the consolidation treatment the polychromy was stable. There are shiny spots in depressions of the surface (borders of armour plates) and inside cracks

*Checked*: March 2001, October 2001

*State of preservation and detected damages*: In March 2001 no changes had been detected. In October 2001 a lot of small shiny, sticky spots were visible on the front and on the edges.

*Weight control*: No weight control, because the weight is above the maximum limit of the scale (2 kg).

**007/2000** - 3-step-treatment with Plex, 33/60/80; 2 x xx? kG, 1 MeV, 2.0 mA; soaking with water before cleaning and 18 h before consolidation treatment; test with 100% Plex after the second step produced sever cracks immediately

*Evaluation directly after treatment*: The polychromy is stable. The fragment had a wet looking border for more than one week after EB. The red of the ribbon shows fine shrinkage cracks. There are shiny spots in the depressions of the surface.

*Checked*: March 2001, October 2001

*State of preservation and detected damages*: No changes were detected in March 2001 and October 2001. The whole lacquer layer shows a fine system of micro-cracks.

*Weight control*: Weight loss after irradiation: 9.17 % during the first month, 12.28 % during 11 month after irradiation.

# Investigation on fragments with consolidated polychromy with videoholography - detection of deformations of the lacquer layer during climate changes

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## 1. Introduction

The following report deals mainly with investigations on those terracotta fragments which were brought to Oldenburg during a visit of our partners from China and from the “Bayerisches Landesamt für Denkmalpflege” (BLfD) in October 1999. The reference numbers of the fragments are: F006/98, F007/98, F011/98, F012/98 and F001/99 (in the following text Charge1). Since August 2000 the fragments a second charge of fragments brought to Oldenburg was investigated. The specimens were labelled as: F005/98, F008/98, F003/99 and F006/99 (in the following text Charge2). Photos of the fragments with marked investigation areas can be seen in Fig. 3 – 9. They were taken before the deformation measurements were performed.
As agreed during the visit in Oldenburg in October 1999 the following investigations with videoholography were performed:

1. The behaviour of all fragments during two humidity cycles of ambient air were measured. The cycles were nearly the same as they have been used during the first deformation measurements in December 1998 on the fragments F011/98 and F012/98. This has been done to get information about the ageing of the different ways of conservation.
2. Deformation measurements on special fragments were performed after 50 humidity cycles (in the following text long term measurement), to study the development of cracks and eventually to make predictions about further damages.

It was agreed that a few small probes could be taken from the fragments to perform Cryo-SEM investigations at the “Materialprüfungsanstalt” (MPA) in Bremen. The results are reported in detail by the MPA.

At the time Charge2 arrived in Oldenburg again a measurement on all fragments during two humidity cycles were performed to get information about the condition of all fragments.

In Chapter 5 a further development of our measurement method will be described. With this development it is possible to investigate the deformation of every single layer in a multi-layer structure and even get information about the distance between the single layers.

## 2. Short description of measurement principles

To determine the deformations the technique of Videoholography (or Electronic Speckle Pattern Interferometrie; ESPI) is used. The set-up and special characteristics are fully explained in the diploma thesis of Akram El Jarad and in [1]. All investigations are made through a microscope. The fragments are placed in a small climatic chamber, in which the humidity can be adjusted by a PC. All investigated areas in the following text are 1,2 mm x 1 mm in size unless specially mentioned.

## 3. Results

### 3.1 Fragments treated with Plex 6803-1 (HEMA)

First measurements were performed on the Plex-treated fragments F006/98, F011/98 and F001/99. This happened between the 8th and the 29th of December 1999. All fragments were stored in the laboratory in the same manner at a relative humidity of approximately 40% and by this had the same starting conditions.
They were exposed to two cycles of humidity changes of the ambient air while the occurring deformations where measured by videoholography simultaneously. The change in humidity in the climatic chamber is plotted in Fig.1 on page 7 versus measurement time. This change in humidity was nearly reproduced for every further measurement and is almost the same condition that was used for the measurements on fragment F011/98 and f012/98 in December 1998.
After these first measurements, which were performed in the same manner on PU/PEG treated fragments (Chapter 3.2), the above mentioned long term measurement of the fragments F011/98 and F012/98 took place. Before and after 50 humidity cycles the deformations of the fragments were measured. To be sure the results are typical and reproducible on every fragment two regions were measured two times before and two times after the long term measurement.
As a result it could be seen that both of the two measurements showed nearly the same deformations. The results are presented in the following text:

**Fragment F011/98**
First deformation measurements on this fragment were performed in December 1998. The results of this experiment are reported in the "Work Report 1998". At that time during a humidity change from 30% to 90% relative humidity (rh) a very complex deformation structure occurred. The investigated area showed up separated in several nearly circular regions with diameters of 100-200 µm. These regions underwent bowl-shaped deformations. Visual inspection by normal microscope at this time showed a totally intact surface. No associated crack system could be recognised. The maximum deformation of the edges of the single bowls had an amount of about 1µm. This measurements were performed on the ground lacquer. In regions with a red paint layer similar results occurred however, the amount of deformation was ~ 0.5 µm. This lead to the presumption that the red paint layer absorbed some of the movement and the main deformation originated from the ground lacquer.
Measurements in December 1999 during one humidity cycle showed again bowl like deformation structures. But now, these structures were more sharp. The deformations were reversible. This means the deformations occurring during drying are regressive during wetting. The maximum deformation now amount ~3 µm between the center and the edge of one bowl and by this has risen 2 to 3 times comparing to the measurement in 1998. Microscopic visual inspection now showed a net-like crack system where the edges of the cracks followed exactly the shapes of the deformation pattern. These damages gave us the reason to once again take photos of all fragments and store them at ~ 65% rh. Well in advance of macroscopic damages TV-holography had signalled an early warning one year in advance.
Furthermore it appears that the deformation rate versus change in humidity was not constant. While wetting the greatest deformations happened at high relative humidity, while drying at low relative humidity. This means the lacquer reacted to the change in humidity with a time delay.
After this comparative investigation to 1998 we performed the long term measurement with the fragments F011/98 and F012/98. The humidity changed in approximately 50 cycles within 12 days. In Fig. 2 the humidity in the climatic chamber versus time is plotted. Besides the wanted changes in humidity there are a few irregularities. This was due to a not perfect sophisticated controller.
The investigated areas were not exact the same as in 1998 because it was necessary to measure in regions where samples for SEM investigations could be taken.
Before the long-term measurements started we made deformation measurements and after the long term measurements we performed the same deformation measurements at the same places. As a result the bowl like deformation structure could clearly be seen. After the long term measurement the degree of deformation has increased again 1.5 times. The maximum deformations were now ~5 µm. As before the deformation of the red painted regions is slightly smaller.

The hope that the occurrence of the net-like crack pattern has lead to a release in tension which as a result should bring a smaller amount of deformations has shown wrong. The mobility of the single deformation areas has increased.
An additional measurement in August 2000 showed again strong deformations of about 5 µm.
At this time some additional phenomena occurred. It seemed as if there were "vulcanos" with a diameter of a few 10 µm. At the top of the volcanoes some liquid has discharged and later solidified. This volcanoes were situated in a region on the ground lacquer that is marked in Fig. 5 at page 11.

**Fragment F006/98**
Up to now no long-term measurements have been performed on this fragment. Measurements in December 1999 in a region with red paint showed nearly the same kind of deformation as fragment F011/98. The same bowl like structures with diameters between 100 and 200 µm and a maximum deformation of ~3 µm occurred. The red paint on this fragment is extremely thin so we measured directly the behaviour of the ground lacquer and no damping of the deformation like on fragment F011/98 could be seen.
Measurements in August 2000 showed an increasing in maximum deformations up to 5 µm.

**Fragment F001/99**
This fragment was treated in China in 1999. It is totally covered with a red paint layer. With naked eye the very bad condition of the lacquer could easily be seen.
There were a lot of big cracks which origins from the shrinkage that happened during the exchange of water with Plex before the electron beam hardening.
Photos from one part of the fragment were taken through a microscope at different magnifications first at 22% rh and then at 92% rh. The shrinkage of single pieces of colour while drying could clearly bee seen. Some of the cracks broadened up to 100µm. At a following wetting most of the cracks closed due to swelling of the lacquer.
The crack pattern could be divided in 3 different parts.
1. Cracks with a broadness of up to one millimetre, which emerged at the treatment with Plex.
2. Cracks which emerged at drying with a width up to 100 µm. The diameter of the associated structures was a few millimetres.
3. Cracks which emerged at drying with a broadness of up to 10µm. The associated crack pattern formed the typical bowl like structure with a diameter of 100 – 150 µm.

Measurements from August 2000 in a region with crack structure No. 3 showed a maximum deformation of ~10 µm.

**Fragment F005/98**
Measurements in August 2000 showed no bowl like structure. The surface looked very intact. In one region there was a small crack. Here it was possible to see slight deformations.

**Fragment F006/99**
The surface seemed to be in a bad condition. There were several long, thin cracks. At the edges the colour scrolled in such a manner that it could be seen by naked eye. Measurements at a region where two cracks meet showed a maximum deformation of about 21 µm. This behaviour is similar to that of PEG/PU treated fragments which showed a high amount of deformation in affected regions.

**Conclusions**
The measurements at the fragments treated with "Plex" and the microscopic inspection showed a severe degradation of the ground lacquer and the paint layers one year after the conservation.
As suspected from the first deformation measurements a net like crack pattern arose. This leads to a higher mobility of the single sub regions. The hope that the occurrence of the crack system remeded in a reduction of stress could not be verified. After fifty humidity cycles a further rise in mobility by a factor of 1.5 was measured.
Fragment F005/98 is a positive exception, which up to now shows no crack pattern.

## 3.2 Fragments treated with PU/PEG

On both fragments (F007/98, F012/98) deformation measurements have been made.
The results:

**Fragment F007/98**
As in 1998 this fragment showed no measurable deformations of the surface while humidity changes. Visual investigations through the microscope showed an intact surface. There were no cracks visible. However, the problem is that the dose of conservation agent had been much to high and by this the colour has lost her luminosity. For this reason it is not an acceptable conservation method and no further investigation like long-term measurements were performed.

**Fragment F012/98**
This fragment has been treated in a way that is up to now used in China for the conservation of a few coloured warriors. Together with the Plex-treated fragment F011/98 it originally built one unit and has thus a similar colour set-up and is suited for comparable measurements of both conservation methods. The visual microscopic investigation of the fragment showed a few cracks. The deformation measurements in 1999 indicated in this regions an high amount of deformation up to 10 µm. Most of the time only one side of a crack was mobile and by this delaminations could be identified. In regions with no visible cracks no deformation could be measured.
The following long-term measurement with a climatic change plotted in Fig. 2 led again to an increase of cracks. Using a microscope it can bee seen that there are delaminations near the cracks. Most times the upper lacquer has peeled off the lower lacquer. At some places even both lacquer layers have peeled off the terracotta.
After the 50 climatic cycles of the long-term measurement the mobility has increased 1.5 times as seen before at the fragments treated with Plexd. Regions with no cracks show no deformations even after the climatic changes.
During the increase of humidity another phenomenon on the PU/PEG treated fragments occurred. Starting at 65% rh drops were generated. They occurred very inhomogeneous on the ground lacquer. Up to now there are no hinds for a correlation between topographic attributes and the occurrence of the drops. The size of the drops increased with increasing humidity. By reduction of humidity the drops vanished. While drying it seemed as if the lacquer resorbed the drops. It has to be pointed out that the drops occurred only at some points on the surface. The occurrence and the resorption of the drops was filmed. During the occurrence of the drops while wetting some probes were taken from the MPA Bremen and then frozen in melting nitrogen. The investigations at the Cryo-SEM have proven that the drops consist mainly of PEG. It was thus shown that the conservation agent stays at least partly mobile and can leak from the lacquer.
In a discussion with our colleges from the BLfD it was reported that this process can precede until the liquid ran down the fragment. Probably consequences of this drop-building and dilution has not been investigated yet.

**Conclusions**
The deformation measurements have shown that in regions where the surface is intact no measurable deformations occur. If there are cracks the lacquer peels of and the measured deformation have an higher amount as at the fragments treated with Plex. Starting at an rh from 65% in single regions drops occur which vanish again at drying.

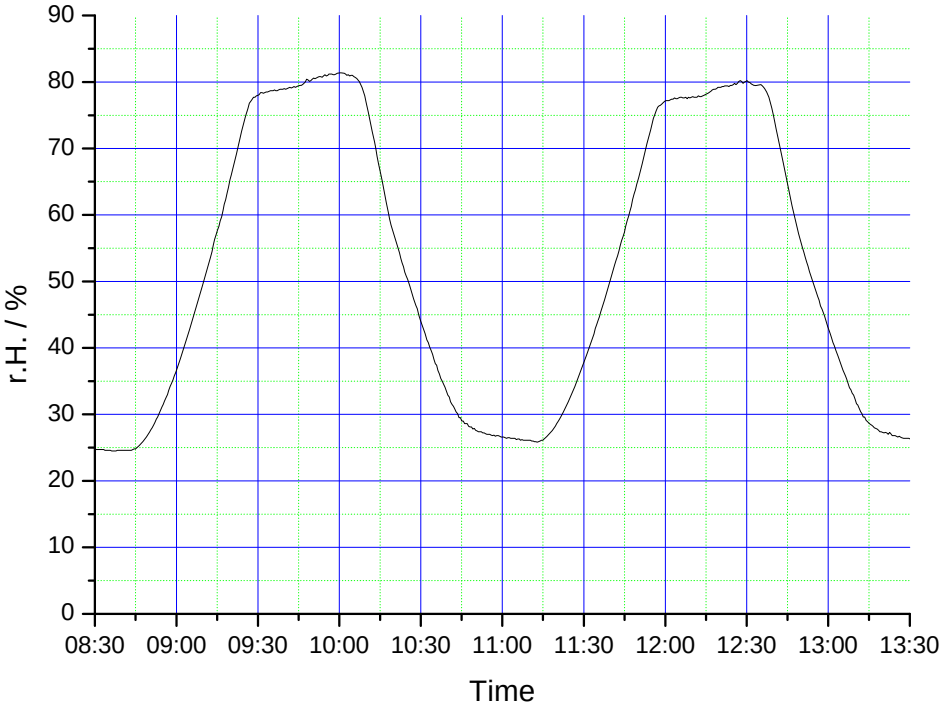



Fig. 1: Typical humidity cycle

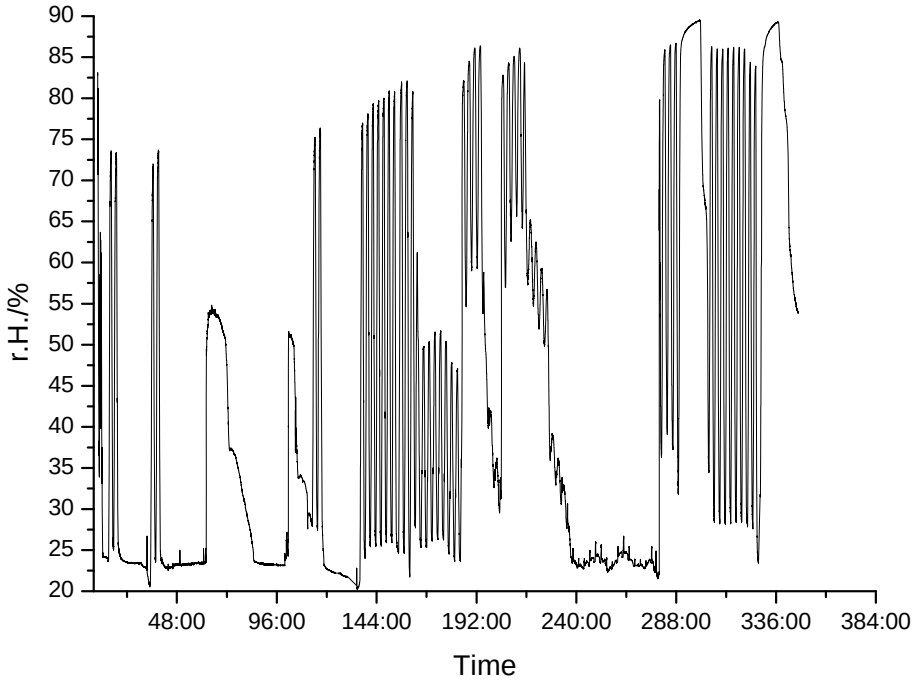



Fig. 2: change in humidity during the long-term measurement

## 4. Table of Results

| Frag.-No. | Treated. | Result 12/1998 | Result 12/1999 | Result 2/2000 | Result 8/2000 |
|---|---|---|---|---|---|
| ***F005/98*** | HEMA-Xi'an | - | - | - | Measurements on the ground lacquer show an intact surface, the edges of a lose part of lacquer with a diameter of 200 µm move up while drying and down again while wetting. max. deformation 3µm |
| ***F006/98*** | HEMA | similar deformation as on the red paint on F011/98 | like F011/98 | - | like 12/1999 but higher amount of deformation<br>max. deformation: 5 µm<br>Similar to F001/99 |
| **F007/98** | PU/PEG – High amount | no deformation measurable, very intact surface | | - | - |
| **F008/99** | PU/PEG | Because of the size no measurements in the climatic chamber were possible | | | |
| **F011/98** | Plex (HEMA) – Dresden | Bowl like structure, edges of the bowls move up while drying, diameter of the bowls 200 µm and smaller; max. deformation 1.5 µm no crack patter visible; red paint layer damps the deformation of the ground lacquer. | like measurement 12/1998 but bowl like structure more distinct; max. deformation 3 µm, crack pattern clearly visible under a microscope even in the red painted regions. | like 12/1998 and 12/1999 but max. deformations 4.5µm. | The measurement region was not exactly the same as 2/2000, similar results,<br>max deformation 3µm |
| **F012/98** | PU/PEG | - | intact surface, only a few cracks visible under the microscope, deformations are only measurable near the cracks but there max. deformations up to 10µm, layers of ground lacquer lose contact, drops of PEG occur at high relative humidity. | like 12/1999 but some more cracks visible, overall intact surface measurable deformations near the cracks, max. deformation 15 µm | like 2/2000<br>Measurements near a crack.<br>One side of the crack moves<br>max. deformation 2 µm<br>The other side does not move |
| **F001/99** | Plex –Xi'an | - | Surface is damaged, a lot of cracks can be seen, from normal bowl like structure up to 1 mm broad cracks. Big cracks broaden up to 100 µm while drying. Cracks close again at wetting. | - | Measurements in regions with the typical crack pattern, max. deformation 10 µm,<br>The highest amount of deformation while drying and while wetting occur at higher humidity. |
| **F003/99** | Plex-Xi'an | Because of the size no measurements in the climatic chamber were possible | | | |
| **F006/99** | Plex-Xi'an | - | - | - | long cracks max. deformation >21µm |

In the following representative extracts of single measurements dated from August 2000 are presented. The picture at the top is always a photo of the fragment taken before the measurements. The relevant measurements are marked. If possible a white light picture of the measured region is placed in the middle. The size of this region is 1 * 1,2 mm². Because of the limited depth of focus these pictures are hard to interpret. The picture on the bottom shows an clipping of the measurement. This picture is a result of the subtraction of a picture taken before and another picture taken after a deformation. The occurring fringe pattern can be interpreted as contour lines of deformations. The deformation-range between two lines is ~0.3 µm.
The measurement regions are marked as followed.


Measurement 1998


Measurement 1999


Long term measurement


Measurement August 2000

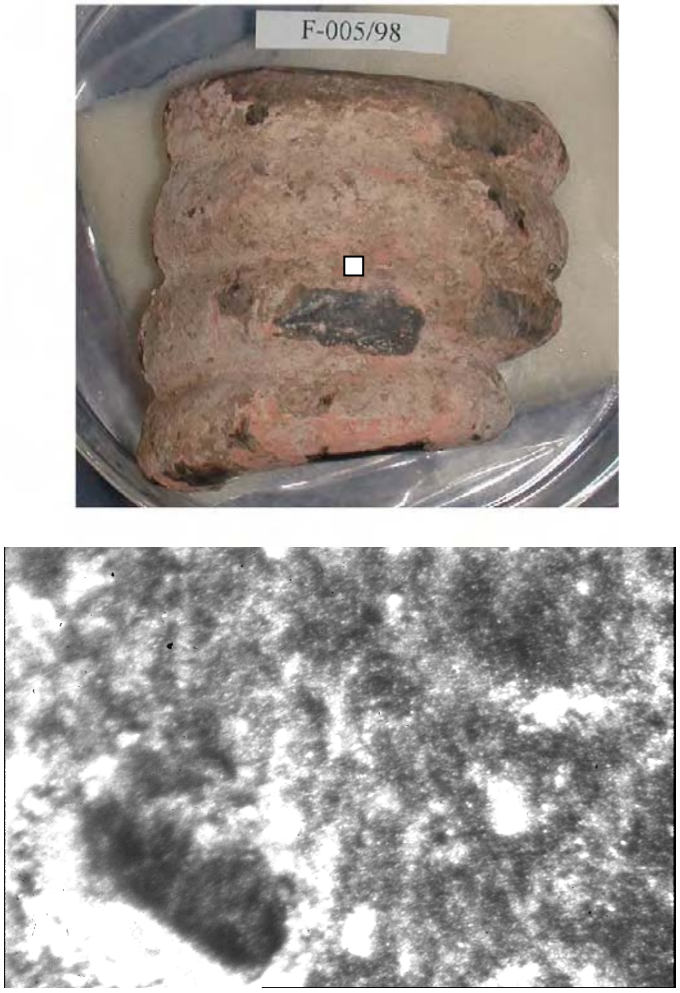



Fig.3 : F005/98 Measurement while drying ( 70 - 68% rh)
The measured region is marked white in the photograph. Only at the crack in the lower left corner some deformations occur which show the typical bowl structure at drying.

„Volcano“

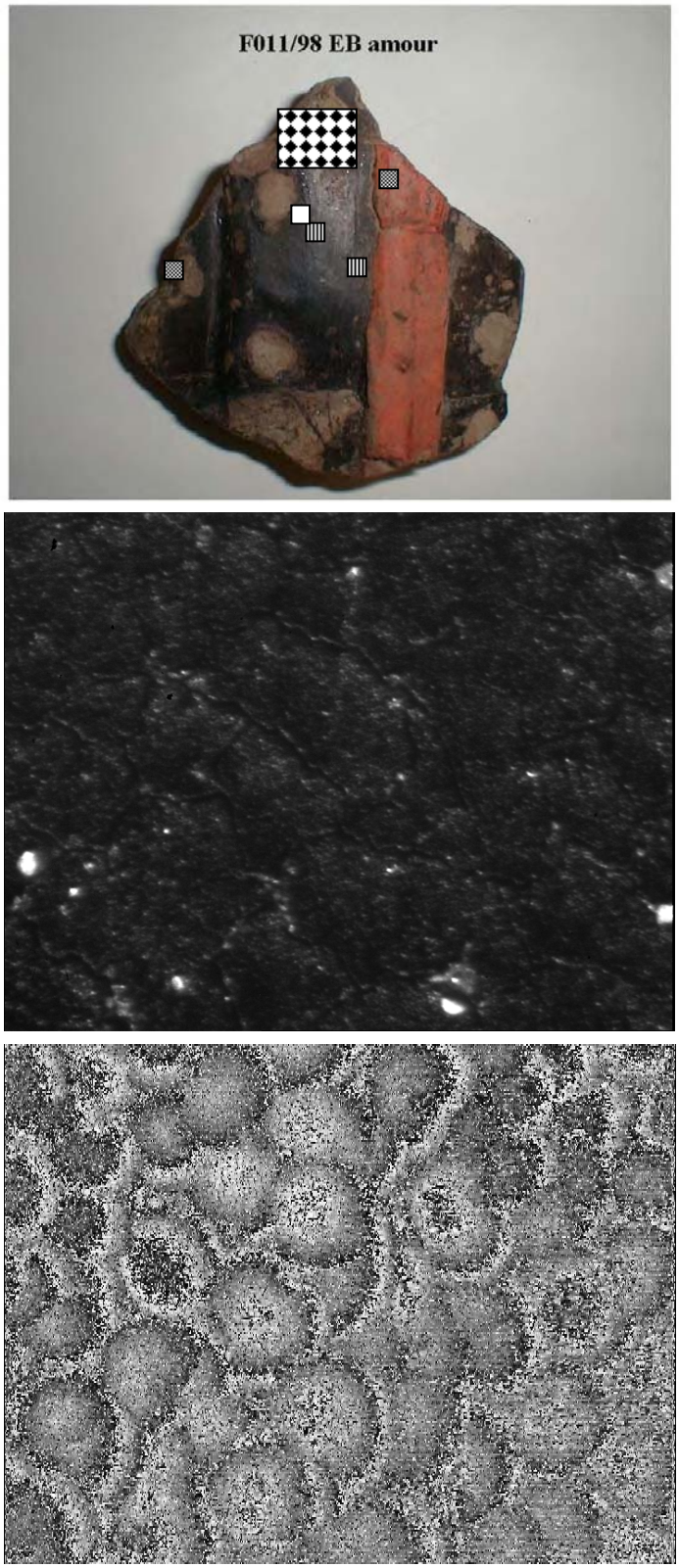



Fig. 4: F011/98 Measurement while drying (70 - 68% rh). The measured region is marked white in the photograph at the top. The typical bowl structure can be seen. The edges move up while drying.

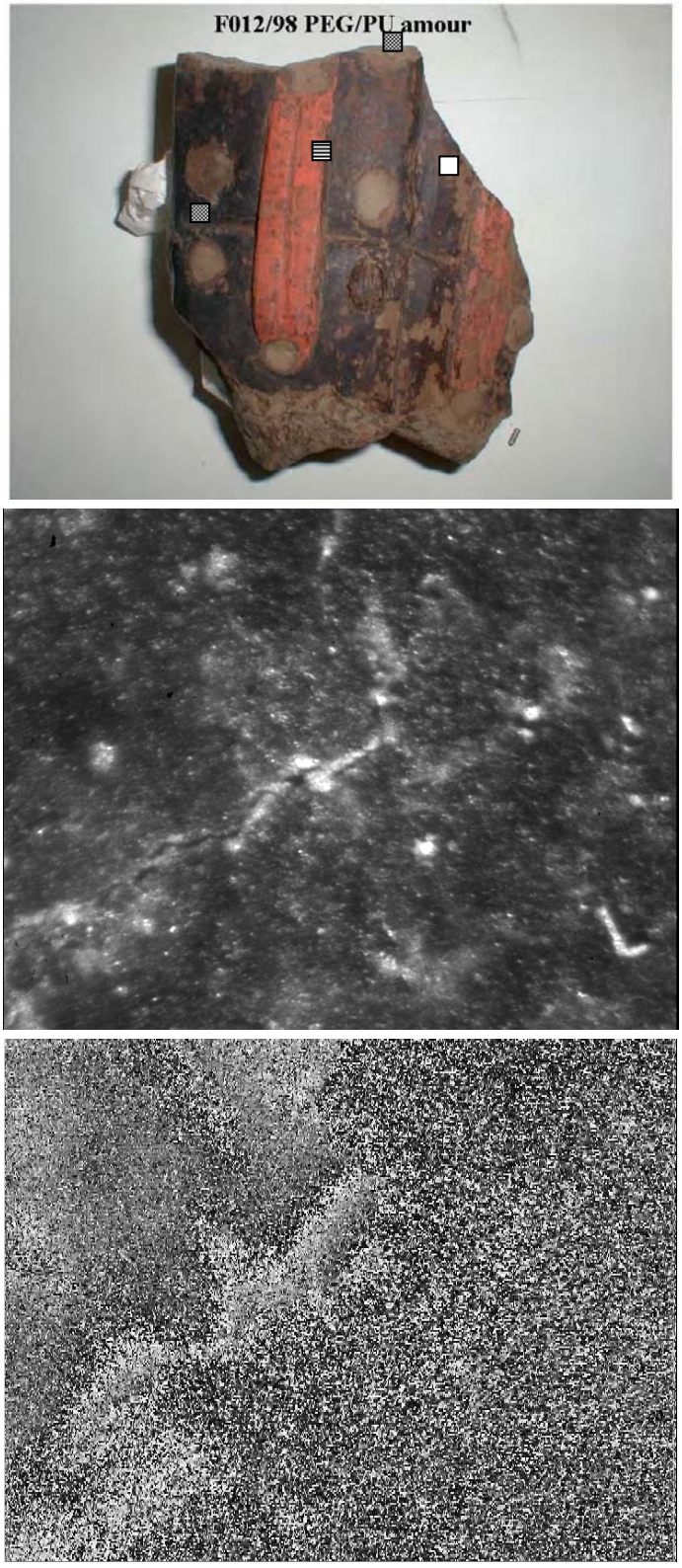



Fig. 5: F012/98 Measurement while drying (70 - 68% rh)
The measured region is marked white in the photograph at the top.
Only directly at the crack some deformations can be measured.

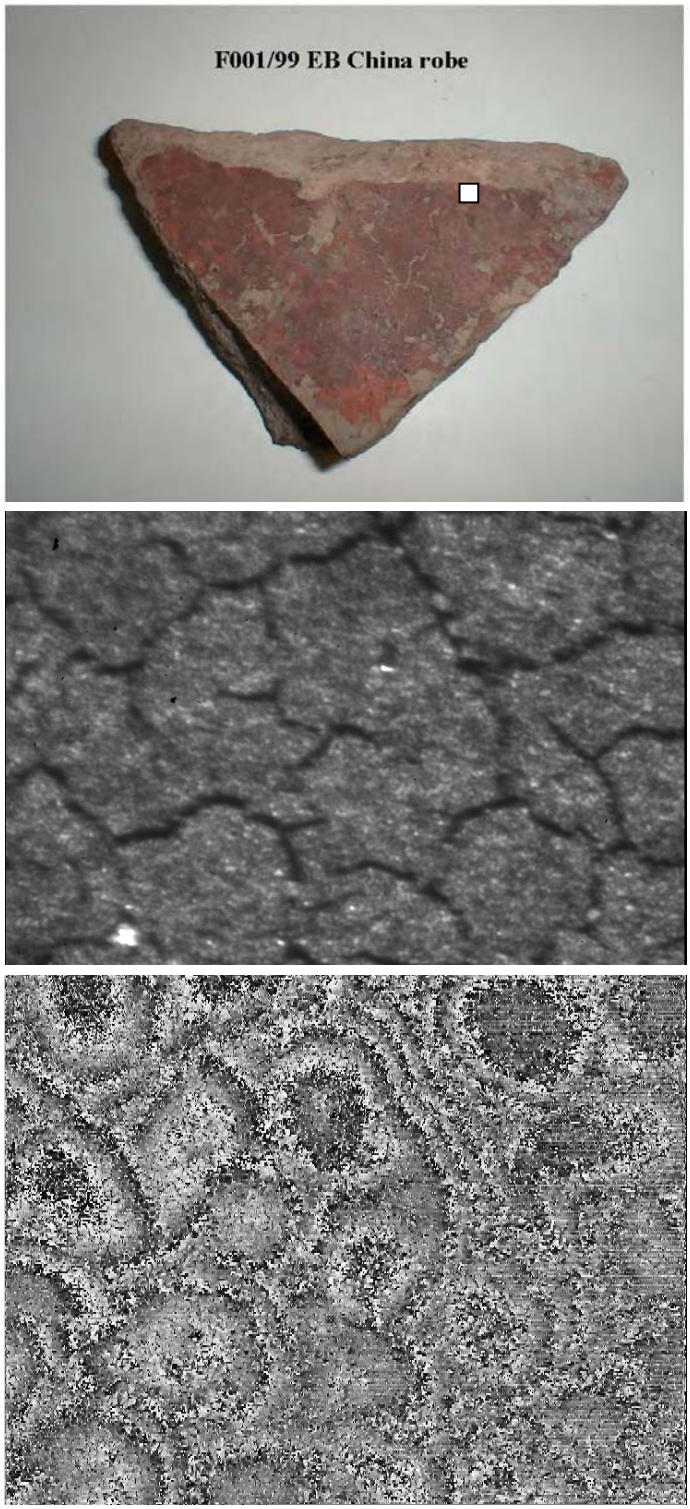



Fig. 6: F001/99 Measurement while drying (70 - 68% rh)
The measured region is marked white in the photograph at the top.
The typical bowl structure can be seen. The edges move up while drying.

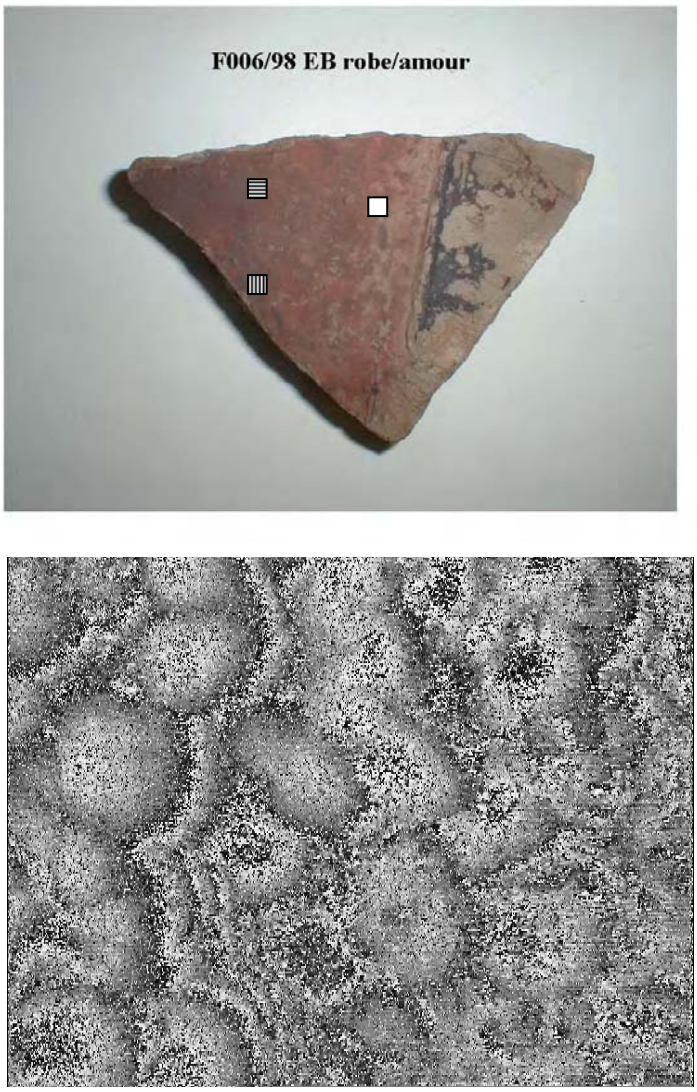



Fig. 7: F006/98 Measurement while drying (70 - 68% r.h.)
The measured region is marked white in the photograph at the top.
The typical bowl structure can be seen. The edges move up while drying.

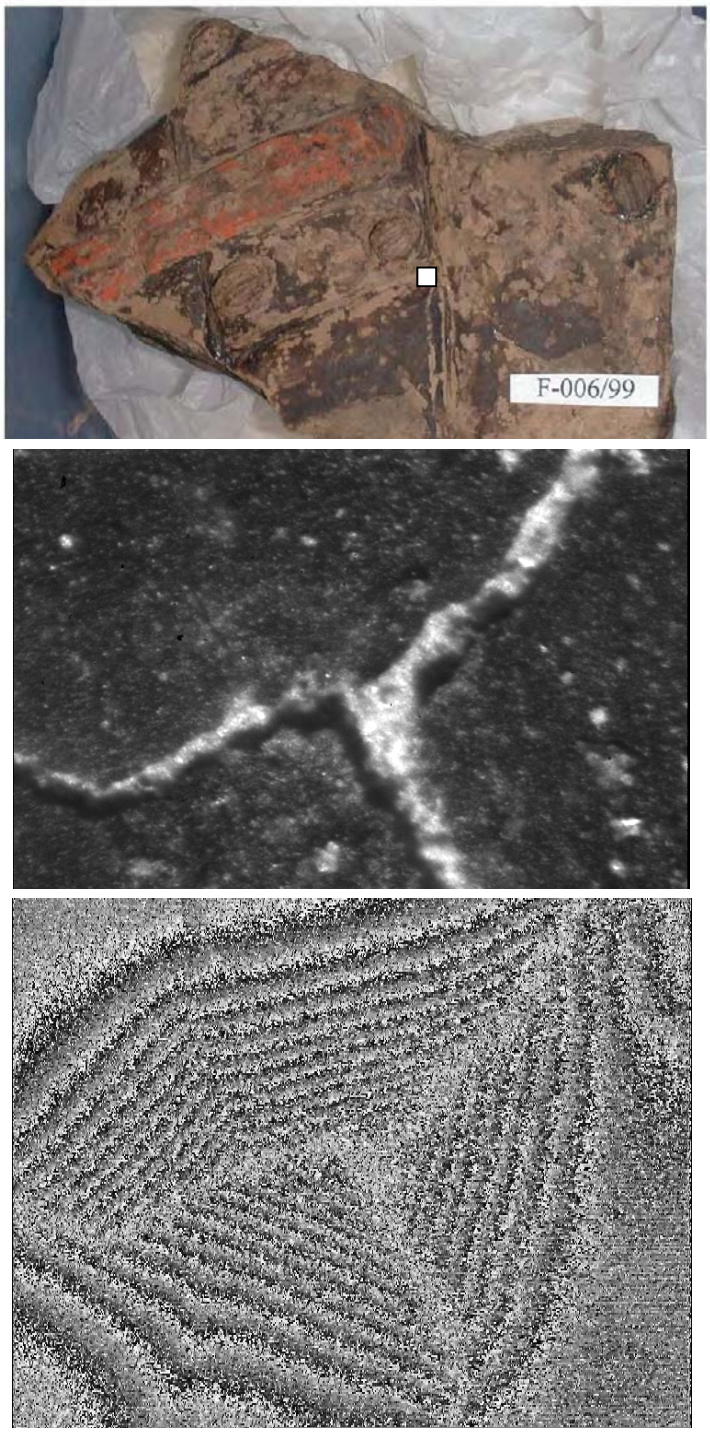



Fig. 8: F006/99 Measurement while wetting (72 - 78% rh)
The measured region is marked white in the photograph at the top.
A high amount of deformation can be measured near the cracks.
The structure flattens while wetting.

F007/98


F007/98


F003/99


F008/98


Fig. 9: Photographs of the remaining fragments

## 5. Sub-surface measurements

Modified ESPI measurements for characterisation of single layers even below the surface

Up to now all measurements are done with a laser whose coherence length is about 10 cm. The light in the object beam can have a path difference of up to 10 cm and even then can interfere with the reference beam. In our case this means that the light reflected from the surface of a fragment and the light reflected from underlying structures of the probe contribute to the deformation measurements. The deformation pattern we get is a consumption of the deformations from every single layer. Most of the light is reflected from the surface and by this the deformation of the surface contributes most to our measurements.
By choosing an appropriate light source it is possible to modify the measurement technique. The superluminescens diode we use has a coherence length of 34 µm. If we vary the path length of the object beam by constant length of the reference beam we can choose a single layer even below the surface and investigate only the deformations of this layer. Necessarily there must be enough light reflected from that layer.
With this modified method we can measure deformations of the single layers separately. A first measurement has been performed in August 2000. At this single region on fragment F006/99 at humidity changes the top layer of lacquer showed a higher amount of deformation than the bottom layer. By the way the top layer moved it was possible to determine that the top and the bottom layer have no contact at the edges. Further more this method gives the possibility to measure the structure of the top and of the bottom layer and by this determine where they lose contact.
The set-up and special characteristics are fully explained in [2].

Literature:

[1] G. Gülker, K. D. Hinsch, and A. Kraft; *TV-Holography on a Microscopic Scale: Deformation Monitoring on Polychrome Terracotta Warriors;* Vortrag und Proceedings; Interferometry in Speckle Light; Lausanne; Springer; p. 337-344; 2000

[2] A. Kraft, G. Gülker, K.D. Hinsch; *Low-coherence videoholografy for sub-surface deformation measurements in layered objects;* Vortrag und Proceedings; SPIE's 45th Meeting; Bellingham; Vol.4101 p. 89-96; 2000

# SEM-EDX-Analysis of Pigment Layers

August 9, 2000

Munich, Geological Institute, Klaus Rapp
Participants: Siegfried Scheder, Catharina Blaensdorf, Stephanie Wallner, Zhang Zhijun, Rong Bo, Ma Yu
Compiled by C. Blaensdorf

## Introduction

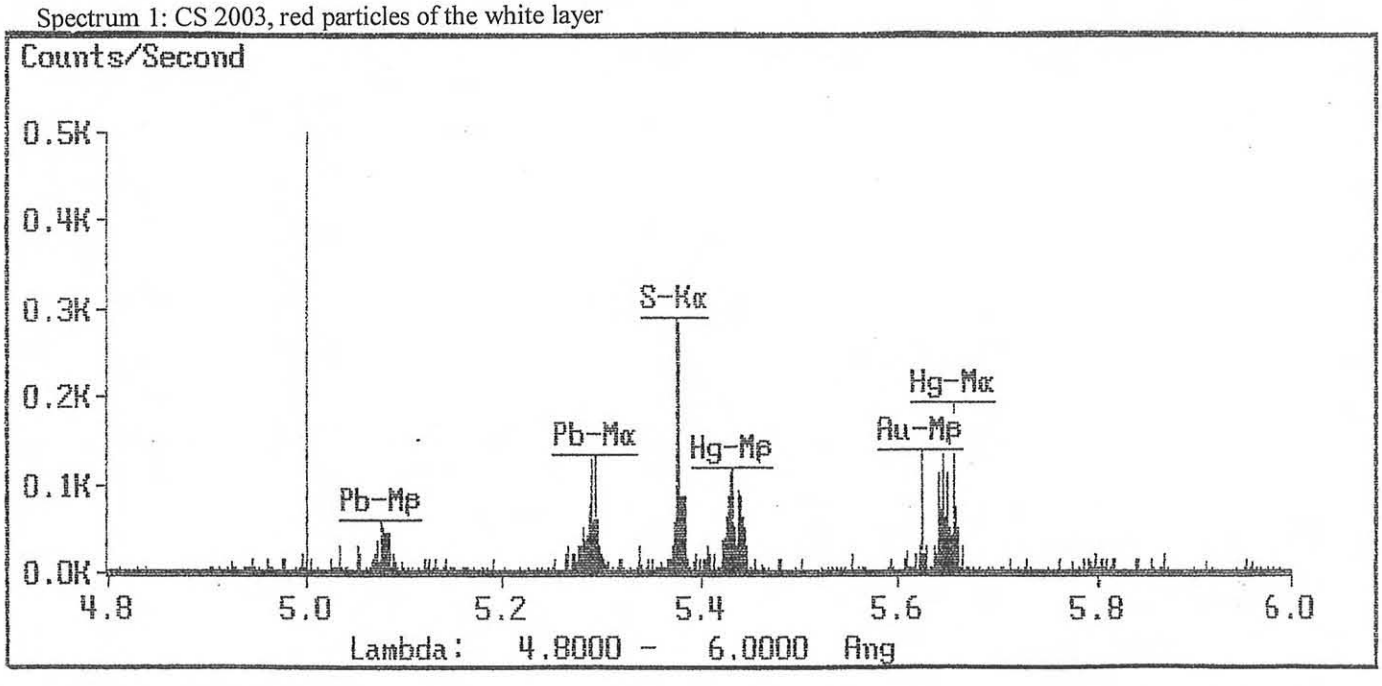
Aims of the visit in the Geological Institute have been investigations on the polychromy of the terracotta army and on lime stones from the stone armours.
The questions about the polychromy concerned the identification of the yellow pigment from the fragment B-0107 (cross sections CS 2003 and CS 2004) and the examination of some green and blue pigment layers which show orange-yellow or brown areas ("colour changes").
The results have been as follows:

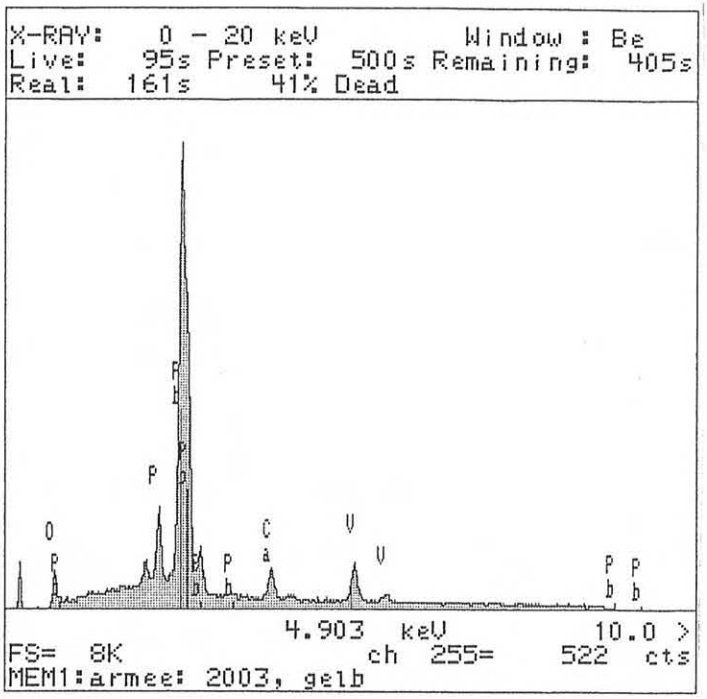
## CS 2003 (yellow and white pigment layers)

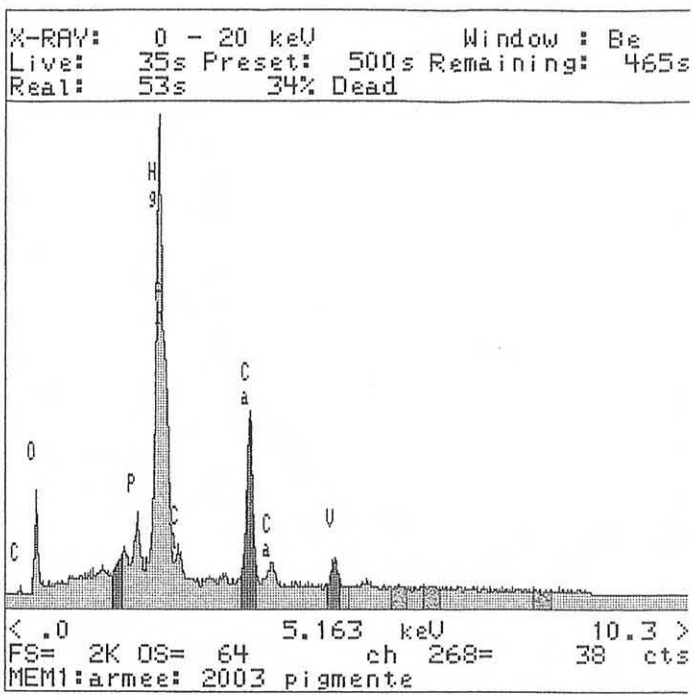
The cross sections CS 2003 and 2004 come from the fragment B-0107, a piece of soil with adhering paint layer from pit no. 1. The exact location and the exact origin of the fragment is not known. It is the only example of a yellow layer in the polychromy of the terracotta army detected so far. The fragment has broken into several pieces which recently had been embedded and mounted in plaster without regard to there original position. The polychromy consists of two layers: a thicker white layer on top of a thin yellow layer. On the yellow remnants of lacquer are visible (fig. 1-3). The cross-sections (fig. 4 and 5) show that the yellow layer is very thin and its pigments are rather coarse; the white layer contains white and a larger amount of small red particles (nevertheless visually it appears white not pink).
The yellow pigment was analysed in China and determined as orpiment. It was examined under the polarised light microscope (PLM); the sample did not contain any orpiment crystals.

*Results of the examination*
- white layer: Ca, P (maybe Ca $PO_3$); red particles: HgS (see: spectrum 1)
- yellow layer: Pb, P, V, Ca, Cl (see: spectrum 2a, 2b and 3 (2b = repetition of the measurement 2a; Cl was marked additionally)

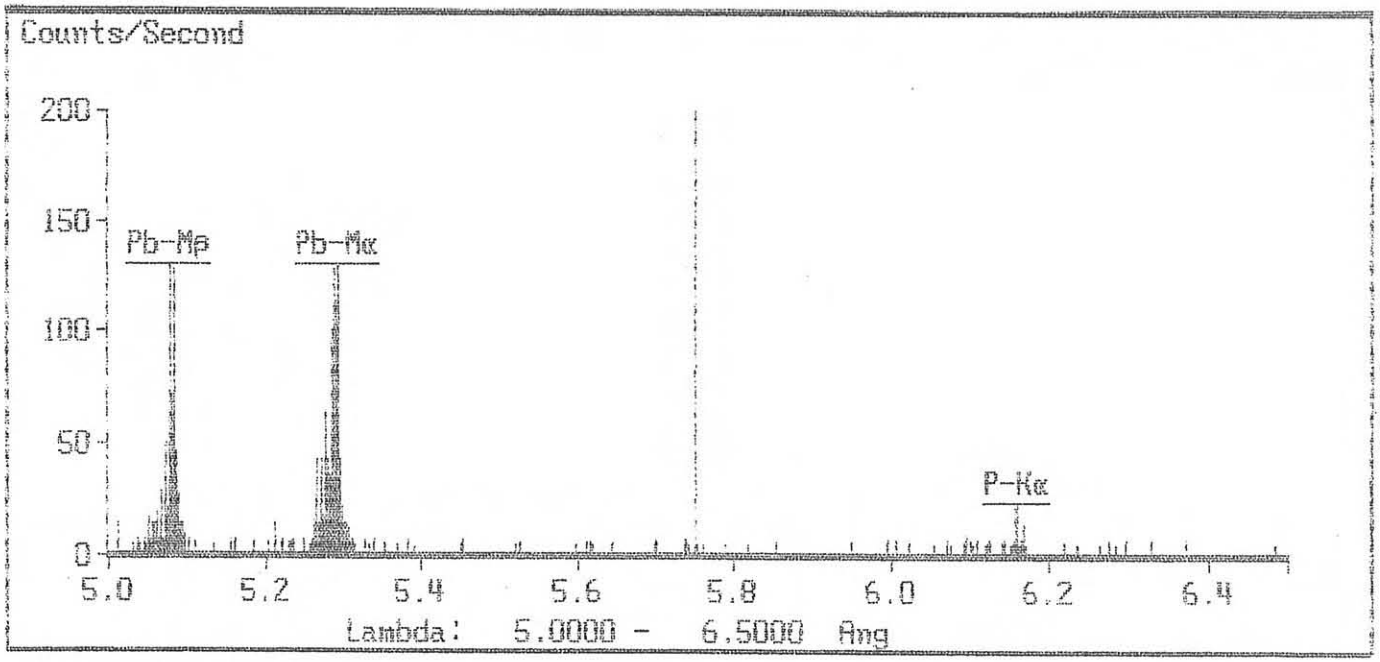
Spectrum 1: CS 2003, red particles of the white layer






Spectrum 2a and b: CS 2003, yellow layer. The peaks of Vanadium (V) are visible.




Spectrum 3. CS 2003, yellow layer. Identification of lead (Pb).

The *white* layer consists of apatite as white pigment and HgS as red pigment.
The *yellow* pigment does not contain any As or S and therefore clearly is no orpiment. The high content of lead could indicate lead oxide (PbO). PbO was known in ancient China.[1]
The amount of Vanadium is too big to be regarded as an impurity of the lead. There is a mineral containing Vanadium and lead, *Vanadinite*, $Pb_5[Cl(VO_4)_3]$. Its colour ranges from orange, orange-red, ruby-red, reddish yellow to yellow-brown to "straw yellow".[2] It is not known if it has ever been used as a pigment.

[1] According to Zhang Zhijun yellow lead oxide has been used as early as the Shang (17.-11. centuries BC) or the Zhou (11.-8. centuries BC) Dynasty.

[2] Hochleitner, Rupert, v. Philipsborn, Henning, Weiner, Karl Ludwig: *Minerale. Bestimmen nach äußeren Kennzeichen.* Mit Kristallzeichnungen von Klaus Rapp. Stuttgart 1996. Vanadinite: 78, 3 % PbO, 19,3 % $V_2O_5$, 2,4% Cl. P and As can substitute V up to: P:V=1:4,7; As:V=1:1. CaO can substitue PbO up to 3 %. In thin layers translucent. Very high refraction of light.

Fig. 1. B-0107: Three soil fragments with remnants of polychromy; from pit no. 1 (exact origin not known). Situation in 1993


Fig. 2. B-0107, July 2000. The three fragments are mounted in plaster.

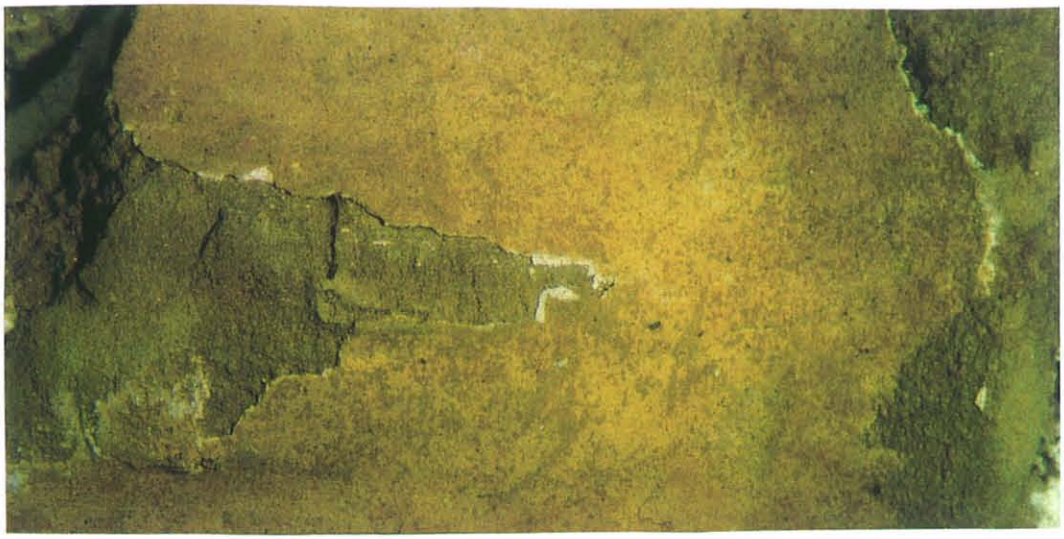


Fig. 3. Detail of B-0107. On top of the yellow layer small remnants of the lacquer and some soil are visible. Below the very thin yellow layer there is a thicker white layer which becomes visible at the borders of the polychromy.

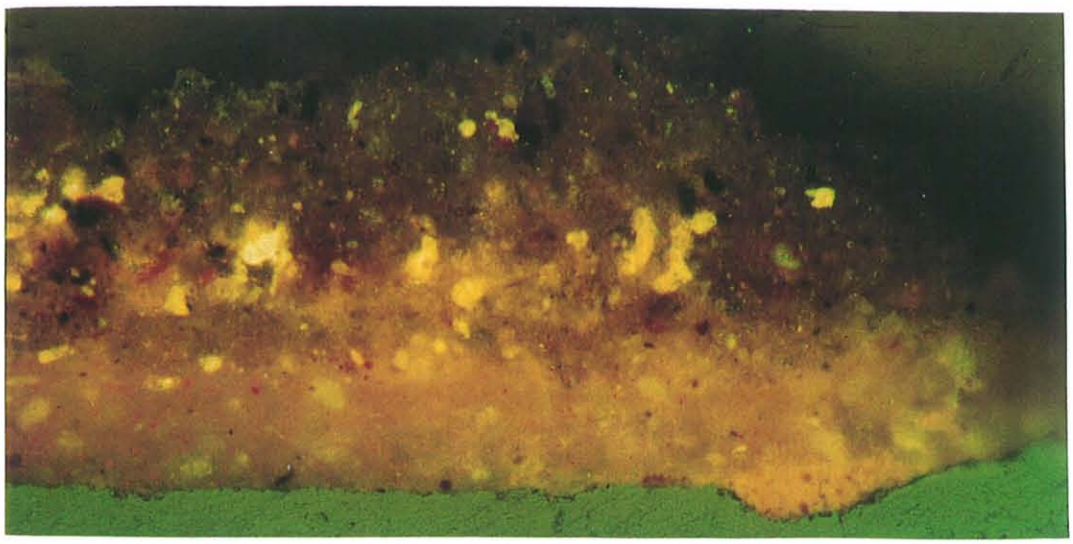


Fig. 4. CS 2003; the narrow side of the photo corresponds to c. 0.6 mm

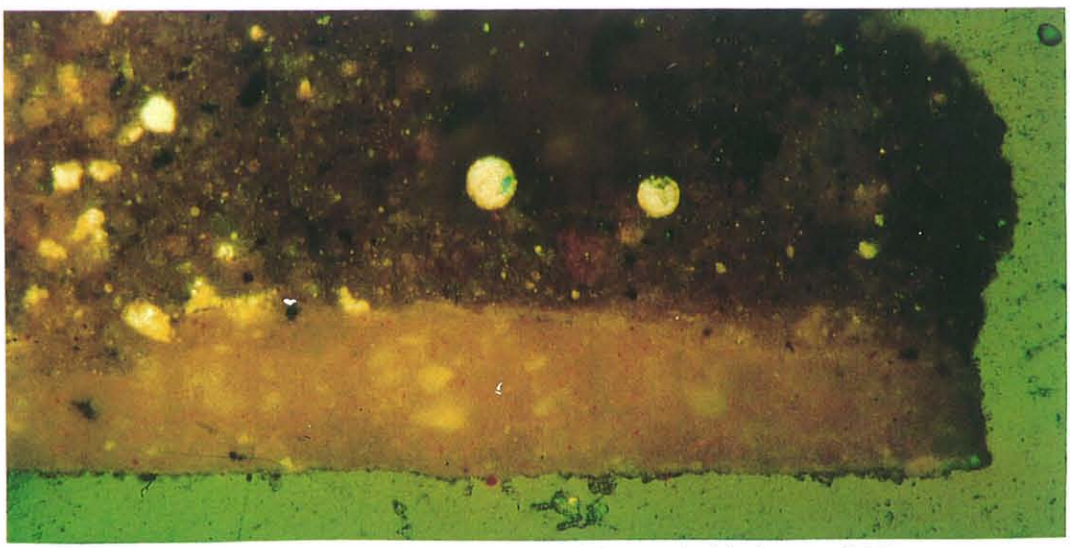


Fig. 5. CS 2004; narrow side of photo = c. 0.6 mm; thickness of white layer c. 0.17 mm

## CS 2007 (pigment layer with green and orange)

The sample comes from a leg of figure no. 2 in T21G18 of pit no. 2 (kneeling archer). It was brought to Germany as an already embedded cross section (fig. 6). According to the Chinese experts the colour of the leg had been green and the orange is a colour change and no artistic effect. On top of the pigment layer there is a thick layer of soil; the lacquer layer had been lost totally.

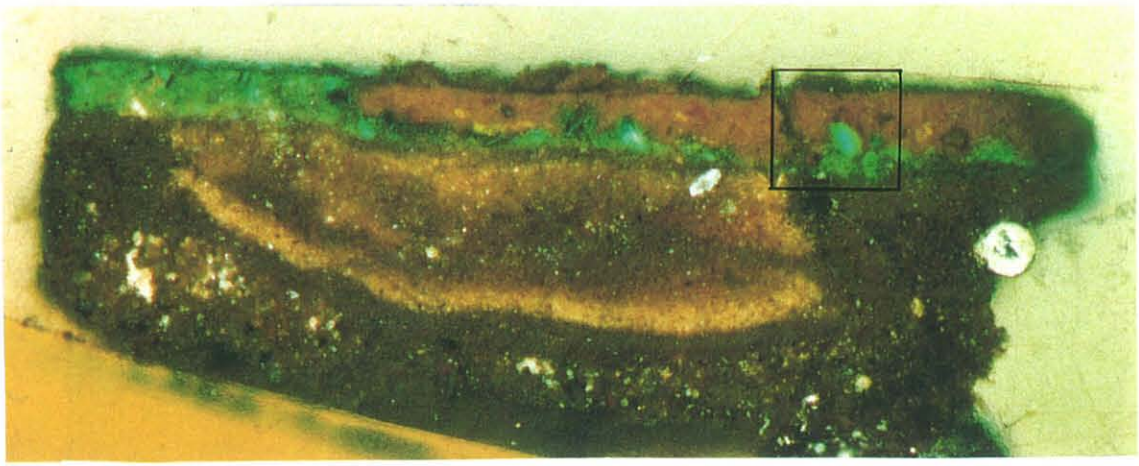


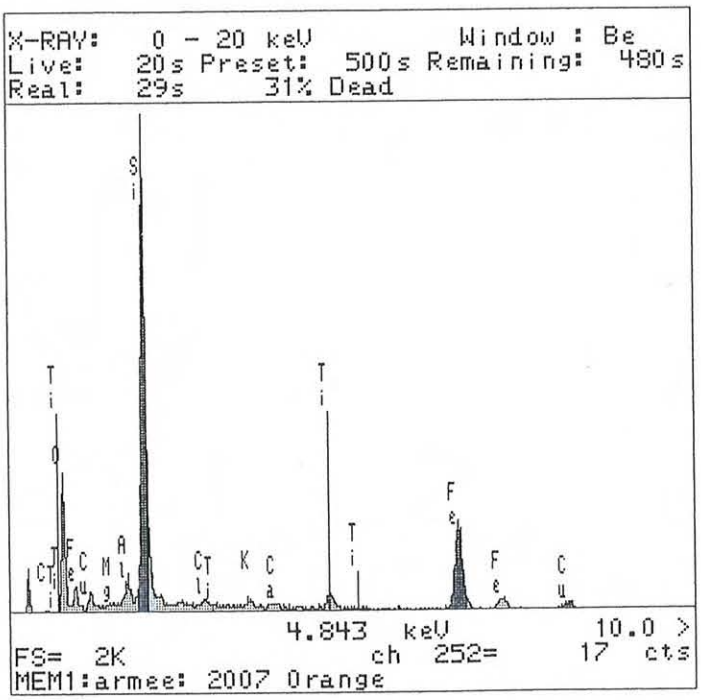
Fig. 6. CS 2007; narrow side of the photo = 1.04 mm. The cross section is upside down here, because the SEM-pictures have been taken in this position. The black frame mares the detail visible in fig. 7 and 8.

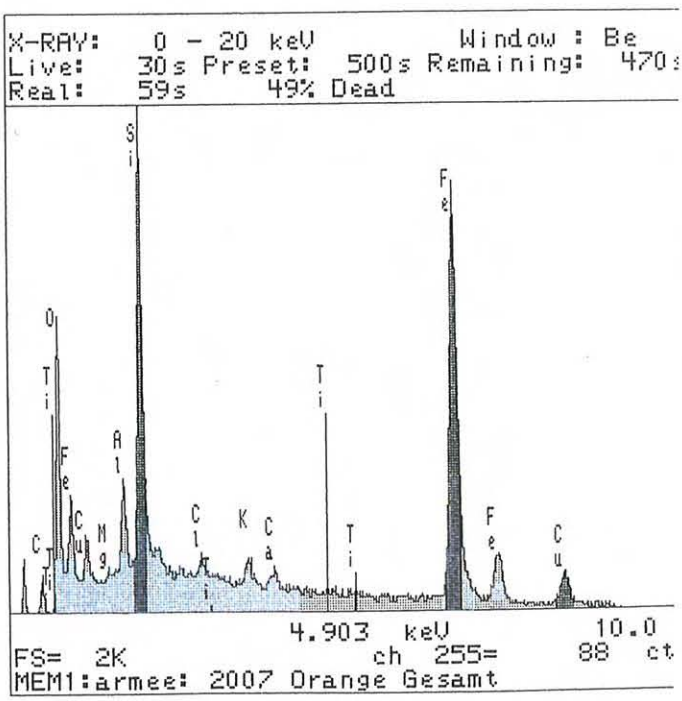
*Results of the examination*

- orange: K, Al, Si, Fe, Ti, (Cu)
- green: Cu, Fe, Si,(Ti)
- soil: Na, K, Mg, little Fe

The *orange* layer contains elements typical for earth pigments, the colour is due to the high content of iron. Darker, almost red looking areas contain more iron (fig. 7 and 8, spectra 4 and 5). The small content of copper can be interpreted impurity from the iron; it does not indicate the existence of a copper pigment. The titanium (Ti) could indicate $TiO_2$ as deterioration product of mica (content of earth).

Spectra 4 and 5: CS 2007, orange part of the pigment layer



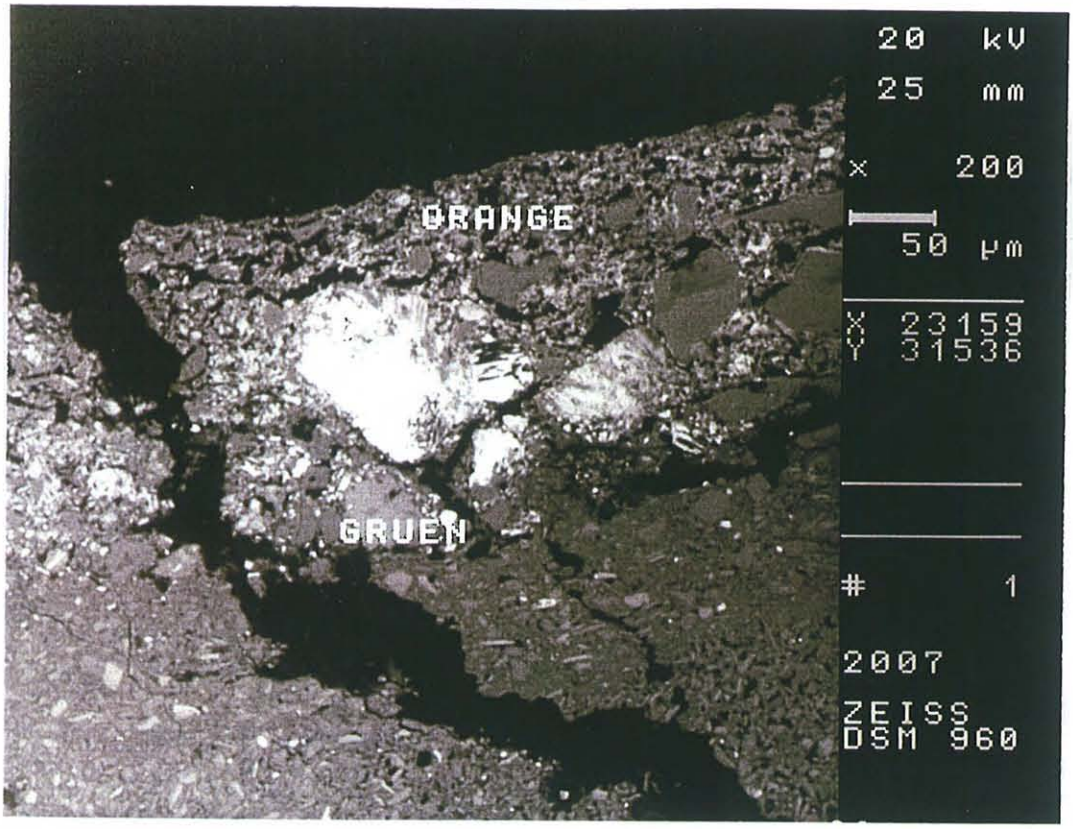



Fig. 7. CS 2007, area with green and orange particles, the lower part is the soil. The area is indicated on fig. 6 by a black frame. The crack running through the cross section is visible (black).

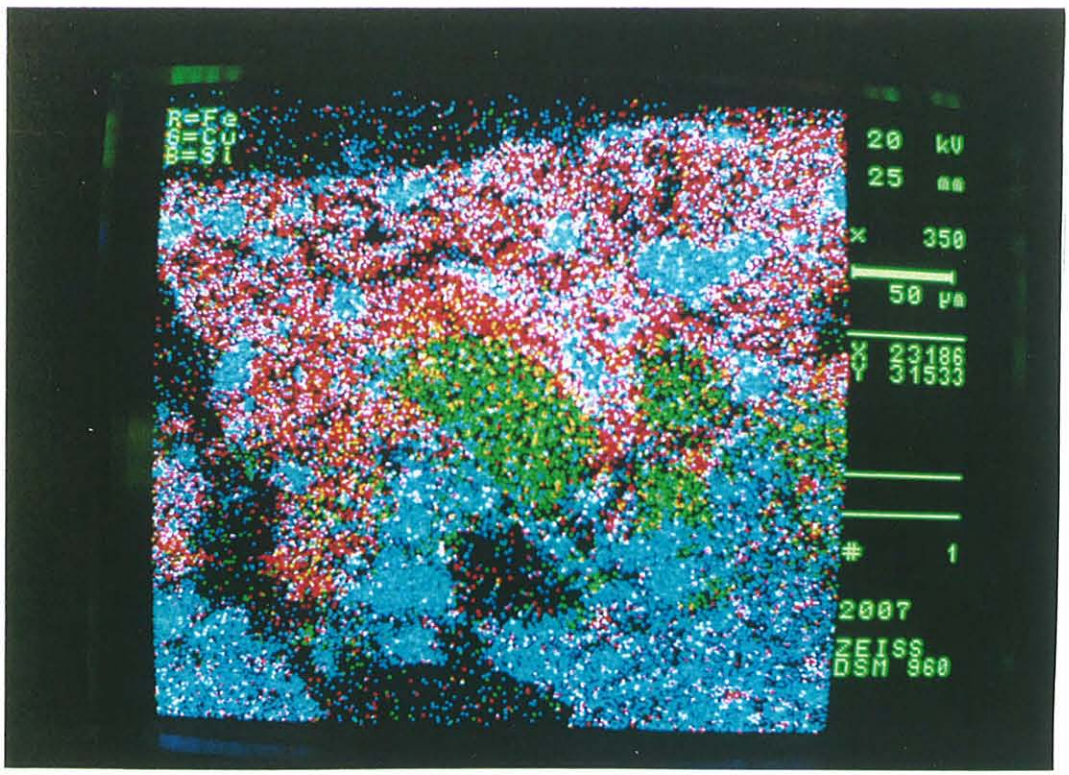



Fig. 8. CS 2007, area with green and orange particles (same as fig. 7).
Red = iron; green = copper; blue = silicate

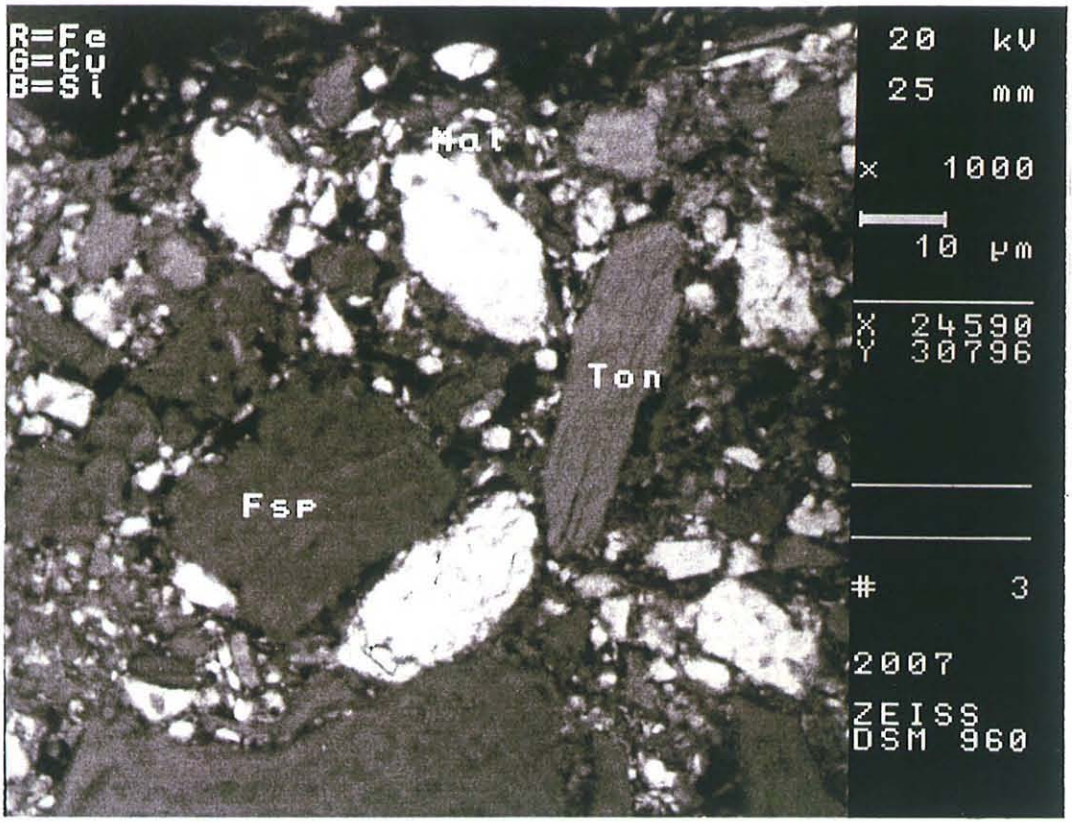



Fig. 9. CS 2007, green area from the right side of the cross section where the pigment layer is totally green. The malachite particles appear almost white.

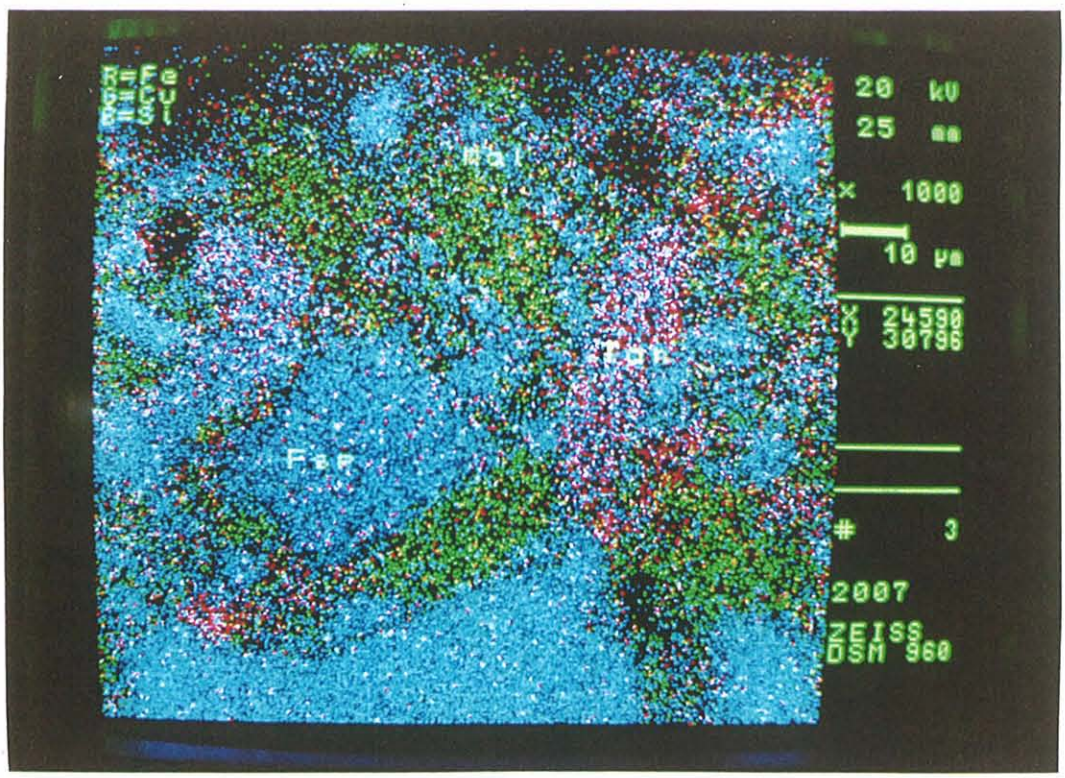
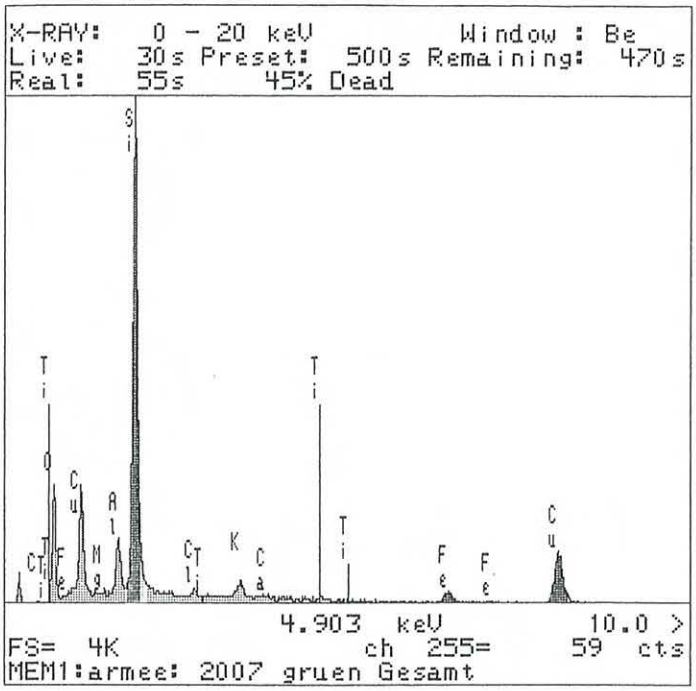



Fig. 10. CS 2007, green area (same as fig. 9).
Red = iron; green = copper; blue = silicate




Spectrum 6: CS 2007, green area

Investigations on the *green* layer focussed on a part where the whole paint layer is green (fig. 9 and 10, spectrum 6) as well as on a part with single green particles inside an orange layer. The green layer gets its colour from malachite (big particles with high concentration of copper). Besides there are clay minerals and felspar (fig. 9 and 10; on fig. 9 the very light particles are the malachite particles; fig. 10 shows their high content of copper, indicated by green dots). There might be a small content of green earth. Small amounts of iron also indicate a content of earth, a part of the pigment or from the soil.

The *soil* (on top of the paint layer) contains elements typical for clay minerals and little iron. The different coloured layers (range from brown to white, fig. 6) can be interpreted as deposit layers. The layers differ slightly in structure and composition (quantitatively, fig. 11): The brown ones contain more iron and no Na, the very fine structured white layer contains Na and very little iron (fine sediment layer).

*Conclusion*

The green and the orange areas of the pigment layer are different in structure and contain different elements. The possibility of a transformation of the green pigments into the orange ones can be excluded. The colour of the orange layer is due to the high content of iron, not to organic compounds. The soil contains considerably less iron than the soil and more silicate. In the middle part several sediment layers can be observed. The orange layer is very unlikely to be a sediment having developed out of the soil.

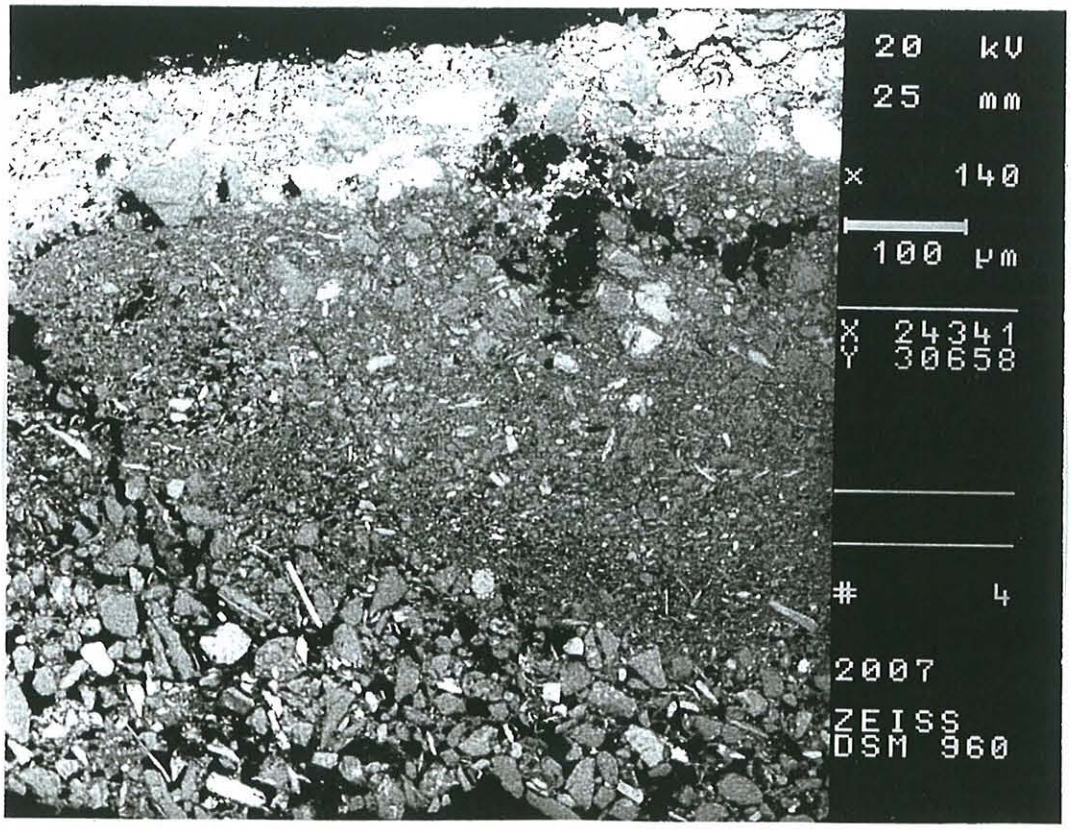



Fig. 11. Sediment layers of soil The light appearing layer on top is the (copper containing) pigment layer.

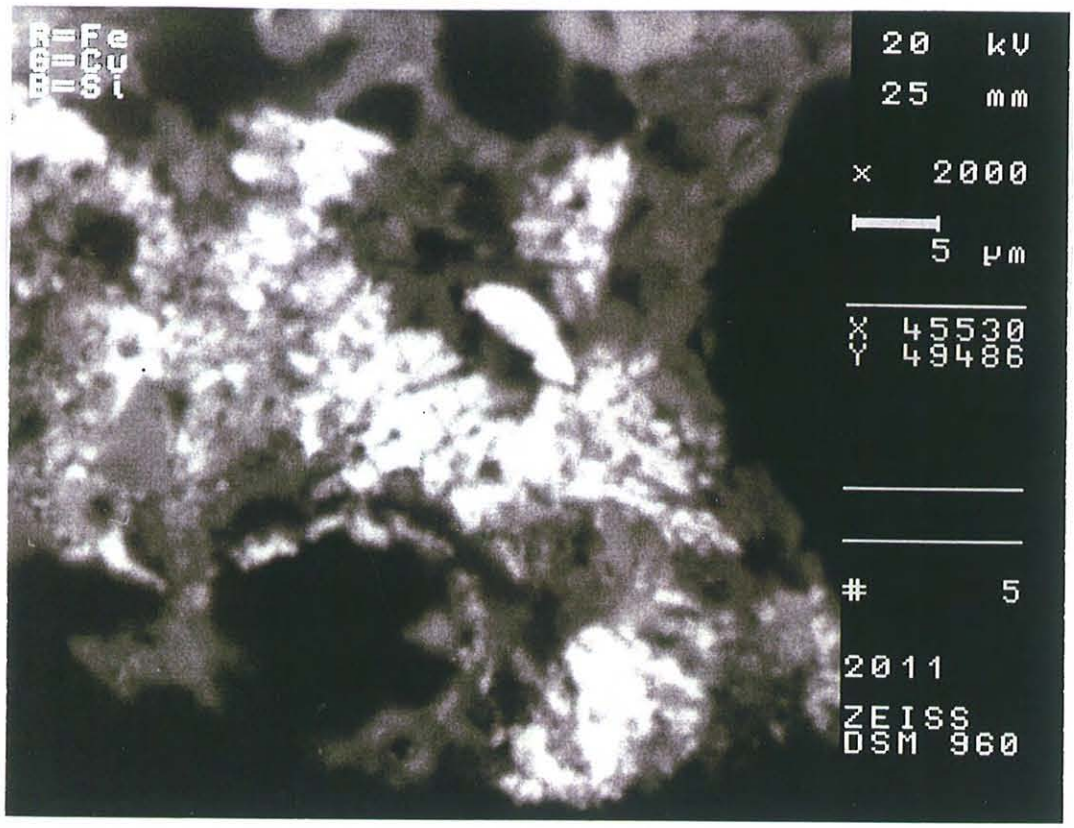



Fig. 13. CS 2011, blue area in the lower edge of the cross section. The area is marked with a frame on fig. 12.

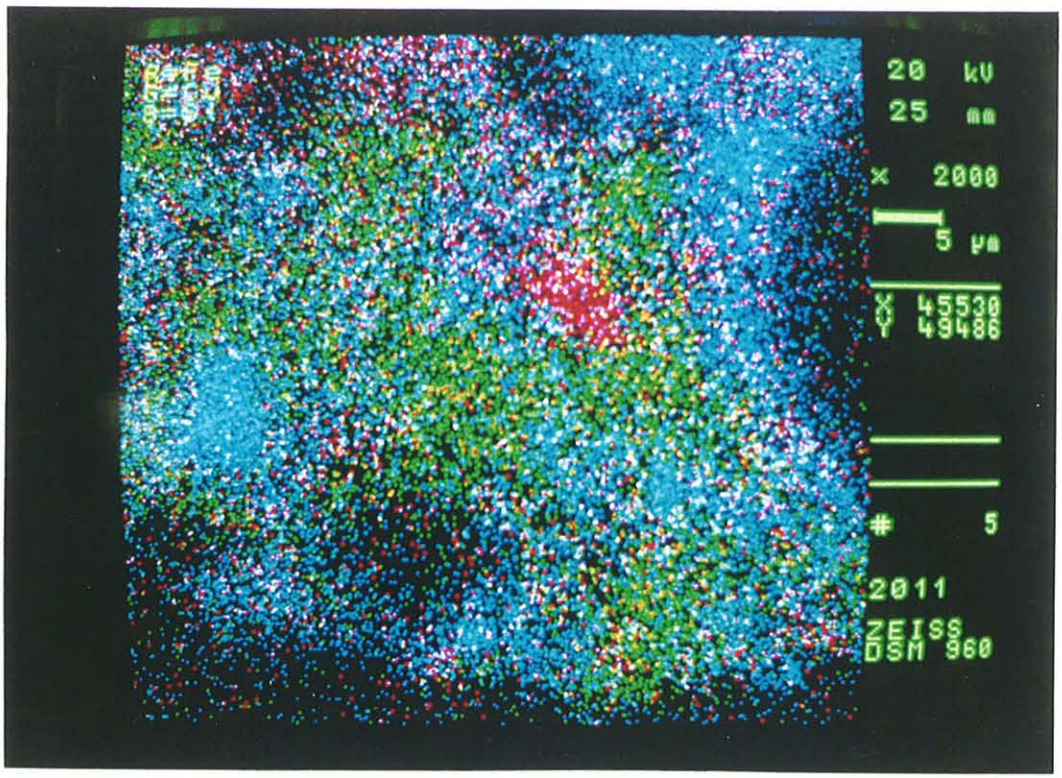



Fig. 14. CS 2011, blue area (same as fig. 13).
Red = iron; green = copper; blue = silicate

**CS 2011 (pigment layer with blue and brown)**

The sample comes from a leg of figure no. 4 in T21G18 of pit no. 2 (kneeling archer). It was brought to Germany as cross section (fig. 12). The colour of the leg was interpreted to have been blue and the brown to be a colour change. The paint layer is mainly brown, it contains smaller and bigger blue particles and areas which are spread equally over the whole length and thickness of the pigment layer.
On top of the pigment layer there is a layer of greyish-brown soil; the lacquer layer is partly preserved in the right part of the cross section.

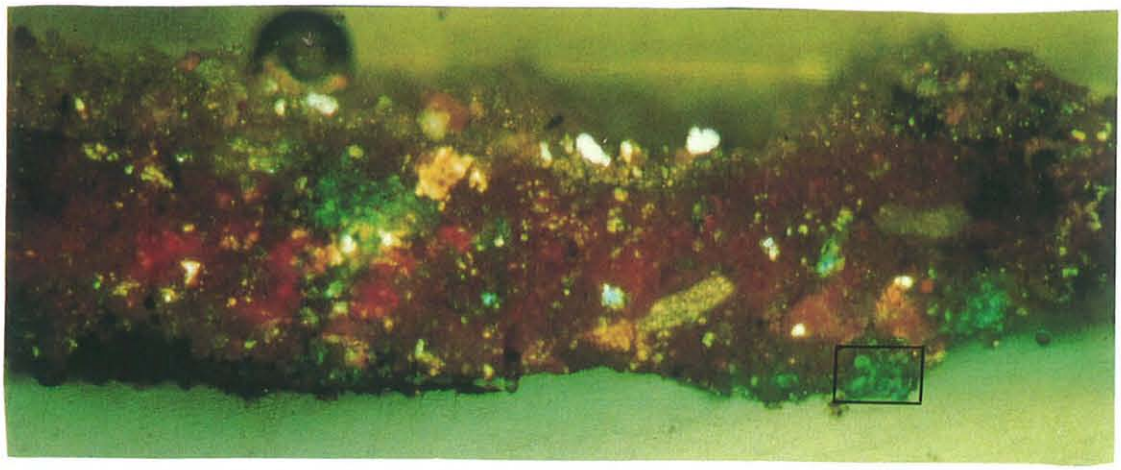
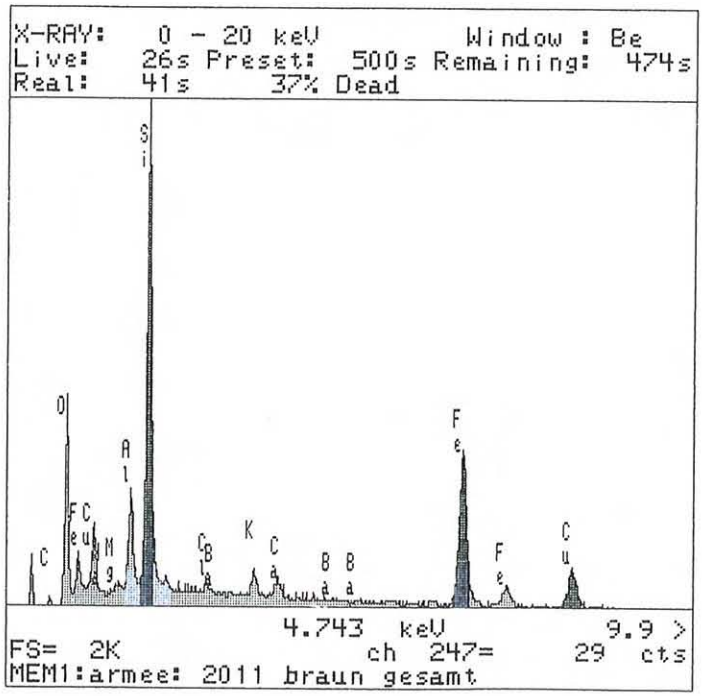


Fig. 12. CS 2011. The narrow side of the photo corresponds to c. 0.26 mm. The frame marks the detail shown in fig. 13 and 14.

*Results of the examination*

- blue: Cu; red particle inside a blue cluster: Fe (fig. 13 and 14)
- brown: Cu (very fine), Si (quartz), Fe (matrix, very fine), Ca, K, Al, Mg (clay minerals)

The bigger *blue* particles visible in the lower part of the cross section were examined. They contain copper and could be identified as azurite. A very small particle inside the blue one contains iron (iron oxide).
The *brown* layer consists of a matrix with extremely fine iron containing particles (below 1µ), clay minerals, quartz (fig. 15 and 16; spectrum 7) and a considerable amount of very fine copper containing particles. It seems that also in the areas which appear brown there are very small copper containing (blue ?) particles, maybe too small to give colour to the layer.
The composition of the *soil* is comparable to the one in CS 2007.




*Conclusion*

The pigment layer could be a well prepared mixture of blue and brown. The brown has not developed out of the blue. Neither does it seem to be a derivative of the soil. The brown shows almost the same colour as the soil on the *Qing gaoni* in CS 2012, but has a different structure. In CS 2012 the soil is very coarse with particles of a size about 100µ (compare fig. 21).

< Spectrum 7: CS 2011, brown area of the pigment layer

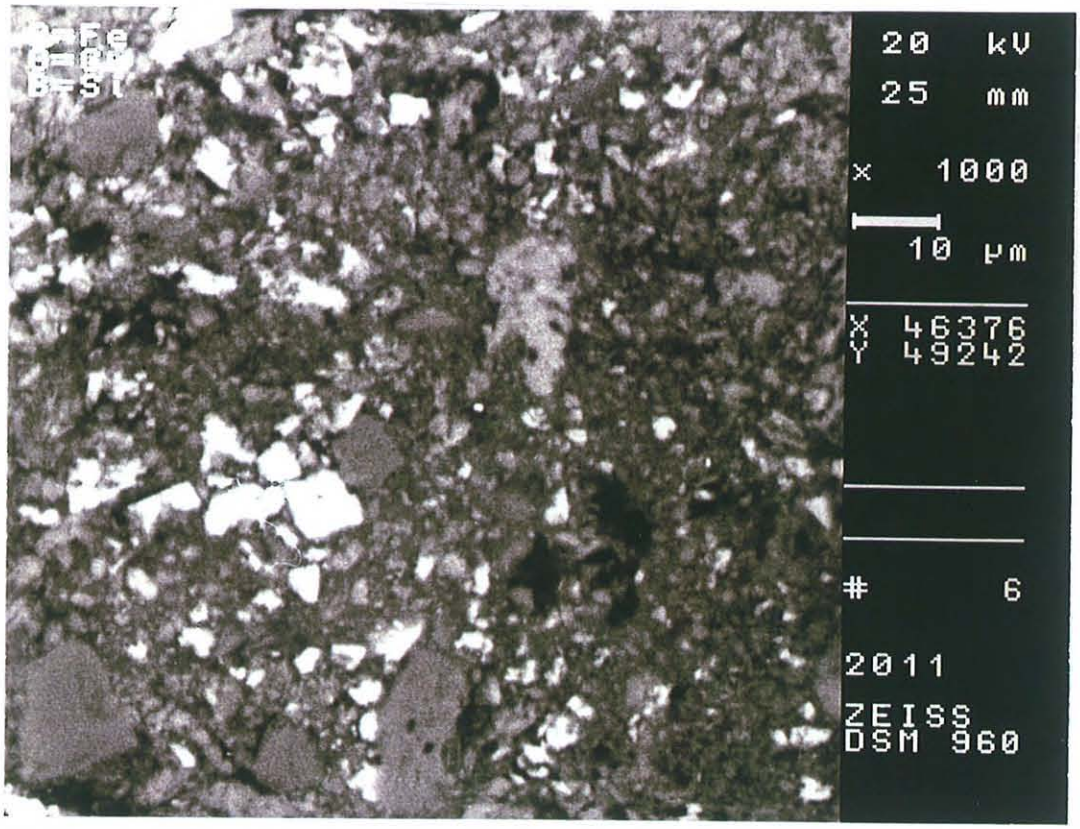



Fig. 15. CS 2011, brown area (in the middle of the cross section) with very small blue particles.

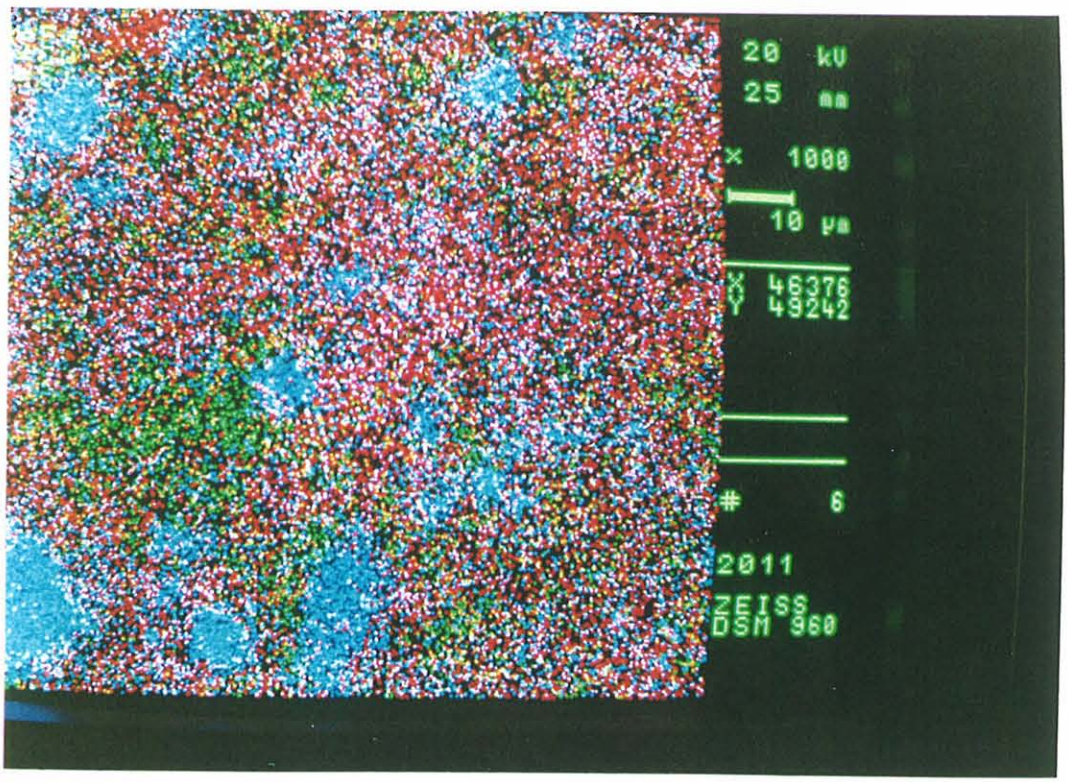



Fig. 16. CS 2011, brown area (same as fig. 15).
Red = iron; green = copper; blue = silicate

## CS 2005 (brown, previously green ?)

The sample comes from a leg of a figure in T21G19 of pit no. 2. It was brought to Germany as cross section (fig. 17). According to the Chinese experts the colour of the leg had been green and has "converted" into brown. In the cross section there are not any green particles visible. There is a layer of charcoal (?) between the pigment layer and the overlaying soil; the lacquer layer partially is still well preserved.

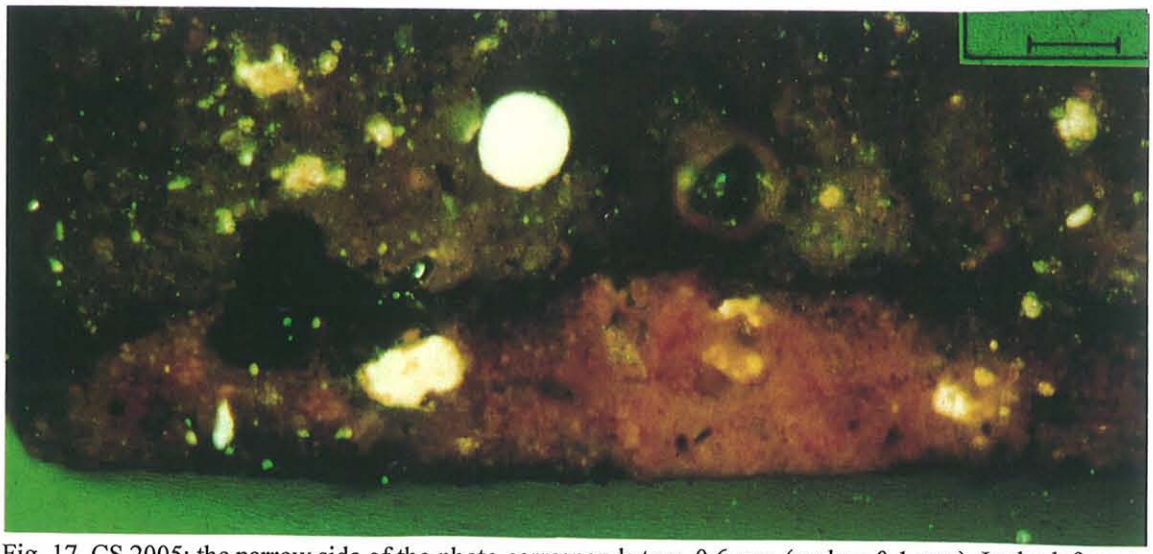


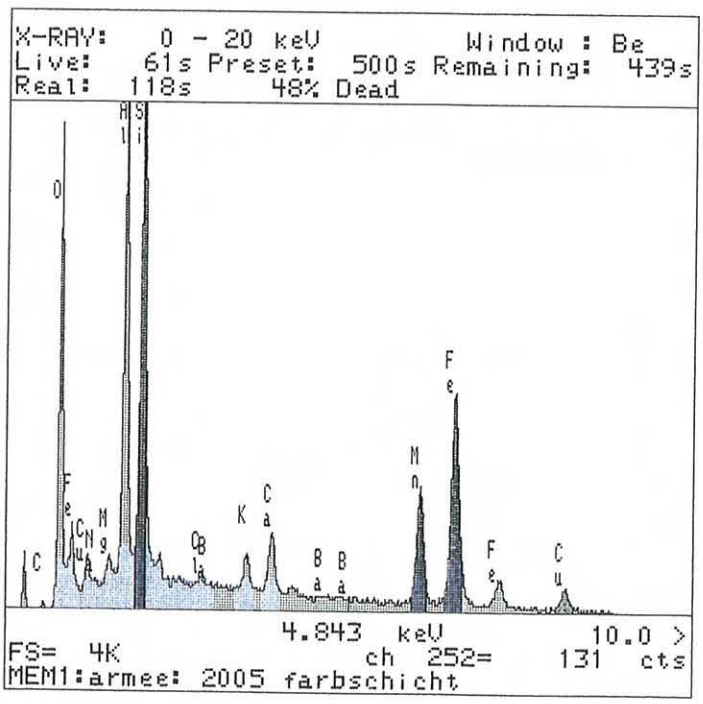
Fig. 17. CS 2005; the narrow side of the photo corresponds to c. 0.6 mm (scale = 0.1 mm). In the left part remnants of the lacquer layer are visible below the brown pigment layer. On top of it there is one bigger piece of charcoal as well as smaller ones indicating a continuous layer of charcoal.

*Results of the examination*

- brown: Fe, Mn, Al, Si, very little Cu

In the *brown* layer there is a distinct border to the soil, partly indicated by the layer of charcoal. The brown colour is given by iron (fig. 18 and 19). No evidence could be found that this layer has ever been green. The content of copper can be regarded as impurity of the iron. There are some particles containing manganese (spectrum 8). Maybe the pigment was a manganese containing earth, i. e. umber. Umber can be greenish, but is not as bright green as the malachite used in other pigment layers on the terracotta army.

The *soil* on top of the brown layer is very coarse.




Spectrum 8: CS 2005. Spectrum from particles with higher content of manganese

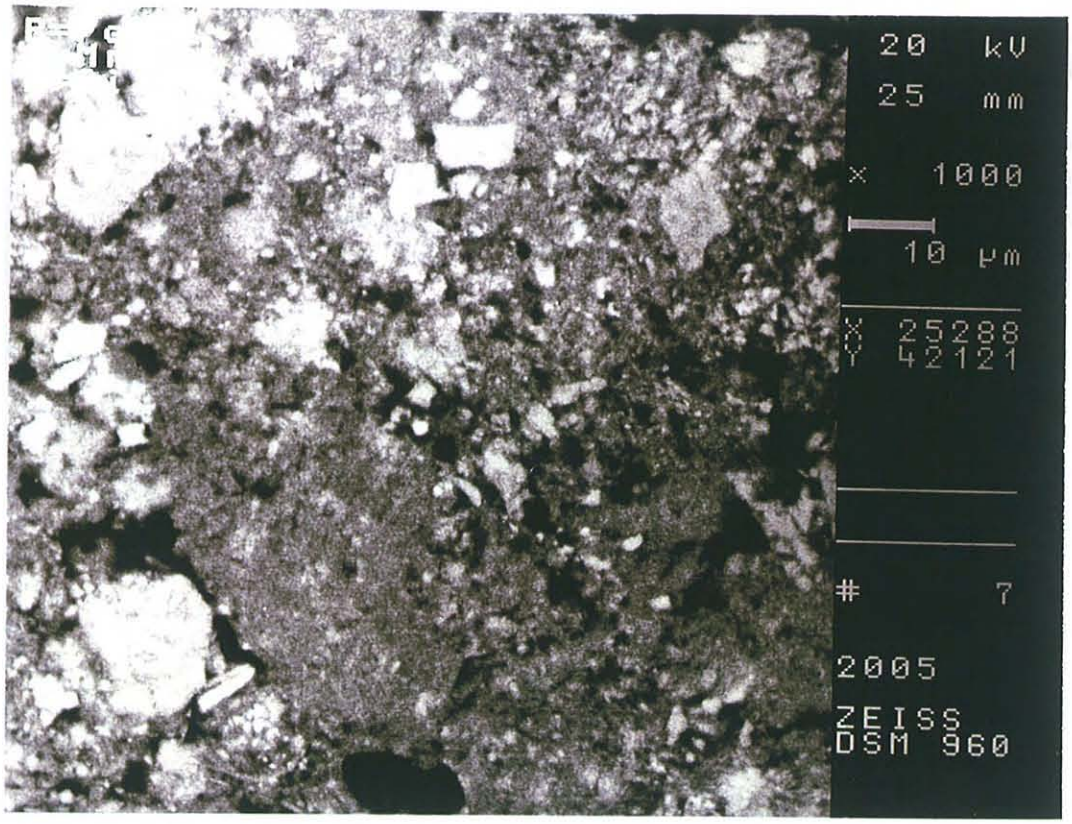



Fig. 18. CS 2005, brown pigment layer

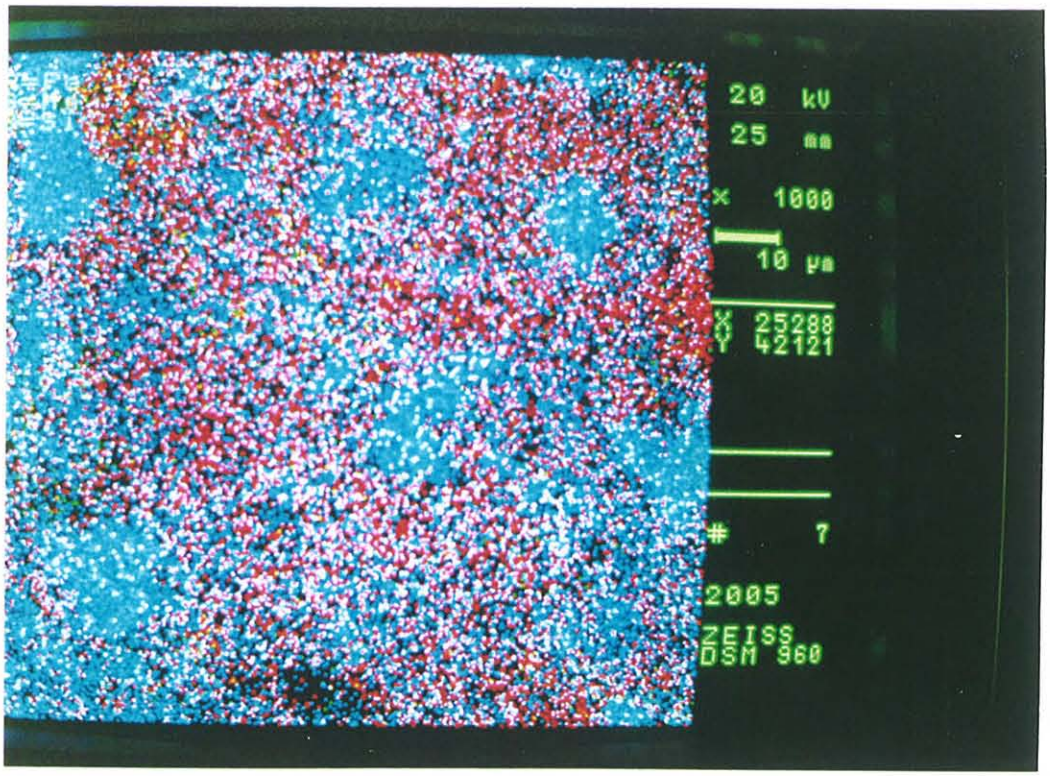



Fig. 19. CS 2005, brown pigment layer (same as fig. 18).
Red = iron; green = manganese; blue = silicate

**CS 2012 (*Qing gaoni* and soil)**

The *Qing gaoni* is a layer of special clay applied on the woven mats on top of the wooden beam roof of the pits probably to seal them against intruding water. The name refers to its colour (*qing* = green or blue). The sample CS 2012 was brought to Germany as cross section (fig. 20). The *Qing gaoni* appears greyish while the adhering soil (on top of the *Qing gaoni* ?) is reddish brown. The sample was taken to compare this soil layer to the brownish parts of the pigment layers in the samples CS 2007, 2005 and 2011.

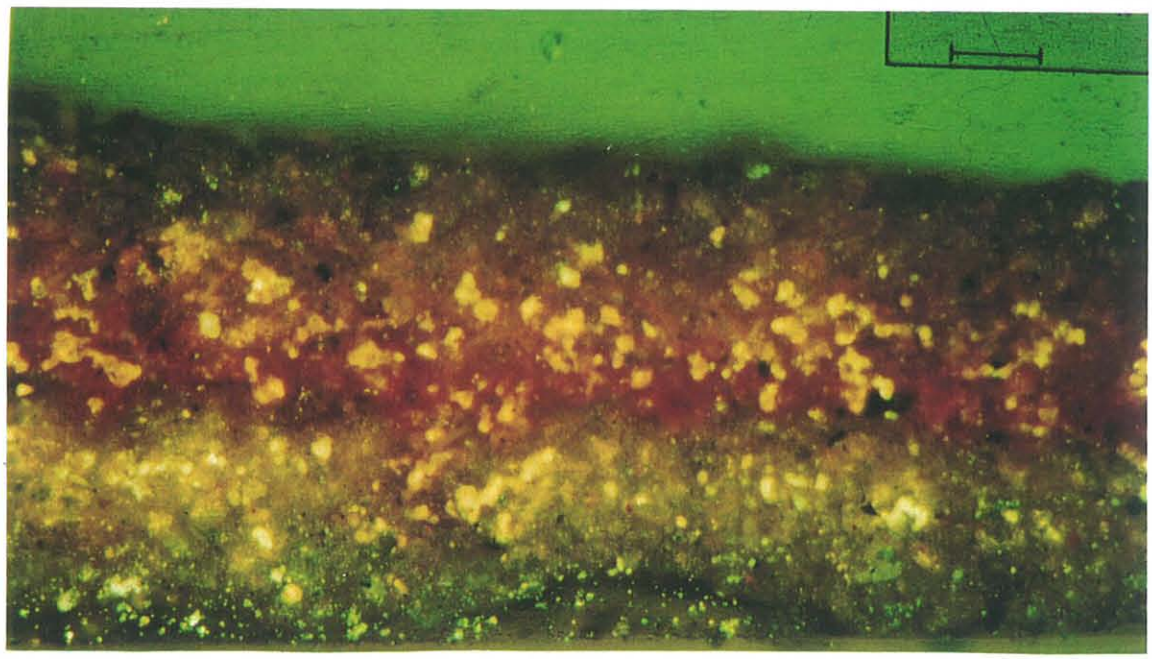


Fig. 20. CS 2012; the narrow side of the photo corresponds to c. 0.74 mm (scale = 0.1 mm). The lower, reddish zone is the soil, the upper greyish zone the *Qing gaoni*.

*Results of the examination*

- Si, Fe

The *soil* is coloured due to the content of iron. The structure is very coarse compared to the pigment layers on the terracotta figures.

The structure of the *Qing gaoni* is comparable to the one of the soil. No closer examination or determination of elements was performed, because it was not important in this context.

By comparison to the pigment layers with soil on top there is no sharp and distinguished border between the *Qing gaoni* and the soil layer (fig. 21 and 22).

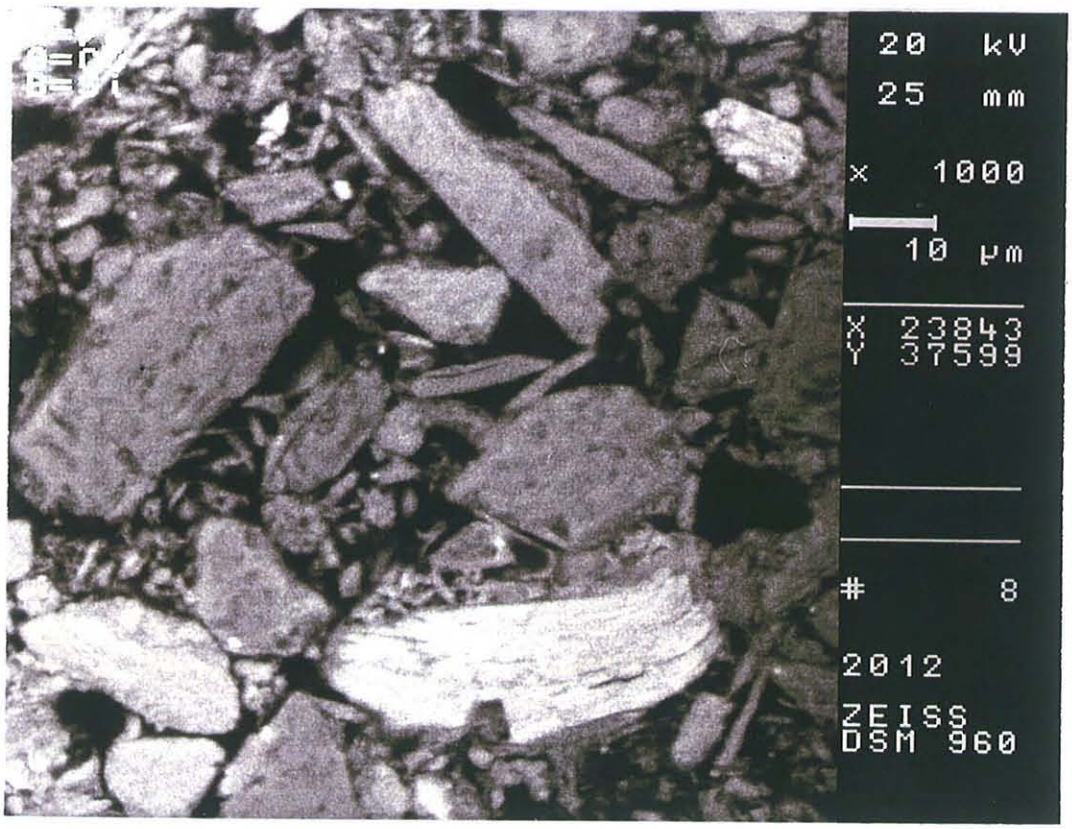



Fig. 21. CS 2012, reddish brown soil (lower part) and *Qing gaoni* (upper part).

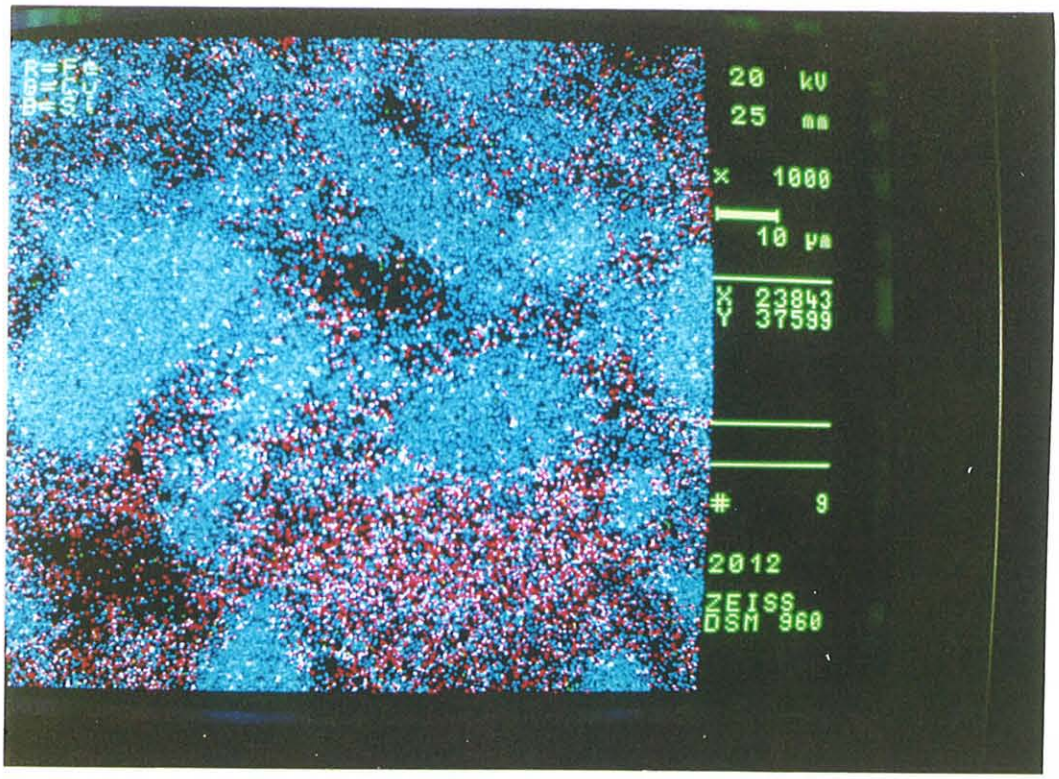



Fig. 22. CS 2012, reddish brown soil (lower part) and *Qing gaoni* (upper part, same as fig. 20). The layers can be distinguished by the higher content of iron in the soil. The border between the layers does not mark clearly.
Red = iron; green = copper; blue = silicate

# Assembling of the broken terracotta figures from the burial complex of Qin Shihuang

Fig. 1. Restored figure with fillings and completions, begin of retouching, pit no. 1, May 1999

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1 Introduction
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# Assembling of the broken terracotta figures from the burial complex of Qin Shihuang

C. Blaensdorf

## 1 Introduction

After the discovery in 1974, the terracotta army from the burial complex of Qin Shihuang soon became famous for the thousands of life-size terracotta figures. The army fascinates with the long rows of warriors and horses standing side by side in narrow corridors. But the figures are not unearthed in this situation: All figures are broken, lying on the floor and one on top of the other. Therefore the task to reassemble the figures arose directly after the beginning of the excavation. The work started in 1975 and still continues.

The problems of restoring the broken figures have been discussed between Chinese and German experts since the beginning of the co-operation work in 1991. However, research and practical work focussed on the conservation of the polychromy of the figures and the preservation of the soil structures of the pits. These problems were - and still are - the most urgent ones to solve.
Since 1998 the problem of reassembling ("restoring"[1]) the broken figures got more attention within the co-operation project. This resulted from a critical evaluation of the work carried out so far as well as the continuation of excavation in a larger scale in pit no. 2. During the Meeting of the Steering Committee in May 1998, the joining of the broken figures was explicitly defined as subject of the co-operation work.[2] The work stay of Chinese experts in Germany in 1999, for the first one focussing on the assembling of the broken figures as main subject.

The excavation of the terracotta army is not finished yet. Only the small pit no. 3 has been totally excavated. Meanwhile new burial pits are found round the grave mound; during test excavations at least four richly furnished pits have been explored. They contain objects of stone and bronze, but also more terracotta figures. In pit no. 0006 figures of civil servants have been found, in pit no. K9901 statues of acrobats (*baixiyong*).

The production of the terracotta figures has been described in detail by the archaeologists in excavation reports on the terracotta army. Base for restoration tests is scientific research on the properties of the terracotta and possible restoration materials. The results are described in the following contributions.
This text tries to give a summary on important facts of the production techniques, the process and characteristics of the breakage and on restoration methods, their problems and new ideas.

## 2 Description of the terracotta figures

The terracotta army is set up inside three pits.[3] All figures face east, so east can be regarded as front or entrance side. The total number of figures is estimated on ca. 7000 warriors, 130 wooden war chariots with four horses each (i.e. 520 chariot horses) and 150 saddle horses (from the cavalry). The distribution on the three pits is demonstrated in the following table (table 1[4]).

| Pit no. | type of troop formation | size of the pit | | number of warriors | chariots | horses |
|---|---|---|---|---|---|---|
| 1 | infantry and chariots (mixed) | 62 x 230 m | 12600 $m^2$ | 6 000 | 50 | 200 |
| 2 | archers (unit 1)<br>war chariots (unit 2)<br>infantry, war chariots, cavalry (u. 3)<br>cavalry (unit 4) | 26,6 x 38 m<br>52 x 48 m<br>68 x 16 m<br>50 x 20 m | 5988 $m^2$ | 800 to 1000 | 80 | 470 |
| 3 | guard of honour or head quarter | | 520 $m^2$ | 66 or 68 | 1 | 4 |

1 The reassembling of the broken figures is called „Restoration of the Figures" by the Chinese colleagues from the Museum of the Terracotta Army and in Chinese publications in English language.
2 See Co-operation agreement from May 1998, top 4.).
3 A fourth pit with a size of 4600 $m^2$, located between pit no. 2 and 3, had never been finished and is empty.
4 Numbers from: Wu Yongqi, The Museum of the Terracotta Army, Arbeitsheft 83, p. 308-332.

In general the figures are classified according to their military rank and their artistic style. Regarding the position of their bodies, the figures of the warriors can be separated into the following groups:

a. standing warriors,

b. standing archers

c. kneeling archers.

a. Most of the figures belong to the type of the *standing warrior*, all together about 6 600 figures. This comprises all warriors from pit no. 1 and pit no. 3 as well as the figures from the units 2, 3 and 4 from pit no. 2. These figures stand upright and straight, with both feet on one base slab. The position of the arms differ depending on the type of troop formation: Infantrymen (fig. 2), adjutants of the charioteers and cavalrymen have their arms tight to their bodies, the forearms are either stretched or bent. The hands have different positions, closed or stretched, often holding weapons. The charioteers (fig. 3) stretch their arms out in front of them to hold the reins.

b. The *standing archers*, about 160 figures from unit 1 of pit no. 2 and one figure from pit no. 1, are depicted in a striding position. The feet are standing on two separate base slabs. The arms do not have contact to the body; the right one is stretched, the left one bent in front of the chest (fig. 4).

c. The *kneeling archers*, about 172 figures from the unit 1 of pit no. 2, are depicted with their right knee on the ground, the left foot set up next to it. The figures do not have a base slab. They are standing on the knee and the tips of the toes of the right leg as well as the left shoe sole. The bent arms lie tight to the body (fig. 5).

The horses stand on all four hooves, they do not have a base slab. Chariot horses and saddle horses do not differ in their position. The cavalrymen are not sitting on the horsebacks, but standing in front of their saddled horses, holding them on the reins.

The newly discovered figures of twelve civil servants from pit no. 0006 correspond to the standing warriors in height and technique, but differ in the artistic style. Their hands are hidden inside the sleeves.
The figures of the acrobats from pit no. K9901 are very different as they only wear skirt, i.e. the body is mainly visible. Some of the figures are short and slim like boys, others are tall, muscular and fat. Their position shows much more motion than the soldiers: Some raise their arms or bent their legs.

The *height* of the figures without base slab in average is about 180 cm (max. 202 cm). This means they are even taller than life-seize. The kneeling archers have a height of 120 cm. The horses measure 170 cm in height and 205 cm in length. The tall figures from the acrobats measure 1,90 m without the missing head and without the base slab.
The *weight* of the figures is 120 to 200 kg. The horses have a higher weight than the warriors.

Fig. 2. Infantryman

Fig. 3. Charioteer

Different types of warriors:
Fig. 2 and 3. Standing warriors
Fig. 4 and 5: Two types of archers

Fig. 4. Standing archer

Fig. 5. Kneeling archer

### 3 Technique of production of the terracotta figures[5]

The figures are made of a light grey clay. The composition is similar to the loess soil in Lintong. The clay material probably was taken from the surrounding of the burial complex.

The figures were mainly formed by hand, using coiling technique or clay slabs. Only hands, feet and heads have been produced in moulds. The parts of the body and the limbs were made separately and connected with clay slip. In this way the *rough form* of the entire figure form was made.
Afterwards the rough forms got a *fine modelling*. Details of the faces, hair and clothes of the warriors, the muscles, mane and tail of the horses were finely formed and structured. They were either engraved or modelled from additionally applied clay material. The rhombus pattern of the belts seems to be impressed by a mould. For the design of the suits of armour and the saddles, small details made in moulds were applied with clay slip. A wooden mould for a connection stitch element of the armours has been found inside pit no. 1. The little loops on the back of the warriors with armours are made of terracotta and served for the fixation of wooden and basket-work quivers.

The figures are *hollow inside*. The void of the body was connected with the ones of the limbs. Sometimes holes are drilled through massive parts as base slabs, feet and lower legs. This method was advantageous for the work process as well as for the firing. Holes in the bottom of the "skirt" of the figures and in the sides of the horses serve for a sufficient ventilation during firing (see. fig. 6 and 23).

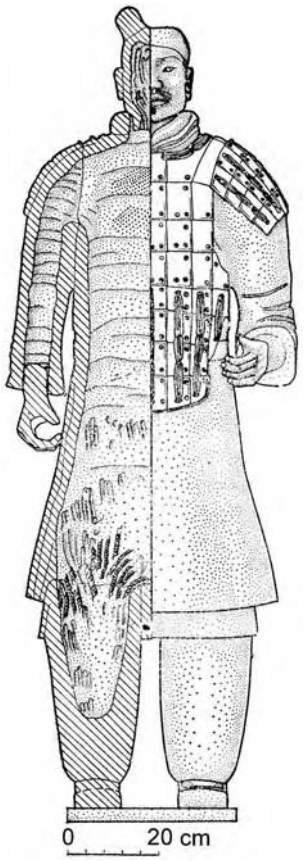


Fig. 7. Section through a standing warrior

On the insides of the figures there are numerous traces of the work process, i.e. fingerprints, marks of tools, supports and temporary connections with strings and joints of clay coils or slabs. The inner sides therefore carry important information about the production of the figures (see fig. 7 and 18).

The terracotta of the bodies and the hollow legs has a thickness of 3 to 5 cm. The arms and parts which do not carry much weight mostly are thinner (1 to 4 cm). Only parts of relatively low thickness (up to a diameter of 10 cm maximum) are massive, e. g. hands, some of the forearms and lower legs and the base slabs.

The horses were made in the same way as the human figures. The hollow bodies are made from clay slabs, legs and tails are massive. The newly discovered figures of the civil servants and the acrobats are made analogue to the warriors.

The figures have been fired as one complete piece. Only the heads and maybe sometimes the hands were fired separately and connected with the figure afterwards. The horses were fired as complete statues. The kilns had an open fire. The channel leading towards the centre of the kiln was filled with fire-wood (or other material).
The firing of entire figures of this size in on part can be regarded as a great achievement. Today, for the production of replicas of the warriors, the workers always cut the modelled figures into several parts to avoid cracks or the bursting of the figures during firing. After firing the figures were painted.

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[5] All information on the production process - as far as not indicated otherwise - from: Archaeological team / Archaeological Institute, *Qin Shihuangling bingmayong keng yihaoyeng fajue baogao 1974-1984*. Beijing 1988 (Excavation report on pit no. 1 of the terracotta army of the burial complex of Qin Shihuang) as well as Yuan Zhongyi, *Qin Shihuangling bingmayong yanjiu*. Beijing 1990 (Research on the terracotta army of the burial complex of Qin Shihuang).

## 4 Causes of damage

Today, all figures are broken. The pits show traces of fire and man-made damages. The first and largest destruction maybe took place only four years after the death of the First Chinese Emperor. Literature sources record that the capital and the palaces were destroyed during the revolts in 206 BC. Probably the rebellious troops also invaded into the half-finished burial complex, robbing the weapons of the terracotta figures, demolishing the burial goods and setting the wooden constructions on fire.

Visible effects of this destruction are the charred wooden roof beams that partly have collapsed. Charcoal often covers the surfaces of the figures. Partly the terracotta figures have been fired again: the grey terracotta turned brick-red (fig. 1). Few of the red-fired terracotta fragments are extremely deformed. (fig. 21). In the eastern part of pit no. 1, the figures are broken into many small pieces. The fragments are scattered over larger areas. Obviously these figures were smashed deliberately. Other areas as well as parts of pit no. 2 and the entire pit no. 3 do not show any traces of fire.

Over a long period sediments from rain falls and floods form the river and the soil from above the roofs filled the corridors. The rammed earth of the partition walls was pressed down, the wooden roof beam bent downwards. Originally the partition walls had been 3,20 m high, i.e. there was 1,20 m of air above the heads of the figures. In pit no. 1, today they are often not even 2 m high any more, so the heads of the restored figures can be seen from the side of the pit, sticking out over the partition walls(see fig. 28). In pit no. 2, several heads of a still standing figure has broken through the remnants of the roof. All voids, also inside the figures are totally filled with soil today.
A lot of figures in the better preserved areas often are still in their original position, sometimes even standing. They are only broken into bigger parts. All fragments can be found nearby. These figures seem to be only damaged by the pressed-down construction of the pits and the penetrating soil.

The figures of the acrobats seem to be clashed deliberately; the wooden floor is charred. The civil servants were all found lying face-down next to each other. The pit does not show traces of fire.

Another problem is that the restored figures break during transports for exhibitions. Often the legs of the horses break off as well as the feet of warriors.

## 5 Position of breaks and size of fragments

Thus, there are two main reasons for the damage of the figures: the deliberate clashing as well as the falling down and cracking caused by the pressure of the soil. A detailed classification of the type of breaks, the size of fragments and the reasons for the damage is not made yet.
Principally, except for the extreme damage by fire and the man-made destruction, typical breaking zones show a dependence on
a. the technique of production and
b. the exposition of special parts to mechanical stress.

a. Often the figures are broken on joint of terracotta parts, i.e. joints of limbs to the body or joints of terracotta slabs. On many figures the technique of the production was revealed only because the figure broke exactly on these joints. Typical breaks at joints are: between legs and body, joint of the upper and the forearm, horizontal breaks in the level of the waist. Applied details as the connection stitches often fall off. Sometimes a separation of the layers was observed: the fine-modelling detached from the rough form.

b. Typical breaking zones of the standing warriors are “weak point” as the ankles of the feet, the connection of the legs and the arms to the body. The collar which had to hold the head, is often broken or chipped off. The base slabs are broken asunder in different directions; the feet are broken in the middle (crosswise on the instep). Thin massive legs of warriors and horses often are broken several times, while the thick legs, depicting thick shin guards and made as hollow tubes, are frequently not broken at all. The hollow bodies have been crushed, especially when they had been lying in a horizontal position (horses; lying figures). Here the breaks run in all directions and are found in all parts without any recognisable system.

Sometimes there are gaps between the fracture edges. Small parts have chipped off along the fracture edges, caused by the breaking of the soft, low-fired terracotta. In previous years also the rough cleaning with metal brushes caused a loss of surface structure of the fracture edges.

| part of pit no. 1 | position - no. of fig. | type | number of fragments (size in cm) | | | | areas with many fragments | losses | | damages from man-made destruction |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | big (10x10) | small (5x5) | tiny (below 3 x 3) | total no. | | dimen-sion* | position | |
| ?? | 03 | A | 26 | 98 | 60 | 166 | all | 4.5 | arms; legs base slab | |
| vanguard, north | T1K(1)-89 | W | 52 | 16 | 17 | 85 | F-robe | 0.08 | L-arm | |
| | T1K-57 | W | 42 | 37 | 12 | 91 | skirt of robe | 1.5 | arms | |
| | T1K-58 | W | 17 | 36 | 23 | 76 | F-chest; back | 0.1 | L-shoulder R-arm | |
| vanguard middle | T10K-15 | W | 29 | 31 | 23 | 83 | L-chest | 1.2 | back L-arm | |
| | T10K-16 | W | 16 | 29 | 0 | 45 | R-chest R-arm; wrist | 0.15 | L-arm F-chest | red below head |
| | T10K-46 | W | 21 | 10 | 6 | 37 | L-shoulder | 0.2 | L-shoulder R-collar | |
| | T10K-74 | W | 23 | 19 | 8 | 50 | part of back below shoulders | 0.135 | back; no R-arm; no head | |
| 1st corridor from north, 0-20 m from east end | T1G1-01 | W | 36 | 36 | 5 | 77 | B-pants | 0.5 | L-F-chest; arms; back | |
| | T1G1-10 | W | 40 | 9 | 5 | 54 | arms | 0.3 | L-chest L-arm; F-collar | |
| | T1G1-32 | W | 16 | 32 | 13 | 61 | back B-robe | 0.13 | L-collar F-robe | |
| | T1G1-32 (?) | W | 42 | 10 | 46 | 98 | S-robe; S-waist | 0.12 | back; L-wrist; mouth; B-belt | |
| 1st corridor, 20 -40m | T1G2-50 | A | 31 | 30 | 13 | 74 | F-chest | 0.06 | F-collar; F-chest; F-robe | red; deformed |
| | T1G2-28 | W | 19 | 25 | 17 | 61 | B-F-robe | 0.3 | back; B-arm F-robe | |
| | T1G6-58 | A | 23 | 32 | 6 | 61 | F-chest; skirt of robe | 0.02 | L-arm skirt of robe | B-robe red |
| 2nd corridor, 0-20m | T2G1-1 | A | 35 | 34 | 19 | 88 | skirt of robe; head | 0.5 | L-skirt of robe; back | |
| | T2G1-4 | A | 31 | 33 | 18 | 82 | B-collar B-shoulder | 0.3 | L-S-collar and robe; F-chest | L-shoulder red |
| | T2G1-5 | A | 23 | 31 | 20 | 74 | chest; back R-leg; R-arm | 0.3 | R-arm R-F-robe; legs | |
| | T2G1-19 | A | 19 | 35 | 14 | 68 | L-arm; F-robe; back; F-chest | 0.015 | L-arm forehead | |
| | T2G1-24 | A | 19 | 19 | 8 | 46 | R-chest | 2.4 | arms; R-F-chest L-collar | |
| | T2G1-32 | A | 29 | 16 | 9 | 44 | back | 0.02 | back R-arm | |
| | T2G1-79 | A | 30 | 9 | 17 | 56 | chest; skirt of robe | 0.13 | back; L-wrist | |
| | T2G3-47 | A | 28 | 21 | 5 | 54 | back B-robe | 0.12 | chest B-robe | |
| middle part ??, 0-20m | T10G1(?) -4 | W | 39 | 15 | 11 | 65 | F-chest | 0.2 | arms L-F-chest | |
| | T10G1(?) -10 | W | 15 | 9 | 4 | 28 | R-arm | 0.5 | arms; no abdomen; no head | |
| 6th corridor, 0-20 m | T10G6-59 | A | 19 | 31 | 11 | 61 | F-robe | 0.1 | S-F-robe | |
| 7th corridor, 0-20 m | T10G7-45 | A | 16 | 12 | 13 | 39 | back | 0.3 | back L-F-chest | |
| | T10G7-47 | A | 11 | 20 | 3 | 34 | legs | 0.06 | collar legs | |
| 11th corridor, 0-20 m | T20G11-37 | A | 24 | 9 | 7 | 40 | shoulders | 0.05 | collar | red above the skirt of robe |
| | T20G11-B30 | A | 23 | 13 | 9 | 45 | head | 0.11 | head | |
| W = without armour, A = with armour; L = left side; R = Right side; F = front; B = back; S = side | | | | | | | | | | |

Table 2. Investigation on situation of breaks on 30 standing warriors from the restoration area in pit no. 1

If the figures are severely deformed by heat and/or the long storage in the soil a fitting assembling of the fragments is impossible (fig. 21). Very few figures also show swollen features, covered with open blisters, caused by the fire of the arson or by the bad quality of the terracotta.

In May 1999 an attempt was made to survey the situation on about 140 figures in the rear (western) part of pit no. 1, which serves as restoration workshop. The figures were totally or partly glued together, but did not have fillings and retouches yet. Most of them come from the eastern part of pit no. 1, especially from the vanguard in front of the corridors[6] and the first 40 m inside the rows. Some figures belonged to pit no. 2.
Most of the figures, in average were broken into 60 to 70 pieces of which most were bigger pieces and only some smaller (below 8 x 8 cm). Figures with less than 50 pieces were rare. Figures that were broken into small fragments (5 x 5 cm and smaller) consisted of 140 to 200 fragments. The majority of the figures were not complete. The missing parts differed in size and number. Very often the fracture edges did not fit perfectly anymore.

Table 2 (p. 107) shows the results of a more detailed examination carried out by the Chinese colleagues in summer 1999. All figures come from the three rows of the vanguard and the first 40 m from east to west of the 11 corridors of infantry and war chariots (i. e. the first two excavation sectors of 20 x 20 m). Mainly they are from the first sectors from the east (0 m to 20 m from the eastern end of the pit).
A larger number figures are from G1, the first corridor in the north. The remotest corridors on the north and south are the flanks. There are only two soldiers next to each other instead of four, one facing east, the other north (or south). Because these corridors are more narrow than the nine corridors in the centre, more figures are still upright here, more or less in their original position.

The table has been evaluated regarding the total number of fragments per figure and the distribution of sizes of fragments. One has to consider that a lot of very small fragments are missing, because they could not be identified. If all fragments had been found, the total amount and the number of tiny fragments would be much higher.[7]

| total number of fragments | number of figures with total number of fragments |
|---|---|
| below 20 | -- |
| 20-29 | 1 |
| 30-39 | 3 |
| 40-49 | 5 |
| 50-59 | 4 |
| 60-69 | 6 |
| 70-79 | 4 |
| 80-89 | 4 |
| 90-99 | 2 |
| above 100 | 1 |

Table 3. Total number of fragments per figure

Table 3 shows that relatively few figures consist of less than 40 fragments. 40 to 49 pieces, 50 to 59, 60 to 69, 70 to 79 and 80 to 89 can be found with the same frequency, with a slight peak between 60 and 69 pieces. More than 90 pieces were very rare.

The following table (tab. 4) shows the distribution of the sizes of fragments. Most of the figures consist of 16 to 30 big pieces (10 x 10 cm or bigger) and up to 35 small pieces, as well as up to 15 tiny pieces. More than 20 tiny pieces are rare, maybe because they can only be recognised when found next to the bigger ones. Less than 10 big pieces were not be present what means that no very bad damaged figures were examined. These results correspond to the observations made in May 1999.

6 The corridors run from east to west; the vanguard corridor in front of them, runs crossways from south to north.
7 The column with the dimension of missing parts in table 2 is not reliable, because the measurement and the calculation of the dimensions was not correct.

| | number of figures with this number of fragments | | |
|---|---|---|---|
| number of fragments | big (10 x 10) | small (5x 5) | tiny (3 x 3) |
| 0-5 | -- | -- | 6 |
| 6-10 | -- | 6 | 7 |
| 11-15 | 2 | 3 | 6 |
| 16-20 | 8 | 5 | 2 |
| 21-25 | 6 | 2 | -- |
| 26-30 | 5 | 2 | -- |
| 31-35 | 3 | 8 | -- |
| 36-40 | 3 | 3 | -- |
| 41-45 | 2 | -- | -- |
| 46-50 | -- | -- | 1 |
| 50-55 | 1 | -- | -- |
| more fragments | -- | 1 | 1 |

Table 4. Distribution of sizes of the fragments

The following figures show three examples of broken warriors from pit no. 1:

Fig. 7 shows a typical situation: The warrior no. 100 from T19G10 is broken into larger and smaller fragments, some smaller pieces are missing. The base slab is broken apart, one leg is broken. Both legs are broken of at the connection zone between legs and robe. Except for the right hand, the figure is complete.

Fig. 8 shows the statue of the general from pit no. 1. Only the lower part of the robe is broken into smaller pieces. The upper body with the arms is not broken at all. Such as good state of preservation is rare in the eastern part of pit no. 1, but rather common in the unit of the kneeling archers in pit no. 2. Because of their pose, frequently the body is not broken into pieces; only hands, feet and the head are usually broken off.

Fig. 9 shows a rather heavily damaged warrior from pit no. 1: The body is broken into many. pieces. The head and a part of the right upper arm are missing. For a restoration of the figure, larger completions had been necessary in the lower part of the robe. The ankles of both feet are broken, like it often happens on thin massive legs. Though this figure looks quite fragmentary, this is not the worst case of damage found in pit no. 1.

Fig. 7. Warrior no. 100, from T19G10, pit no. 1

Fig. 8. General from pit no. 1

Fig. 9. Severely damaged figure from pit no. 1

## 6 Method of assembling the fragments

### 6.1 Workshops

Since the erection of the hall above pit no. 1, the rear (i. e. western) part of the pit is used as restoration workshop for the terracotta figures, as storage room for the restored figures and those that have returned from exhibitions.
Five excavation sectors of 20 x 20 m (T 8, 9, 17, 18, 27) where the excavation has not been started yet, serve as workshop area for the assembling of the figures. In the southern part (T 8 and 9) isolated fragments are laid out on plastic foils. In the sectors T 17, 18 and 27 (middle and north) the figures are built up from the assigned fragments (fig. 12 -14).
Two adjoining excavation sectors (T 16 and 26) serve as storage areas. Here the excavation had been stared, but the openings have been refilled again. T 26 is used to store restored figures. The level is about 1.60 m lower than in the untouched areas (fig. 15).

Besides the hall of pit no. 1, also rooms in the workshop/laboratory building have been and sometimes still are used to gluing of terracotta figures (see fig. 10). The figures of the acrobats have been restored in the storage room[8]. The figures of the civil servants have been consolidated and glued together in a side-room of the temporary hall of pit no. 0006.

Working inside the pits has the advantage that the fragments and the completed figures do not have to be transported over longer distances. Furthermore, in pit no. 1 there is a lot of space, so many fragments can be laid out and many figures can be assembled on the same time. The disadvantage is, that these places are not equipped as restoration workshops: Electric installations and light are rare, there is no water supply. Because the loess is dry now, everything gets very dusty in short time. From time to time water is sprinkled on the soil surfaces to reduce the dusting. In the side-room of pit no. 0006, there are tables, light and water.

All the figures that are restored in pit no. 1 do not have polychromy anymore or only small remnants. The polychromy of the civil servants and the acrobats has been preserved before the figures were glued together.

### 6.2 Method of gluing

The method has been slightly changed and advanced during the last years. Principally, the same methods and materials are used since 1975.

When terracotta fragments are removed from the excavation, fragments belonging to one figure are taken out and stored together. Smaller units of single fragments and pieces that could not be identified yet, are laid out on plastic foils in the rear part of pit no. 1 (fig. 17). If adjoining pieces are found, these are marked or assembled provisionally. For the provisional fixation lumps of plaster (gypsum) are used being placed on the outside or inside of the figures (fig. 16), sometimes also strings or bandages. Before the fragments can be glued together, the plaster lumps have to be scratched off again.

Before the gluing the fracture edges are cleaned. In previous years, wire brushes have been used to remove the soil from the fracture edges. This treatment causes losses, because the metal is much harder than the terracotta. Afterwards the fragments do not fit well anymore.
After most of the soil has been removed, the fracture edges are cleaned from remnants of soil and dust with paint brushes, scalpels and spatulas. If necessary, they are degreased with alcohol. During a provisional assembling without adhesive the exact position of the fragments is marked with control signs in the shape of lines, triangles, square, circles with a black, shiny material (ink ?, epoxy resin ?; fig. 18, marks for gluing visible on fig. 13). Sometimes the fragments are also given numbers with the same black colour (Chinese numbers ( ), see. fig. 19).

Since the beginning of the restoration work in 1975, epoxy resin is used as adhesive for gluing the terracotta. The used epoxy resin with the serial number “E-44” is produced in Xi’an; its properties are

[8] The room has a large door towards the outside and is used for packing objects for exhibitions, storing transport boxes and parts of not used laboratory equipment, but one corner is also used for conservation and restoration work.

comparable to “Araldite 2011”, an epoxy resin from the company Ciba.[9] The epoxy resin is mixed with a “polyamid gum” (polyamide) which serves as hardener.[10] It has a brown colour; detailed information was not available.[11] This type of epoxy resin has a high adhesive strength. The Chinese experts think that this is necessary because of the high weight of the figures and mechanical stress during transports.

The epoxy resin is used as delivered from the company, but with addition of retarding agents. In this way, the setting time is 24 hours, so there is still time for corrections. In pit no. 3 instead of the polyamide “ketimide” (ketimine or ketoimine)[12] was used, because the fragments had been glued while still damp.

After the major amount of fragments has been assigned, the warriors are glued together, starting either at the feat or the collar. Smaller units are assembled, when several fitting pieces have been found.
As soon as possible the figures are placed on the feet. The body is assembled part by part, later on the arms and smaller pieces are added. The heads which originally had been put inside the collars without further fixation, are fixed with epoxy resin or plaster nowadays.
The adhesive is spread on the entire surface of both fracture edges. The pieces are pressed together and fixed in the correct position until the adhesive is hardened. On the outside of the figures a surplus of adhesive coming out of the joint, is removed with alcohol or other solvents. On the inside the surplus of adhesive is not removed; thick drops and traces of run down material are often visible. These traces are dark brown, brittle and refer to the viscous consistence of the adhesive (fig.19).

For temporary fixations during gluing mostly strings and ropes are used, sometimes also wooden supports and frames (ropes: see fig. 10, 12 and 13). Smaller units of fragments are placed into sand boxes for the time of the hardening of the epoxy resin. Furthermore, lumps of plaster are put on both sides (outside and inside) over the joint as temporary fixation. Often this method is used to bridge gaps and smaller missing parts, i.e. the plaster also serves as filling. Projecting surpluses are removed afterwards from the outside. On the inside they remain (see fig. 19). Often smaller voids are totally filled with plaster (i.e. parts of forearms).

### 6.3 Additional support systems

On the inside of the bodies often a glass-fibre lamination is applied as support for the body. The fabric is soaked in epoxy resin and applied in stripes, covering the inside of the body from the bottom of the body (end of the robe/height of the knees) up to the waist (see fig. 20). If the figures are broken into many small fragments or if a lot of fragments are missing, the lamination continues up to the shoulders with strips inside the arms. The support system gets very stiff. If fragments have to be inserted afterwards, holes have to cut into the lamination.

In addition to gluing and the lamination, sometimes metal cramps are used. They are inserted mainly in the lower part of the robe (level of the thighs, called skirt” by the Chinese), especially if this part is broken between the legs (fig. 23). If cramps are used in the part of the robe, the holes for the metal cramps are drilled from outside through the terracotta (diameter ca. 1 to 1.5 cm, see fig. 22, also fig.10). The size of the cramps varies between 5 and 25 cm. Mostly the cramps are inserted from the inside, but in some cases also from the outside. In this case a groove is made for the cramp which afterwards can be covered with plaster and retouched (fig. 24).

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[9] An analysis (IR spectrum) was made in 1998 by Stefan Simon in the Zentrallabor of the Bavarian State Department of Historical Monuments from the adhesive on the glass-fibre lamination. Also Chinese literature states that the material is comparable to “Araldite 6030” of the company Ciba-Geigy. This epoxy resin type is not produced anymore; it corresponds to the product “Araldite 2011” (product name from 1999) from Ciba Speciality Chemicals (AW 106 (epoxy resin), HV 953U (hardener); contains Bisphenol A-epoxy resins, N(3-Dimethylaminopropyl) 1,3-propylendiamine).

[10] The exact purpose of the polyamide was described differently in the previous years: According to explanations from 1991, it first was used instead of the epoxy resin, but replaced later, because it was too hygroscopic, reacted to climate changes and developed tensions. They were afraid that the glued joints might open up again (C. Thieme, in: Travel Report 1991). At the same time, it was mentioned as additive to the epoxy resin, either as adhesive or as retarding agent. In 1998, we were told that it is added as hardener or plasticiser (oral information from Zhang Zhijun). - The different explanations are a problem of translation. The polyamide obviously serves as hardener or “second component” of the adhesive.

[11] Product of the company “Donghuan”; English description on the tin: “A so-called type of low moleculare polyamide resin 650.”

[12] see: Travel Report, 1991: The material was called „ketimide“, which might be a mistake of translation.

Steel dowels or bars are inserted in the legs, if they are broken in many pieces or are not complete anymore. They are fixed with epoxy resin and added fillers.

After the joining of the figures missing parts and gaps are filled with plaster (fig. 1) and retouched in the colour of the terracotta. For retouching, gypsum mixed with polyvinyl acetate, pigments black ink and soil dust is used.

For the transport inside the pit serve wooden beams are put under the figures. If the figures have to be transported lying, they are carried on boards on straw and maize straw cushions. For the removal or inserting into the corridors pulley blocks are used which are mounted on the roof construction of the hall (fig. 28).

### 6.4 Changes and developments

The gluing and joining system visible on the figures in the rear part of pit no. 1 represents a state of conservation techniques which is not up-to-date and not the actual state of knowledge anymore. Partly the figures are standing there, have been restored years ago. The work progress is very slow, but it looks like it is still continuing.[13]

The figures of the acrobats, the civil servants and the newly excavated figures from pit no. 2 have been restored with a slightly changed and improved joining technique.[14]
For the gluing of the acrobats (1999 and 2000) and the civil servants (2001) another type of epoxy resin was used. In contrast to the material used in pit no. 1, the hardened material is not brown, but colourless and milky-opaque and obviously higher viscose.
Supporting systems as the glass-fibre lamination and the metal cramps are not used anymore. Because all or most of the fragments could be assigned and the assembling is performed carefully, an additional support had not been necessary. All figures are glued very carefully, inserting also very small parts and keeping the visible surface (i.e. the outside) clear of adhesives. As all these figures still show polychromy, this was very important. On the acrobats the gaps along the breaks and missing parts have not been filled.

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[13] In May 1999 about 140 more or less assembled figures stood in the sectors T 17, 18and 27. Another 100, already restored figures were standing in the excavation sector T 26 (glued, gaps filled, retouched). In October 2001 11 rows of about 15 figures (165 figures) were standing in T 17, 18 and 27. 81 restored figures were standing in T 26. The arrangement of figures and fragments had changed. There were tools and tins with adhesive, so obviously the work is still going on there.

[14] These figures have been restored after the work stay in May 1999 which focussed on the problem of joining techniques and adhesive materials.

**7 Problems of the assembling technique and the actually used materials**

Problems of methods and materials used so far show some problems lie in the choice of the material and the way of their application.

The Chinese experts see the main problem in the extreme hardness and the missing reversibility of the epoxy resin. Smaller fragments often are identified and assigned only after the figure is already almost completed; sometimes corrections have to be made during the assembling of a figure. Therefore, it is a problem, that the epoxy resin cannot be solved again after the setting time of 24 hours. To open the joints again, the adhesive is destroyed by heat with Bunsen burners.
Because the epoxy resin has a higher cohesion strength than the terracotta, the figures tend to break next to the old crack under mechanical stress (i.e. during transports, especially for exhibitions abroad).
Another problem is the long-term stability of the conservation materials. The hardened epoxy resin appears dark-brown and brittle. The lamination inside the figures gets very brittle after some years and can be torn into pieces easily. Nevertheless so far, problems of the stability have almost not occurred.

The carefulness of the work is also important for the stability as well as the visual impression. If the fracture edges are not cleared from dust, the epoxy resin does not adhere well and can be splintered off. Often too much epoxy resin was applied on the fracture edges: The surplus not only run down soiling the surface; the quality of the gluing is also effected: The thicker the adhesive film, the lower the adhesion strength and the more evident are the problems of ageing. A too thick application on the fracture edges also makes it more difficult to achieve well fittings joints of fracture edges.
The plaster sticks perfectly well on the terracotta. This also means that it is very hard to remove it from the surfaces; often white spots remain. Metal tools which are used to remove the plaster damage the soft terracotta. Therefore, it is not a suited material for temporary fixations.

Not much attention was laid on a careful and considerate treatment of all parts that are not directly visible, especially the insides of the figures with the traces of production. In many cases in pit no. 1 also the outside of the figures has not been treated very gently.
If small parts as fingers break off again, sometimes adhesive tape or plaster lumps are used for a temporary fixation (fig. 25 and 26). These materials are not a suited; they never should touch the polychromy.
Fillings and completions with plaster frequently are not carried out neatly and carefully. The plaster covers the surrounding areas, often in the width of one or more centimetres. Some completions are modelled very finely, but often the plaster is applied much too thick. Sometimes the completions crumble and powder off (fig. 27).

## 8 Demands and considerations for the improvement of the methods

Alternatives for the restoration method have been discussed since 1991.[15] The demands on materials and methods were defined in 1999 as follows:
a. Determination of an appropriate adhesion strength of the adhesive
b. Good ageing properties and long-term stability of the adhesive with special regard on the climatic conditions inside the pits.
c. Easy to handle and low price. Because of the large number of figures, a lot of manpower is required for the work. The workmen mostly are not trained very well. Relative long setting time are necessary to allow corrections to be made.
d. Use of reversible materials, i.e. adhesives which can be solved again.
e. Compatibility with the methods and materials for the consolidation of the polychromy.
f. As little damage of the surfaces as possible - on the outsides and the insides.
g. Better methods for temporary fixations
h. Improvement of filling techniques

a. If the figures are joint with adhesives without additional supporting systems (lamination, metal bars) a sufficient adhesion strength should be guaranteed. It depends on the properties of the terracotta as well as stress of the particular fragment what is sufficient and suited. Investigations on the terracotta can show the properties like tensile strength, but the fragments underlie different conditions: Fragments that do not carry much weight do not require as much adhesion strength as those from supporting parts of the figures (i. e. legs, body). If there are no fragments missing and the fracture edges are fitting well, there is some mechanical connection and support which does not work if a larger number of pieces is missing and there are gaps between the fragments.
The adhesion strength also should not be too high to avoid new breaks next to the glued joints.

b. The ageing properties of modern adhesives are only partly known as many of these products only exist since some decades maximum or maybe only some years.
The climatic conditions inside the pits are of special evidence, because they mean an additional stress for the adhesives. The soil and the archaeological finds are very humid before and during excavation. After the excavation or when the excavation is stopped for a longer time, the pit dries out. The erection of buildings (exhibition halls) over the pits also support and accelerate the drying. German experts could observe the process of drying-out on pit no. 3 (excavated 1987 to 1989) and pit no. 2 (first major excavation campaign in February 1998). Both pits showed severe problems with mould during the first year after excavation, the humidity was extremely high. During the second year the mould disappeared. In 2000 all the pits looked relatively dry. Factors as the distance from the ground water table, the construction of the hall and ventilation/air condition also have an influence on the velocity of drying. Over a longer period the outside climate becomes most important for the climate conditions. The differences between the seasons and the daily changes are rather high. From the Chinese side values of 5-25 °C and 40 to 70 % RH are regarded as suited for the preservation of the terracotta figures. In the moment, these values cannot be reached.
Therefore the used restoration material have to be resistant against these climate changes. Their swelling and shrinking (contraction) properties should be similar to the terracotta. They should also be insensitive against occasional decreases of the temperature below the dew point (condensation) and short periods of heating up by sunlight (pit no. 1) or lamps (spotlight).

c. General properties as setting time, an easy method of application, the price as well toxic aspects are important criteria for the choice of an adhesive. Long setting times allow corrections, but also require a good support system. On the other hand, the hardening time has to be long enough to position even big and heavy or fragments of complicated shape exactly. If reversible materials were used, maybe shorter hardening times could be sufficient; if a fragment gets out of place, the joint could be opened

[15] In 1991 (?) experts from the Roman Germanic Central Museum in Mainz recommended to use „Zaponlack“ (a German product based on cellulose nitrate) instead of epoxy resin which they regarded as not suitable. - During a work stay of German experts from the Bavarian State Department of Historical Monuments in 1993, decision was made to start investigations concerning better suited epoxy resins and alternative adhesives. The subject was discussed on several meetings, but research work and practical tests just started in 1999, after the subject had been taken up in the co-operation agreement. - In 1998, in preparation of the work stay of the Chinese experts, there was a long discussion with Dr. Pick and Mrs. Kern from the Bavarian State Department for Historical Monuments, department of Stone restoration, Castle Seehof/Bamberg (August 26, 1998). - In 1999 a discussion of the situation took place in the workshop of the Roman Germanic Central Museum (RGZM) Mainz. The restorer Mrs. Pluntke also demonstrated the methods and materials used in Mainz and explained their experiences (Oct. 7, 1999).

again. All used materials must be available in China, because high amount are required. These aspects are taken in account, but tests will also include materials which do not fulfil all these properties.

d. The use of reversible materials is necessary to ensure that joints could be opened again if required. This is not possible with two-package systems as epoxy resins. Therefore other material systems have to be tested which can be opened by solvents.

e. The materials for the conservation of the polychromy should not affect the gluing of the fragments. This means that the materials for both treatments should not have a negative effect on each other. If that is not possible, the fracture edges have to stay clear of materials during the consolidation of the polychromy.
On the other hand, the handling of the fragments during gluing and materials for temporary fixations must not damage the sensitive polychromy. Therefore, fixations with plaster lumps or strong robes cannot be used. A neat work is absolutely necessary, because traces of adhesive cannot be removed from the polychromy. A surplus of adhesive coming out of the joint has to be prevented.

f. The original surfaces should be respected and protected as far as possible, also if there is no polychromy left. Because plaster can only be removed with great difficulty and always leaves remnants and white spots and margins, it should only be used as filling material. The fillings should be performed without spreading plaster in the surrounding area.
Also the inner surfaces have to protected, because their information about the production technique. A surplus of adhesives or plaster and the entire covering with a lamination are interferences that damage or destroy this information.
Drill holes for cramps should be as small as possible and always be conducted from the inside, without breaking through on the outside of the figures.

g and h. Temporary and permanent support systems have to fulfil the same demands as the adhesives in respect on their properties, long-term stability, reversibility and minimum damage to the terracotta figures. The same applies to the materials of the fillings and completions.

## 9 Results of the first series of tests

Examinations have been carried out on the properties of the terracotta itself and of possible sample material. The results are presented in the following contribution. Some properties of glued terracotta as tensile strength have also been tested and determined for several adhesives.
The properties of adhesives used in terracotta, ceramic and partly also stone restoration were compiled from the literature and from experiences of restoration workshops. A summary of the results is given in this Annual Report (see: Übersicht über Klebemittel).
A principal problem is that information about terracotta figures or objects of that size and weight is rare. There is not to much scientific literature about terracotta restoration at all. Experiences made on terracotta vessels and small objects can only partly be adopted to the situation in Lintong. Stone figures or objects have the same problem of a high weight, but have a completely different material, built-up and structure.
Information about long-term stability, especially under conditions as they are in Lintong, is hard to find. So far, we can only orientate on tests carried out in laboratories and on observations on the figures in Lintong.[16]

Climate measures with hygrothermographs are conducted at least since 1987 (pit no. 1), but probably not continuously over a longer period. The development of the climate situation in pit no. 2 is monitored since 1998 (also see contribution in this Annual Report).

If control signs or marks are needed to define the exact position of a fragment, chalk can be used instead of ink or epoxy resin. Chalk marks can be wiped off easily.[17]

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[16] The restoration began in 1975, so there are 26 years of experience now. Unfortunately long-term effects and problems are not recorded in detail.

[17] Chalk is used in the RGZM for marks on terracotta.

The materials actually used for the gluing of the terracotta and the consolidation of the polychromy are compatible. Neither the PEG/PU nor the Plex have any negative effect on gluing with epoxy resins, even if Paraloid B 72 is used as a primer.[18]

The discussion focussed on the improvement of the actually used methods and materials, but there are also suggestions to replace certain materials or to try different methods.

Materials and systems for temporary fixations and supports before and during gluing have been discussed widely. Plaster is not suited, adhesive tapes also have to be avoided.[19] Strings and ropes can be used if there is no polychromy left.
For the assembling of the figures, the Chinese experts suggested a support system made of a metal frame and metal sticks that can be fixed on the frame. The figure would be built up inside the frame, the sticks could be adjusted to support the fragments during gluing or even during a provisional assembling before gluing. An accessory support system of this kind had been used for the restoration of the bronze chariots, giving satisfactory results. Furthermore, big sand boxes were suggested, which could be built up in several steps.

During the discussion about gluing materials and temporary support systems ideas about alternative joining systems and permanent support systems have been considered.
On the German side possibilities to built up a support system inside the figures have been discussed. The general idea was a construction which could hold the fragments and support the entire figure without irreversible interventions on the terracotta. The support system would carry most of the weight and reduce the stress on the fragments and the joints. Furthermore it should have good ageing properties. The use of irreversible adhesives with a high adhesive strength and glass-fibre laminations that are glued on the inner surface could be excluded in this way.
As materials steel bar systems inside the figures, cores of polystyrene or glass-fibre have been suggested. The fragments could be fixed on these inner “skeletons” on single points with steel dowels. The use of steel needles and dowels placed inside the fracture edges has also been discussed.
One idea was to abandon the use of organic adhesives completely and only work with mechanical bond systems and maybe anorganic adhesives and fillers.
On the Chinese side these suggestions have been taken up sceptically. Building up a support system inside the figure seems to complicate; the same applies to the use of dowels inside the fracture edges. Generally the Chinese experts would prefer to built up the figures only by gluing the fracture edges. As restoration works carried out since 1999 show, with careful and neat gluing a lamination is superfluous.[20]
So far, the discussion about temporary and permanent support system still continues.

The quality of filling and completions could be improved relatively easy. Plaster is a suited filling material. The fillings and completions have to be reduced exactly on the missing parts. The missing part can be backed from the inside to achieve a filling of a fitting thickness. The terracotta surrounding the missing part can be protected against the white dust and splashes of plaster.[21]
For special purposes the filling material can be varied: For the completion of superficial damages a higher adhesive strength is advantageous; plaster mixtures containing adhesives can be used.[22]

In 1999 preliminary practical tests have been carried out on a replica of a figure. The test series is described in the one of the following contributions of this report (see: Test series for the assembling of terracotta figures on a replica of a warrior / Versuche zum Zusammensetzen von Terrakottafragmenten an der Kopie eines Kriegers).

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[18] The water attracted by the hygroscopic PEG could affect the gluing of adhesives solved in organic solvents, but a negative effect was not observed yet.

[19] Adhesive tapes loose their adhesive force after a relatively short time, but often not soluble remnants of the adhesive film remain on the surfaces.

[20] At the restoration of the acrobats no lamination was used.

[21] In the workshops of the RGZM, „Revultex“ is used (latex in ammonium chloride). After drying it forms a thin elastic skin which can be peeled off easily. - Protective coatings can only be applied if there is no polychromy anymore.

[22] German products of this type are for example: Keramiplast (plaster or clay plus fibres and methyl cellulose), also Moltofill (plaster and methyl cellulose). Moltofill fillings often have bubbles inside (Information of Mrs. Pluntke, RGZM).

**Assembling of terracotta figures - Workshop situation**

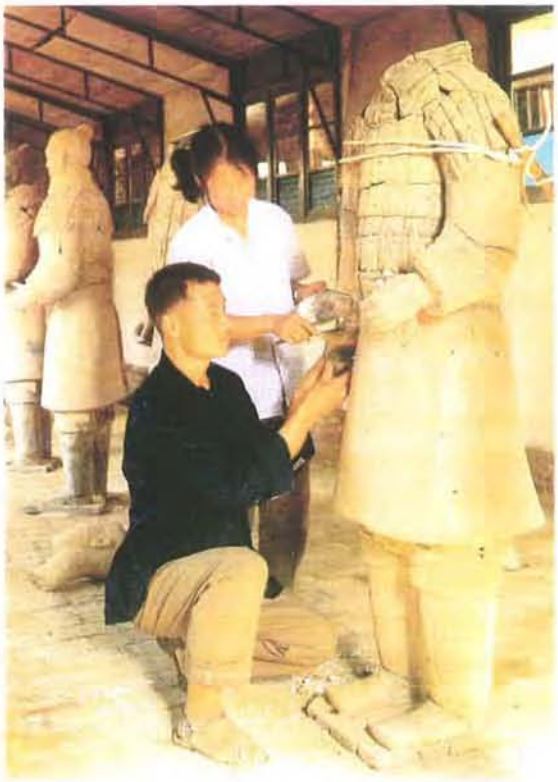


Fig. 10. Assembling of a warrior in a workshop building (around 1982). There is a temporary fixation with a rope round the upper body for the hardening time of the adhesive. In the robe holes are visible, drilled through the terracotta to insert cramps on the inside of the body.

Fig. 11. Assembling of a horse inside pit no. 1 (around 1982).

Fig. 12. Restoration work in the rear part of pit no. 1 (around 1999). During the hardening time, the fragments are fixed with robes. The figure that is glued in the moment is supported with bricks because the legs are (still) missing.

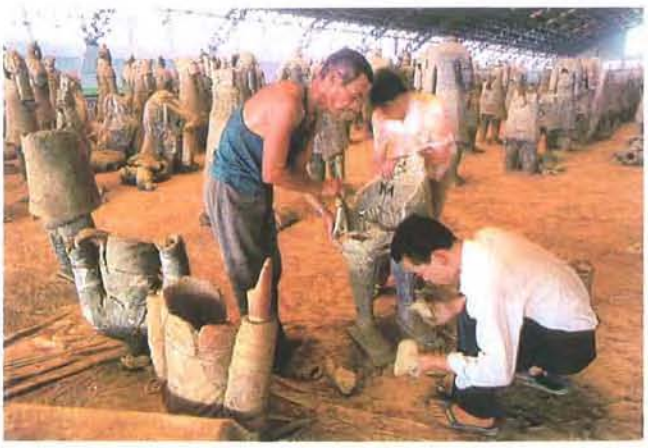


Fig. 13. Restoration in pit no. 1 (1996). The figures are assembled from the feet or the collar. Control marks are visible on the figure that is assembled in the moment.

## Assembling of terracotta figures in pit no. 1

Fig. 15. Restored figures stored in excavation sector T 26 in pit no. 1, in the background sector T 17 where the figures are assembled.

Fig. 14. Excavation sector T 17 in May 1999. The figures are assembled starting from the feet; parts that could not be attached yet are stored in baskets next to the figures.

Fig. 16. Smaller units of fragments assembled from isolated pieces laid out on plastic foil in excavation sector T 8. Provisional fixations are made with lumps of plaster. (May 1999)

Fig. 17. Heads and other parts of broken figures laid out on plastic foil

**Assembling of terracotta figures in pit no. 1 - control marks and plaster lumps**

Fig. 18. Control marks for assembling on the inside of the figures. The upper fragment shows marks from the tools of the production of the figures.

Fig. 19. Inside of a figure: Black control marks and fixations with plaster lumps. The dark brown adhesive has run from the joints.

**Assembling of terracotta figures in pit no. 1 - lamination and damages by the arson of the pit**

Fig. 20. Glass-fibre lamination on the inside of a figure. The glass-fibre fabric is soaked in epoxy resin and applied in strips. On the left side, the lamination had to be cut off to add another fragment. Normally the lamination reaches from the “bottom” of the robe to the level of the waist. Below the lamination there is a metal cramp visible.

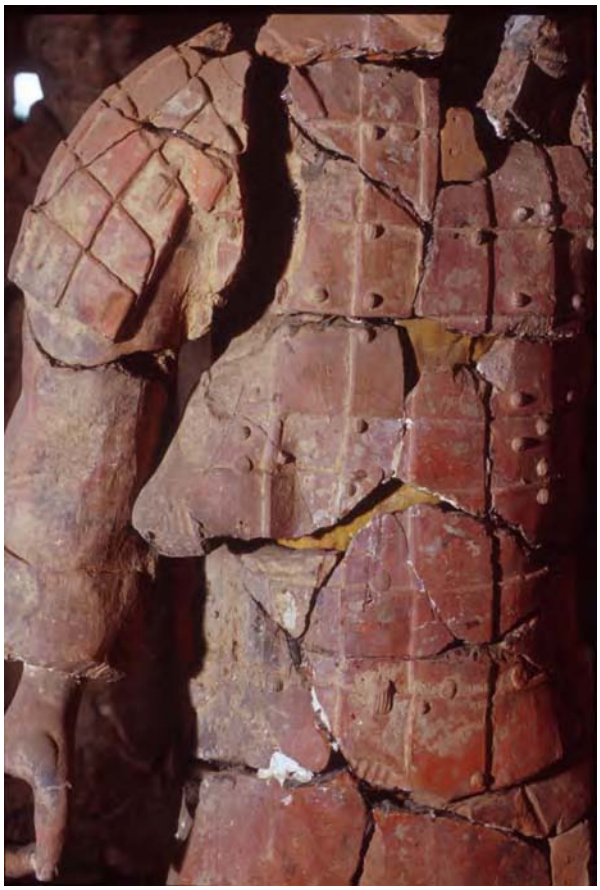


Fig. 21. Detail of a figure damaged by the fire of the arson of the pits. The terracotta has turned brick-red. In the gaps between the fragments the glass-fibre lamination is visible.
Some of the parts are heavily deformed, especially the fragment of the armour below the arm. The figure cannot be assembled in a fitting way anymore. Such extreme deformations are seldom, but often figures or parts of figures have turned red (compare fig. 1); small deformations can be found on a many of the totally red-burned figures.

## Assembling of terracotta figures in pit no. 1 - Metal cramps

Fig. 22. Holes drilled through the terracotta to insert metal cramps from the inside. After the restoration the holes are filled with plaster. Metal cramps are sometimes used in the lower part of the robes.

Fig. 23 (below, left). Metal cramp in the “bottom” of the body (for the stabilisation of the legs).
Metal cramps are often used in this part of the figures.

Fig. 24 (below, right). Metal cramp inserted from the outside, lower part of the robe of figure 16 from T 19G2.

## Fixation of small parts that have broken off again (after restoration)

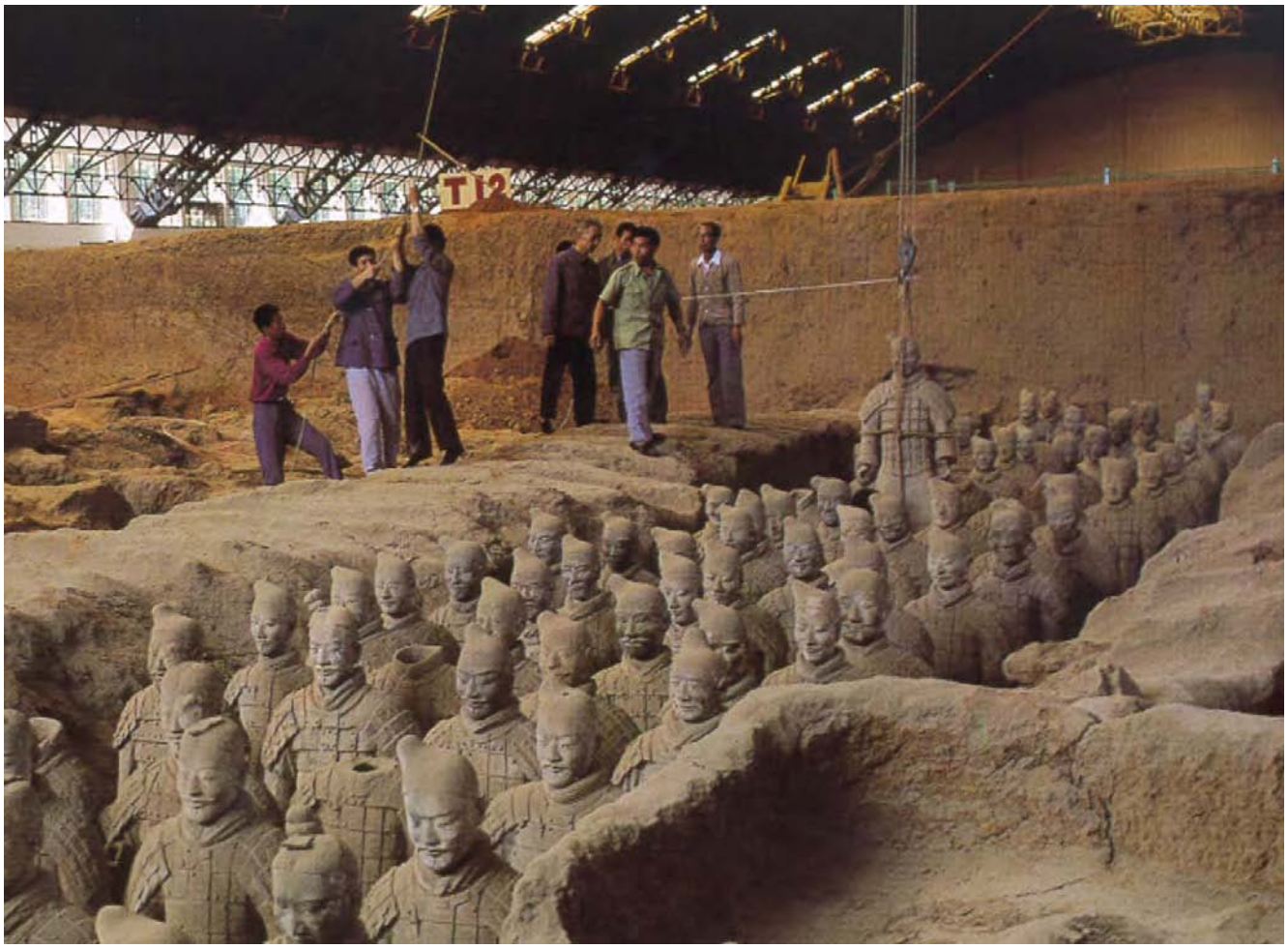
Fig. 25. A thumb fixed with adhesive tape.

Fig. 26. A thumb fixed with plaster.

## Assembling of terracotta figures in pit no. 1

Fig. 27. Plaster completions of button-shaped stitches on the armour. Some of the reconstructed stitch elements crumble off.

Fig. 28. A warrior is put back in its place in the corridor after restoration with the help of a pulley blocks.



## Photo credits

Fig. 1. Blaensdorf, Bavarian State Department for Historical Monuments, during work stay in Lintong May 1999

Fig. 2-6: Archaeological team / Archaeological Institute, *Qin Shihuangling bingmayong keng yihaoyeng fajue baogao 1974-1984*. Beijing 1988 (Excavation report on pit no. 1 of the terracotta army of the burial complex of Qin Shihuang)

Fig. 7-9: Museum of the Terracotta Army

Fi. 10-11: Capon, Edmund (ed. ), *Qin Shihuang, Terracotta Warriors and Horses.* Catalogue of the exhibiton: Terracotta figures of Warriors and Horses of the Qin Dynasty of China. Clayton, Victoria (Australia) 1983, p. 44 and 45

Fig. 12, 15, 17. Museum of the Terracotta Warriors and Horses (Photo CD)

Fig. 13. National Geographic, Vol. 190, No. 4, October 1996 (American Edition), Louis Mazzatenta, *China's Terra-cotta Warriors,* p. 82

Fig. 14, 16, 18-27: C. Blaensdorf, Bavarian State Department for Historical Monuments, during work stay in Lintong May 1999

Fig. 28: Museum of the Terracotta Army / Wu Xiaocong (ed.), *Haudegen des Reiches vor 2200 Jahren*, Xi'an 1992, p. 27

# Investigations on the texture and on the mechanical properties of terracotta fragments from the museum of the terracotta warriors and horses in Lintong (October-December 1999 and Mai-June 2000 in Munich)

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## 1 Introduction

For the working session from 10.10.99 to 08.12.99 in Munich, our colleagues brought eleven non coloured terracotta fragments to Munich. In Mai 2001 they brought along four further fragments. One of the subjects of both workshops was the development of new restoring and gluing methods for the terracotta warriors. For the workshop we also had a whole copy of a standing warrior, made of terracotta. For the improvement of the adhesives and the gluing application it was necessary to get more information about the texture and the hygric and mechanical properties of the original terracotta. Principally the original fragments can be divided into grey and red coloured pieces. Besides the general description of the terracotta material, the investigations should find out differences among the texture and the hygric and mechanical properties of the original terracotta and the modern copy.

## 2 Former publications on this subject

In the last thirty years, several investigations on the terracotta material of the Qin dynasty have been performed. Concerning the terracotta warriors the excavation report of Prof. Yuan is very important. It is partly translated into German, and published in "Forschungsbericht Nr. 7/1992 des bayer. Landesamtes für Denkmalpflege" (SHAANXI SHENG..., 1988). This report contains scientific investigations of the research institute for electrical ceramics in Xi'an on various types of qin terracotta, including terracotta of the famous warriors. The methods are: AAS, X-ray diffraction, thin sections, TG, determination of density, porosity, pressure strength and thermal dilatation.

Investigations at the institute for crystallography at the ETH Zürich were published 1988 in the MRS Proceedings 1988 (MRS-PROCEEDINGS, 1988). The methods in this report are DSC, TMA, TG und XRD....

Both investigations are focused on the reconstruction of the raw material and on the determination of the firing temperature. The Chinese investigations compare terracotta of the terracotta warriors with terracotta tails and floor bricks of qin dynasty and with modern bricks made in Xi'an. But there is no attempt for a differentiation between the different fragments of the warriors. The investigations at the ETH Zürich were performed on one single sample with an uncertain origin. It is not sure, that the sample is belonging to the terracotta army of Qin Shihuang di (T. V., PALMITER U. P.F., JONSON?).

**3)Methods**

3.1. Microscopic analysis

3.1.1 thin section

Samples for thin section were taken of six original fragments and two fragments of the modern copy (see: chapter. 4) sample description and sampling and chapter. 5) documentation of the fragments). The slides are cut in parallel orientation to the fracture edges of the fragment. Of fragment 01-99 three additionally slides in a tree dimensional orientation were prepares (see: chapter 4) sample description and sampling and chapter. 5) documentation of the fragments). The analysis of the texture, structure and the pore space of the terracotta were performed on a Wild Photo makroscope M 400 and a Leitz Polarisation microscope Ortholux II Pol-BK. For the modal analysis the visual comparing method after FLÜGEL (1978) was used. The visualising on the microscope is the basis of the interpretation of the results that are carried out by other methodes.

3.1.2 SEM analysis

For the visualisation of the matrix texture in smale pieces of fragment 01-99 and 05-99 a scanning electric microscope "Stereoscan 250 MK3" was used.

3.2 Water uptake under atmospheric pressure and vacuum, bulk density, pure density and porosity

These investigations help to characterise the porosity of non organic materials. The investigations differentiate the porosity and the mineralised matrix of the terracotta fragments. Seven samples of the original fragments and two samples of the replica were tested by this method. Correspondingly to the description of POSCHOLD (1990), the tests were performed by gravimetric measurings.

3.3 capillary water uptake w-Wert

The capillary water uptake of porous materials is determined by the characteristic values of water uptake coefficient (w-Wert), water penetration coefficient (B-Wert), water capacity $\psi_k$ and saturation $\psi_s$. The physical interdependences of these material parameters are described at Schwarz (1972). The w-Wert is a direct indicator for the capillary porosity of mineralic materials. By calculating the w-Wert with the B-Wert it is possible to get the amount of the capillary active porosity ($\psi_k$) of a sample.

The capillary water uptake was measured with oriented drill cores (diameter 19mm) of the fragments 01-99, 02-99 and of the replica. Of each sample we took one core parallel and one core perpendicular to the fragment surface (see chapter.: 4.). The measuring was performed correspondingly to the instruction manual DIN 52 617.

3.4 Ultrasonic testing

The ultrasonic testing was performed on Nov 08$^{th}$, 99 on original terracotta samples of Lintong excavation site and on samples of the replica by Dipl. Chem. Stephan Simon.

The goals of the investigations were:

-Characterization of replica material in comparison to the original terracotta in respect to their ultrasonic velocity (comparability).

-Investigation of possible anisotropy in terracotta due to the manufacture and burning process

- Correlation of ultrasonic testing results with drill resistance measurements, porosity analyses and microscopic analyses

Methodes and Materials

The ultrasonic measurement device USG 20 (Fa. Krompholz Geotron Elektronik, FRG) was used with point-shaped 46 kHz vibrator (USG 46-T) and receiver (USE-T). The coupling to the terracotta was effected with a permanent elastic silicone sealant. The accuracy of the in-situ-measurements can be assumed to be ±10 %.

Transmission velocity profiles

The most important parameter in ultrasonic testing is the ultrasonic velocity $v_l$, calculated from the transmission time through a well defined measuring distance $l$ (1) (see Fig. 1, left):

(1) $$v_l = \frac{l}{t_k}$$

| | | | | |
|---|---|---|---|---|
| $v_l$ | = | ultrasonic | velocity | (km/s) |
| $l$ | = | measuring | distance | (mm) |

$t_k$= transmission time (µs) = recorded transmission time $t_r$-dead time $t_0$.

Indirect surface measurements

Indirect surface measurements have been proposed by Bouineau (1978) for the investigation of scaling on building facades, which are accessible only from one side. The travel time of the ultrasonic pulse is recorded at continuously increasing distances between emitter and receiver (see Fig. 1, right). If the surface zone is mechanically weaker than the bulk, the thickness of the weakened layer ($a$) can be derived form the distance/travel time diagram (see Fig. 1, case A).

With increasing distance between emitter and receiver at a certain point (point of discontinuity), the ultrasound wave travelling with lower velocity but the shorter track in the crumbly surface zone is passed by the sound wave travelling at higher speed but the longer way in the unweathered core.

The extension of the weathered layer $a$ (cm) is calculated according to (2) (FACAOARU AND LUGNANI 1993):

(2) $$a = \frac{lo}{2} \cdot \sqrt{\frac{v_s - v_d}{v_s + v_d}}$$

$v_s$ is the ultrasonic velocity in the fresh core, $v_d$ is the ultrasonic velocity in the (weathered) surface layer and $l_0$ is the distance, where the discontinuity of travel time takes place.

The calculation, based on Snellius' law of refraction, however cannot be performed, wherever a mechanically harder zone lays upon a weaker core or where the surface is separated from the core by cracks (Fig. 1, case B). Almost parallel shifts in the distance/travel time diagram can be attributed to single vertical cracks (BOUINEAU 1978).

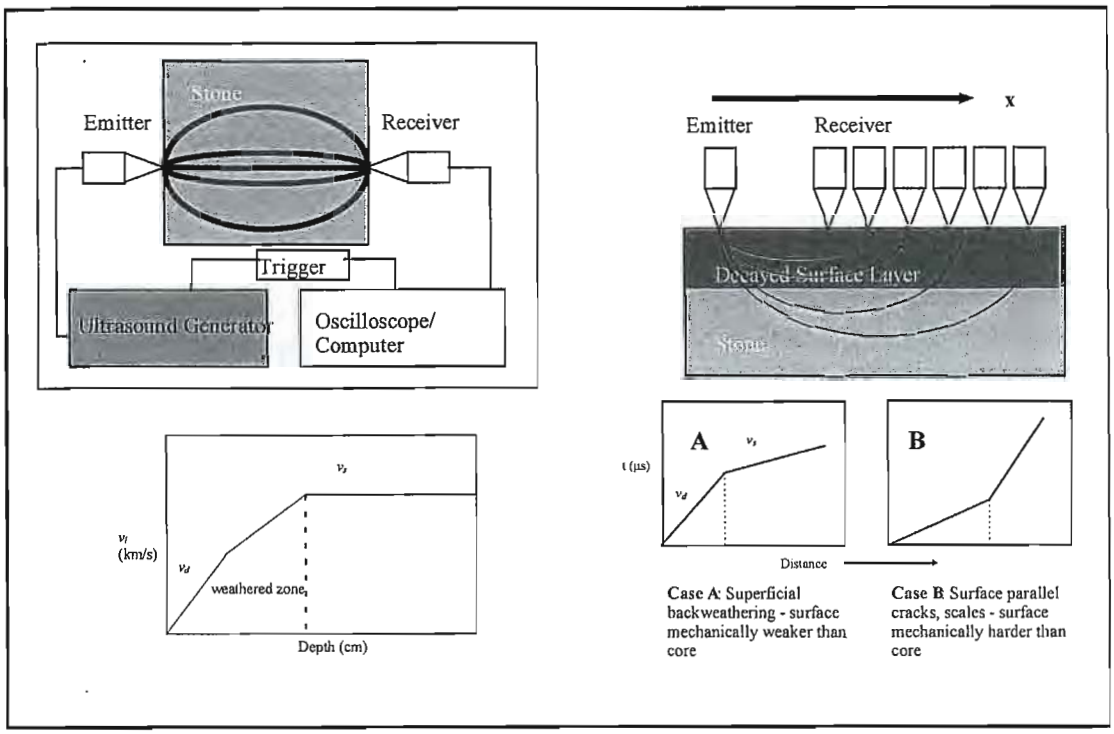



**Fig. 1:** Principles of ultrasonic transmission measurement (left) and indirect surface measurement (right)

## 3.5 Drilling resistance

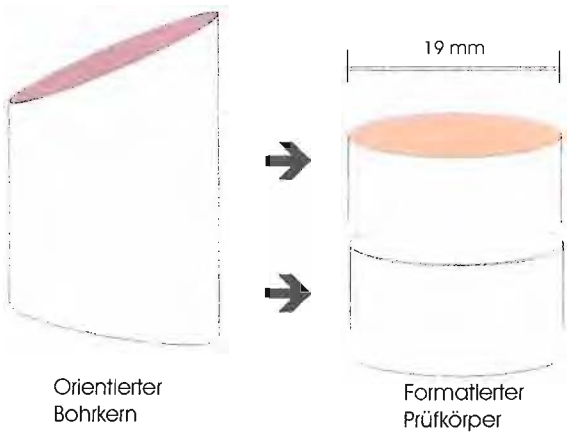
the tests for the drilling resistance were performed by the recently develpoed DFMS decice (Drilling Force Measurement System) produced by the Italian company Sint Technology (Firenze, Italy). This machine was developed within an European research project for less destructiv data aquiring on natural stone monuments. The machine is working with defined rotation speeds and penetration rates. The valuable measuring are the penetration depth (mm ) and the drill force (N) (VALENTINI, 2000). The measurings were performed by Dipl. Min. Birgit Singer. The rotation speed with 600 U/min and the penetration rate with 20mm/min are adapted to the recommended parameters for weak sandstone (SINGER, B., HORNSCHILD, I., SNETHLAGE, R., 2000). The fragments were drilled perpendicular to the surface from inside to outside. This method should enable us to detect sintered parts and harder superficial firing, a weak core ore bigger voids inside the terracotta. After a correcting calculation for the elimination of the drill bit abrasion a direct comparison between the mean values of the drilling resistance of the samples is possible. The drill holes of the drilling resistance measurings are spotted in chapter 5: documentation of the fragments.

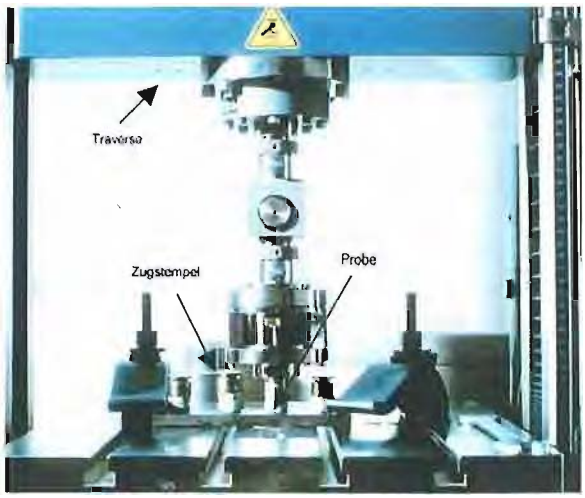
## 3.6 Tension strength

The tests of the tension strength were performed in Mai 2000. For this test are used relatively big amounts of material. Therefore we used also terracotta specimens of fragment 02/00 which wasn't involved in any of the former investigations.

For the determination of the maximum tension strength an universal mechanic testing machine made by the company "Zwick" was used (Type: "ZWICK/Z010" ). This machine is specially composed for small samples. Besides the increasing factor of the force and the size of the samples, the test condition are corresponding to the German advice for the testing of mineral building materials "DIN 51 220/ 51 221". The tension speed was 1mm/min, the pre loading force was 0,5 N. The tension strength test was performed with five samples of three original fragments and with two samples of the replica.

For the tension strength test the oriented drill cores were formatted into small columns of two centimetre length and with plane parallel ends. In the middle of these columns was cut a groove with one millimetre depth. **(Fig.: 2)**. The samples were glued on a metal plate. A iron stamp was glued on the top of the column. The tension force of the traverse is transmitted into the sample by this stamp, that is connected by a cardan shaft to the traverse **(Fig.: 3)**. Araldit 2011 was used as adhesive for the fixation of the samples.




| **Fig. 2:** Preparation of the samples for the tension strength measuring. | **Fig.3:** mechanic testing machine with sample. |
|---|---|

### 4) Sample description and sampling

All original fragments belong to figures of pit No. 1. They com from different figures and are found in the earth in various areas in pit N0. 1. It should be possible to determine significant differences in the strength of the terracotta, that is caused by the manufacturing technique ore the bedding conditions in the earth. Among the fragments are red and grey pieces of terracotta. The red colour is caused by a "second firing" during a firing damage in parts of pit No. 1. Originally all the figures are grey because they were were made in reduction furnaces (SHAANXI SHENG ..., 1988). In the range between grey and red the classification in hues like tint grey, shade grey, orange red and brick red is possible. There is no macroscopic difference within the texture the structure and the fracture appearance of the original terracotta.

The material of the copy is red inside and grey on the flanks. That means, the terracotta was burnt in a oxidation furnace and smoked after the burning. The texture of this material is more fine grained and less quarz bearing than the original terracotta. It is much more shattered in ist fracture appearance as the original fragments. Visible macroscopic cracks, that indicate to polarised grain size distribution, rapide drying of the fresh clay, ore to thermal stress during the firing process are very frequent in the replica. The fragments with the description of the taken samples and the investigations of each fragment are listed in **table 1**. The fragments 07-99; 09-99; and 10-99 were not used in the series of tests.

| Fragment | SEM | thinsection | porosity | drillcore | w-value | ultrasonic | Drilling resistance | Tension strength |
|---|---|---|---|---|---|---|---|---|
| 01-99 | ++ | 01/C02<br>01/C08<br>01/C09<br>01/C10 | 01/P02 | 2 (par/per) | par / per | O;P;Q;R;S ;T | 9;10 | 1x per; 1x par |
| 02-99 | | 02/C 03 | 02/P 03 | 2 (par/per) | par / per | A;B;C | 6;7;8 | 1x per; 1x par |
| 03-99 | | 03/C 01 | 03/P 01 | 2 (par/per) | - | D;E;F;G;H | 11;12 | - |
| 04-99 | | - | - | - | - | AD;AE | - | - |
| 05-99 | + | 05/C 05 | 05/P05 | - | - | I;J;K | 1;2;13 | - |
| 06-99 | | 06/C 04 | 06/P 04 | - | - | AF;AG;AH | - | - |
| 08-99 | | 08/C 06 | 08/P 06 | - | - | L;M;N | 3 | - |
| 11-99 | | 11/C 07 | 11/P 07 | - | - | - | - | - |
| 02-00 | | - | - | 4 (par) | - | - | - | 1x par |
| Replica | | ++ | ++ | +++ | - | U;V;W;X;Y ;Z;AA;AB; AC | 4;5 | ++ |

**Table. 1:** Naming of the investigated fragments with the sample numbers and the measuring numbers. All the samples of the replica are named "replica". The number of the crossmarks ( + ) is corresponding to the number of the measured samples. The abbreviation "par. and. per" apply to the orientation of the samples. - Descriptions are given in **Fig.: 25**.

**5) Documentation of the fragments**

Protocols of the original fragments were prepared for the documentation of the fragments and the respective investigations **(appendix 1)**. On this protocols are documented the samples and the measuring positions. Selected analytic results are added for a direct comparison of the fragments. The fragments of the replica are not documented in this detailed manner. They are sufficiently documented in a report of C. Blänsdorf, C. Köhler and S. Wallner.

## 6) Results

### 6.1 Results of the microscopic analysis

#### 6.1.1 Results of the thin section analysis

A photo list and a description of all thin sections is added in **appendix 2**. Selected photos are discussed in **Fig. 4 to 10**.

**The original fragments:**

Even though the fragments belong to different physiognomic parts (foot, torso, arm...) of different figures, the correspondence of the terracotta material in its composition and structure under the microscope is amazingly high.

*Structure:* All pieces have a matrix dominated, homogeneous structural constitution. The volume of the components is between 5vol.% and 10vol.% in the average. An amount of more than 20vol.% components was not observed. **(Fig. 4 a. 5)**.

The main components are quarz, plagioklas, mikrokline and siltstone fragments. According to the grain size the components are well sorted. Their shape is predominantly round ore elliptic. The edges are sharp ore slightly rounded. Sometimes the feldspars have kept their rhombic outlines. The grain size distribution of the main components is between 0,1mm and 1,2mm. The most common grain size is about 0,3mm **(Fig. 4 a. 5)**.

Supplementary components are biotite, muscovite, micritic lime and opaque accessories (coal and ore minerals). The grain size distribution of the supplementary components is between 0,1mm and 0,8mm. The most common grain size is about 0,3mm.

Seventy percent of the matrix consist of phyllo silicates (biotite, muscovite,...), iron hydroxide Thirty percent of the matrix are fine grains of quarz ore siltstone fragments with grain sizes under 0,05mm. The colour of the matrix varies from grey to ochre to orange and brick red. The colour of the matrix is determined by the firing temperature and to the oxidation grade of the iron containing minerals. The colour of the matrix is the determinant factor for the visual colour appearance of the fragment. Colour changes parallel to the surface of the fragment are common. Strange brown and black rims in the superficial area of the profile (1mm-2mm) in fragment 05-99 and 06-99 can be explained by penetrated black qui lacquer **(Fig. 5).**

The grain size distribution of the matrix minerals is corresponding to the defined grain size distribution off loess sediments. The range for this sediments varies from10µm to 60µm (SMALLEY, J., SMALLEY, V., 1982). The rammed earth of the partition walls has the same grain size distribution (GUDEHUS, O., MICOULITSCH, V., 1997). One possible conclusion of

this results is, that the raw material for the original terracotta was made of loess (matrix), mixed (grogging) with a sieved fraction of a low graded fluvial sand (components).

*Texture:* The terracotta has no macroscopic grain texture. Fine grained "finishings" on the surface -as they are described in the archaeological report- could not be observed (SHAANXI SHENG ..., 1988) on the fragments. Under the microscope it gets obvious, that elongated and needle shaped main- and supplementary components have a surface parallel preferred orientation. This texture is not visible to the open eye, because the most main components have round outlines **(Fig.: 4 and 5)**. In contrast to this, the elongated matrix minerals have an obvious surface parallel orientation in all investigated fragments. The laminated arrangement of the matrix minerals can be explained by the mechanic compressions on the fresh clay while the plastic forming of the figures (kneading, stroking, moulding...). For a better visualisation of this surface parallel orientation of the textured matrix we additionally prepared three oriented thin sections of the fragment 01-99 (see chapter 5 documentation of the fragments). **Figure 7 and 8** show a section parallel to the fracture plane. The **Figures 9 and 10** show sections parallel to the surface at the same edge of the same fragment 01-99. By this comparison the non isotropic texture of the matrix and -as consequence- the non isotropic character of the pore structure is easy to see.

*Pore structure:* The microscopic visible pore space is dominated by round and elongated shrink pores. They form while the drying of the fresh modelled clay. This microscopic visible pore space occupies about five to seven percent of the bulk volume. In the microscope diameters of this porosity range from 0,08 to 1,6mm. The elliptic outlines of the pores are oriented parallel to the surface **(Fig.: 4, 5, 7, 9).** In the core area of some fragments could be noticed an accumulation of the shrink pores. In a few fragments occur surface parallel thermal fissures. Their crack spacing remains under 0,05mm **(Fig. 4 and 5)**

The microscopic observation assumes an additional intergranular porosity within the terracotta matrix with pore sizes under 0,005mm. This porosity is formed by the whole mesh space in the netlike fabric of the matrix minerals. Only the biggest of this pores with diameters between 0,005 and 0,003mm are visible in the polarisation microscope. It seems reasonable that the most share of the bulk porosity (24-25vol.%) is hide in this micro porosity of the matrix (the result of the porosity measuring with terracotta fragments by water uptake under vacuum defined a bulk porosity of about 30% (see chapter.: 6.2)).

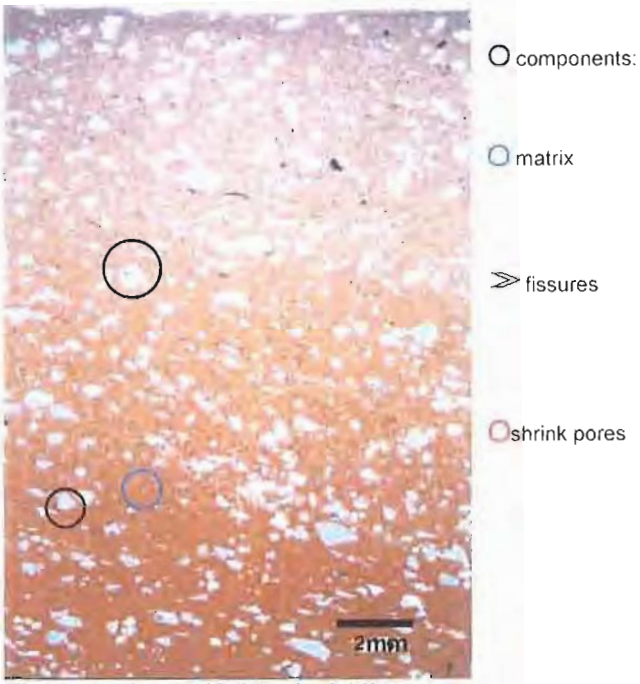



**Fig.4**: section 01/C 01; nicols' II


**Fig.5**: section 06/C 04; nicols' II

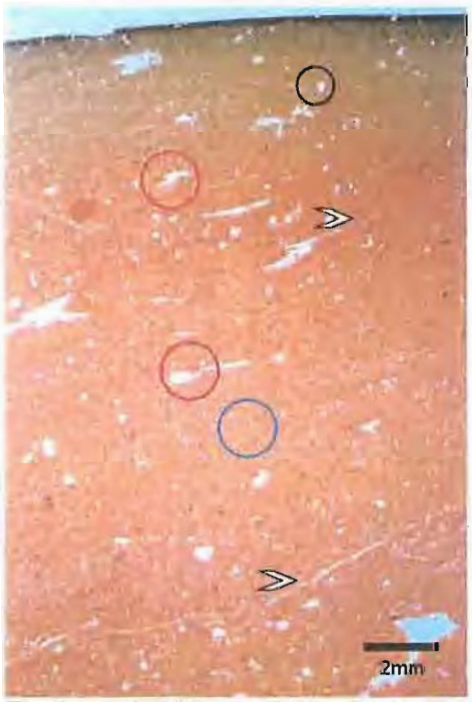



**Fig.6:** section "Replica"; Nicols' II

Explanation:

**Fig.4:** The section is cut parallel to the fraction plane. The surface of the fragment is to be seen on the top. Originally the terracotta had a grey colour. Because of the fire in pit 01 the colour turned to red from the backside. The angular quarze and the shrink pores are white. The share of the components with about 20vol. % is relatively high. The microscopic porosity of this sample is between 5 and 7vol.%. (see.: photo list in appendix2). As in all the other fragments the macro structure of the terracotta remains constant al over the profile. The colour change is caused by the colour change of the matrix.

**Fig.5:** The section is cut parallel to the fraction plane. The formed surface is to be seen on top. At this fragment a fine finishing for the modelling of the surface was not applied. In the lower part of the picture a increasing content of pores can be observed. The dark tone on the surface is caused by soaked qi lacquer. The content of the components with 5vol% shows the lower end of the usual range of the original fragments.

**Fig.6:** The section is cut parallel to the fraction plane. The surface of the fragment is to be seen on the top. The content of the components is under 3vol.%. In comparison to the original fragments the low share of components and the high share of big shrinking pores and fissures is remarkable.

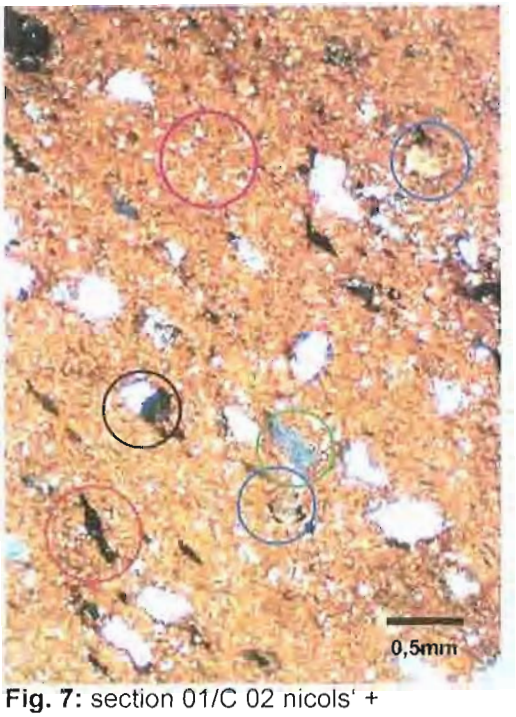



**Fig. 7:** section 01/C 02 nicols' +
The pores are black, the quarz grains are black ore white. The orientation of the section is diagonal. The surface of the fragment is in the upper right edge. The surface parallel orientation of the shrink pores is easy to be seen. Here you can see that the matrix contains up to 30% components with grain sizes under 0,05mm (mainly quarz and siltstone fragments). The limestone components are partly dissolved.

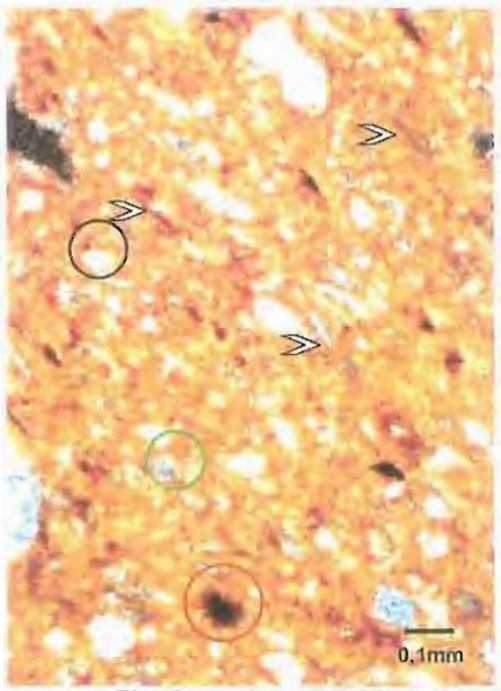



**Fig. 8:** section 01/C 02 nicols' +
Detail of the matrix in **figure 7**. The laminated texture of the matrix is indicated by the elongated outlines of the phyllo silicates. They are oriented parallel to the surface of the fragment. With a better resolution it would be able to see, that the micro structure of the yellow matrix is a porous fabric of laminated and needle shaped crystals.


**Fig. 9:** section 01/C 08 nicols' +
This section is cut parallel to the sueface of the fragment. The singular open pores are blue in colour. The granular texture has no orientation.

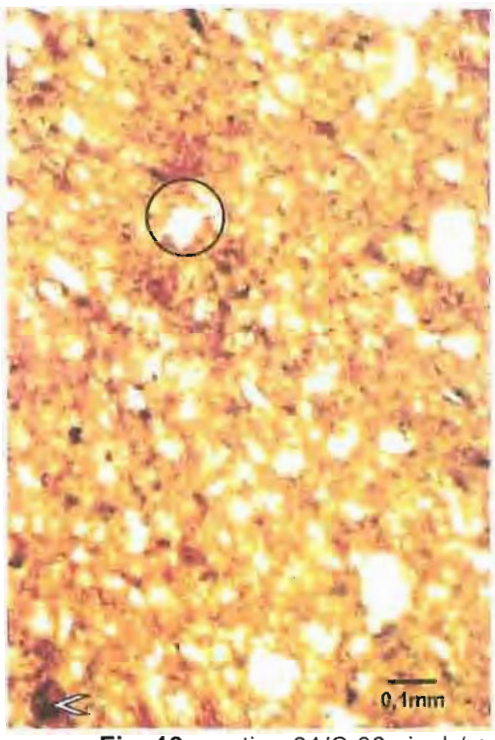



**Fig. 10:** section 01/C 08 nicols' +
Detail of the matrix in **Figure 9**. Perpendicular to the C-axis the phyllo sillicates appear as irregular round plates. Oriented needle shaped outlines can not be observed within the layering of the matrix texture..

**The terracotta of the replica:**

The observations on different thin sections of the replica are highly corresponding because all the samples belong to the same figure.

*Structue:* The terracotta of the replica has a matrix dominated, homogeneous structural constitution. Only a few fine components are swimming in a fine crystalline brick red matrix. The share of the components is under five percent volume. The main components are quarz, plagioklas, and stone fragments. Supplementary components are biotite, muscovite, and opaque accessories (coal and ore minerals). The components are sorted and have rounded edges. They show no fabric orientation. The diameter of the biggest grain is 0,3mm, the diameter of the smallest grain is 0,1mm.

The structural constitution of the matrix is to fine for a visualisation in the light microscope. About 15vol.% of the matrix seem to consist of quarz and phyllo silicates with grain sizes under 0,03mm.

*Texture:* In the structural constitution of the terracotta of the replica no macroscopic ore microscopic texture could be detected. But the surface parallel orientation of shrinking pores points to the conclusion, that the terracotta of the replica has a similar matrix texture like the original fragments, but in a smaller scale.

*Pore space:* The replica has big shrinking pores with more than 2mm diameter. It shows also many long fissures with crack spacing of about 0,03mm. The microscopic volume of the bulk porosity is about 10% of the bulk volume. The porosity of the matrix is not visible under the light microscope.

6.1.2 Results of the SEM analysis

The results of the thin section analysis have shown the surface parallel laminated texture of the matrix. The logical consequence of this texture is an equivalent texture of the matrix porosity. The structural constitution of the matrix and the structure of the matrix porosity are fundamental factors for the understanding of the mechanic and hygric properties of the terracotta. As this microporositi is not visible in the light microscope we tried to visualise the charakteristics of the matrix porosity under the electron microscope.

The supposition of the microscopic analysis was confirmed under the SEM. The laminated, sheeted micro structure of the matrix is shown in **figure 11.** The horizontal orientation of the fabric, composed by the long edges of the phyllo silicates and sperical quarz grains is easy to observe. The diameters of the biggest matrix minerals are under 0,025mm. The majority of the mineral phases in the matrix is smaller than 0,005mm. The free space in the network of mineral phases is linked to a horizontal orientated interstitial porosity. The visual diameters of the pore spaces are between 0,001mm and 0,015mm. Vertical links in this interstitial porosity are less often.

The perpendicular view on the matrix in **figure 12** shows scaly phyllo silicates with round, partly pseudo hexagonal outlines. The interstitial holes of the upper layer have diameters from 0,001mm to 0,01mm. Comparing this two pictures it is clear, that the sum of the visible matrix pores perpendicular to the surface of the fragment **(fig. 12)** is smaller than the sum of the matrix pores parallel to the surface **(fig. 11).** The mineral phases are highly interlocked in the horizontal lamination. Their vertical interlocking is much lower.

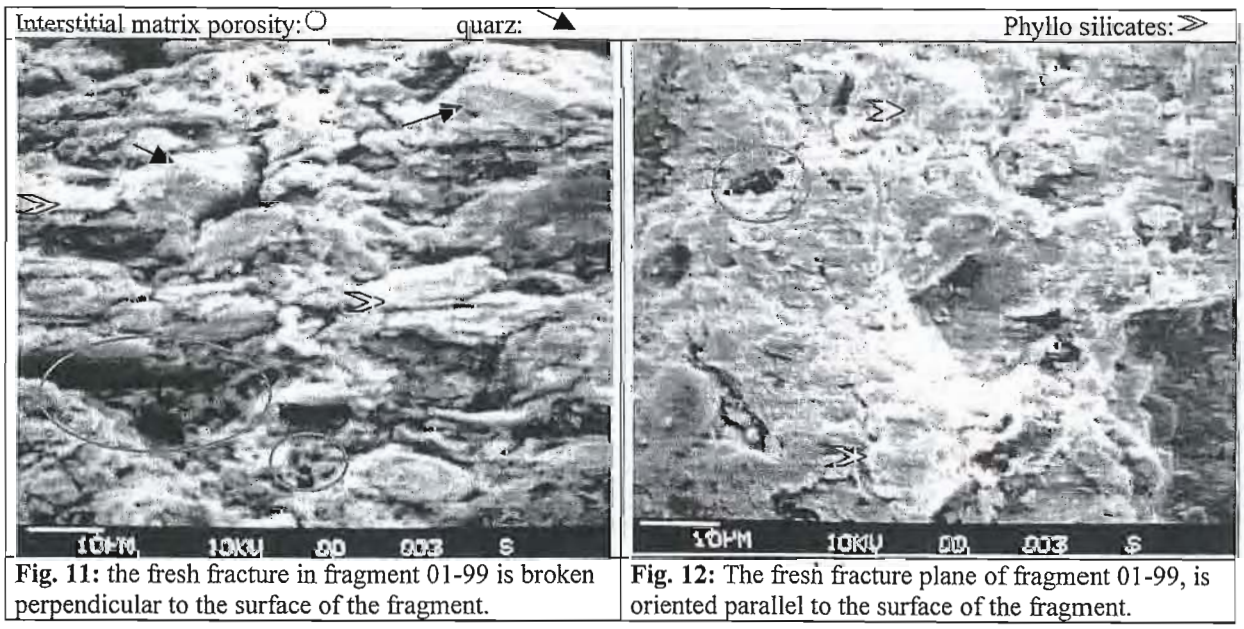



**Fig. 11:** the fresh fracture in fragment 01-99 is broken perpendicular to the surface of the fragment.

**Fig. 12:** The fresh fracture plane of fragment 01-99, is oriented parallel to the surface of the fragment.

6.2 Results of the investigations on pure density, bulk density and porosity

The results of the measuring are listed in **table 2**. For a better comparison of the samples the most important data are shown in two diagrams **(fig. 13 and.14)**.

The differences in the volumes of the porosity that is open for the penetration of water are low. The highest value, belonging to fragment 02-99 is 31,87 vol. %. This is only 5,6 percent more than the minimal value of 29,7vol.%, measured for fragment 11-99. The average of the porosity for the original fragments is 29,7%.

There is no direct coherence between the colour of the fragment and its porosity. Red fragments must not be more porous than grey ones. Concerning the bulk porosity the replica is fairly well adapted to the original.

The values of the pure density of the original terracotta do not leave more than 0,7% of their mean value, that is 2,69 g/cm³. This fact demonstrates homogeneous constitution of the original material. The pure density of the replica is 1,3% higher than the average of the original material. This shows a slight difference in the type of the components (particularly in the ratio of silicate phases to metal-, carbonate- ore organic phases). This difference between original and replica is slight but significant. Differences in the mixture of the raw material ore the burning temperature are possible reasons for this.

The saturation is a value for the volume, that is soaked with water after a 24h immersion under water in normal atmosphere. It is the difference between porosity and the water uptake of the sample **(table. 2, and. fig. 13)**. The pore space of all investigated samples has saturation values from 87% to 94%. With this values, the terracotta has a good accessibility for water.

The microscopic visible porosity is only 5-7 vol.% (see last chapter). That means, that about 25% of the whole porosity are formed by the highly textured matrix pore space, that is not visible under the light microscope.

| | water uptake | water uptake | water uptake | porosity | saturation | pure-density | bulk density |
|---|---|---|---|---|---|---|---|
| sample no. | norm. ath. M % | vacuum M % | Norm. ath. Vol.% | Vol.% | Vol.% | g/cm³ | g/cm³ |
| 11 P07 | 12,08 | 13,30 | 23,86 | 26,26 | 90,87 | 2,68 | 1,97 |
| 05 P05 | 13,58 | 14,48 | 26,24 | 27,99 | 93,77 | 2,68 | 1,93 |
| repl2 | 13,72 | 15,03 | 26,51 | 29,05 | 91,25 | 2,72 | 1,93 |
| 01 P02 | 13,39 | 15,22 | 25,62 | 29,11 | 88,00 | 2,70 | 1,91 |
| repl1 | 13,17 | 15,08 | 25,44 | 29,13 | 87,33 | 2,73 | 1,93 |
| 03 P01 | 14,83 | 15,66 | 28,13 | 29,69 | 94,74 | 2,70 | 1,90 |
| 08 P06 | 14,79 | 16,71 | 27,60 | 31,19 | 88,50 | 2,71 | 1,87 |
| 06 P04 | 15,55 | 17,24 | 28,60 | 31,71 | 90,21 | 2,69 | 1,84 |
| 02 P03 | 15,32 | 17,32 | 28,18 | 31,87 | 88,43 | 2,70 | 1,84 |

**table. 2**: The samples are arranged according to their porosity. The colouring with the original sample numbers represents their real colour appearance.

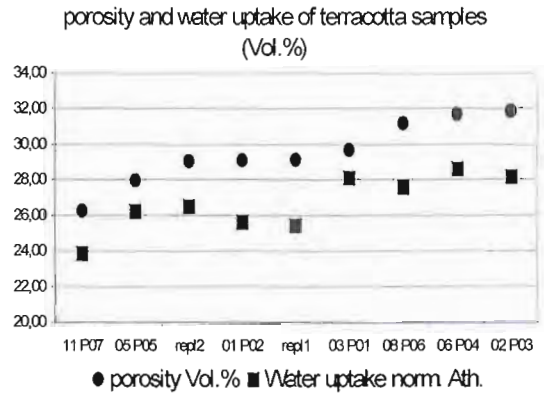



**fig. 13**: The bulk porosity of the fragments is has no correlation to the colour. The saturation values are high.

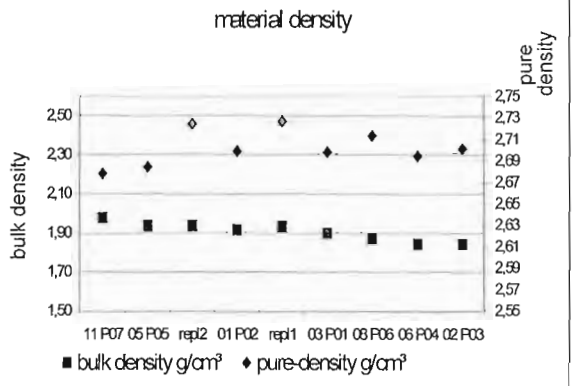



**fig. 14**: the pure density of the replica is higher than the pure density of the originals.

## 6.3 Results of the capillary water uptake w-Wert

Because of the limited dimensions and the small number of the fragments only six drillcores coul be investigated up to now. But the comparison of the results in **figure 15** shows that the capillary water uptake of the original terracotta is combined with its orientation. This fact confirms the idear, that the majority of the capillary pores is within the anisotrope matrix of the terracotta. Water can penetrate more easy into the terracotta from the side than from the surface. Again the different original fragments have similar w- values. There is no evidence for a coherence between the w value and the colour of the fragment.

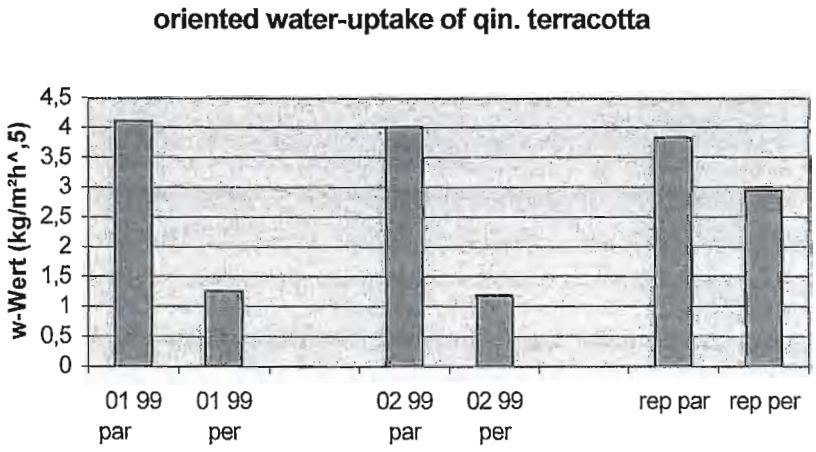



**fig. 15**:
The capillary water uptake of the same fragment at the fraction plane (par) can be four times as high as the capillary water uptake at the surface (per).

6.4 Results of the ultrasonic velocity measurements

The results of the ultrasonic velocity measurements are summarised in **figure 16** to **figure 20.** The whole measuring values are listed in **appendix 3**. This method is not damaging the fragments. Therefore a high number of readings could be taken and evaluated in statistically. For the evaluation the tree dimensional orientation of the fragment in its position in the terracotta figure was taken into consideration. Besides the usual differentiation between perpendicular to the surface (per) and parallel to the surface (par) the measurings parallel to the surface were divided into (vert) - for vertical measuring considering the standing figure and (hor) -for measurings horizontal measurings considering the standing figure. **(see. fig. 25).**

The combination of the data shows that the median of the ultrasonic velocity v (par) is 20% higher than the median of the ultrasonic velocity v (per), that is oriented perpendicular to the surface of the fragment. **(fig. 16)**.

Within the parallel ultrasonic velocity (v par) the velocity that is measured horizontal to the standing figure (hor) is about 15% higher than the vertical velocity. This horizontal orientation is the best transmitter for the ultrasonic sound wave impulse in the original terracotta. The median in this direction is 25% higher than the median of v (per). In this direction the diversification of the values is very small. Fifty percent of the values measured in this orientation are between 2,75 and 2,85 km/s **(fig. 17)**. In comparison to this the Gaussian distribution curve with the values of v (vert) is very wide.

Probably this anisotropy of the ultrasonic velocity is caused by the anisotropy in the structural constitution of the matrix. The interdependence of this anisotropy and the manufacturing process as its reason will be discussed in chapter seven.

The values of the ultrasonic velocity combined to the groups grey, red and replica are shown in **figure 18**. A distinct declining of the velocity from grey over red to replica is visible. Within the comparison of v (per) and v (par) it is clear, that the anisotropy in the replica is higher than in the original fragments. The anisotropy of the red terracotta is the lowest of all **(fig. 19).** The surface parallel fissures in the replica are one reason for the reduction of the ultrasonic velocity in the perpendicular direction. The standard aviation within the directions v per and v par is smaller for the replica than for the original fragments. The small differences for v (par) in the replica (here ony two dimensional anisotropy) point at an other manufacturing technique for the replica.

The data curve of the superficial measuring from T to T on the red backside of fragment 01-99 has no significant kink. The interpretation shown in figure 20 concludes a transition from lower to higher ultrasonic velocity at a depth of 1,6 cm.

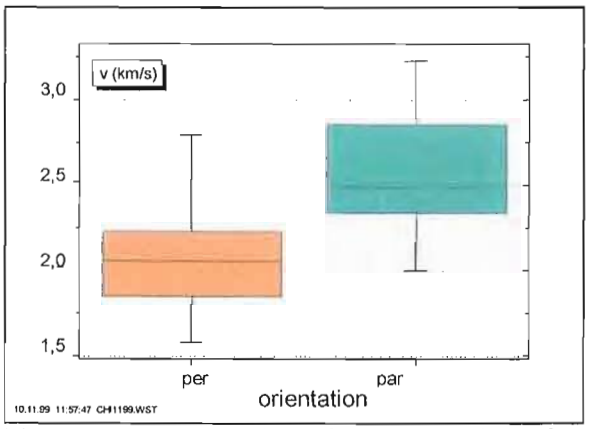



**Fig. 16**: v as a function of the orientation of the measurement trace in respect to the sculpture (perpendicular and parallel to the surface)

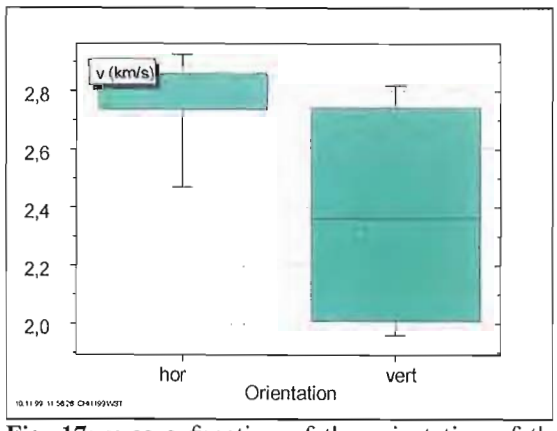



**Fig. 17**: v as a function of the orientation of the measurement trace in respect to the sculpture (horizontal, vertical)

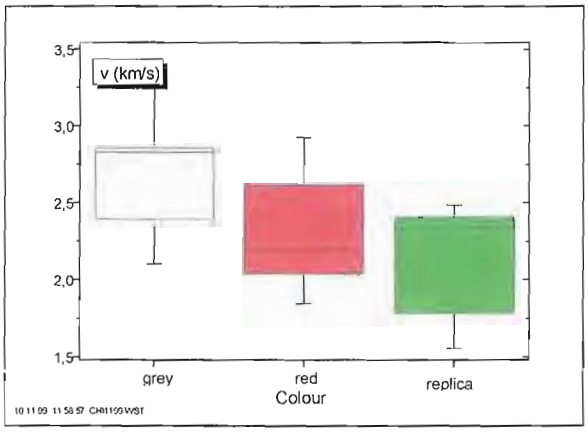



**Fig. 18**: v as a function of the terracotta material

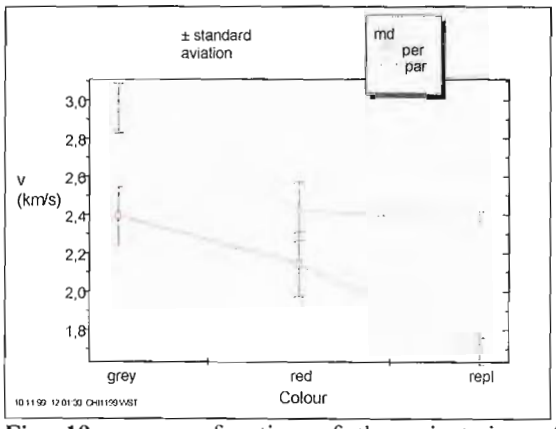



**Fig. 19**: v as a function of the orientation of material and orientation of the measurement trace in respect to the sculpture

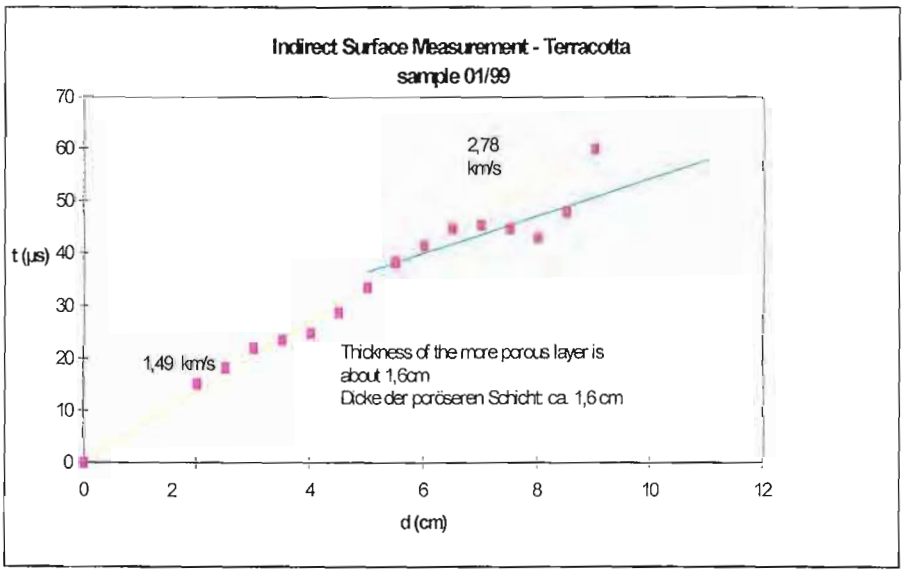



**Fig.20**: Transition time/distance diagram for sample 01/99 measurement T-T on the backside of the fragment. The thickness of "more porous" red layer is approx. 1,6 cm.

## 6.5 Results of the drilling resistance measurements

The results of the drilling resistance measurement are shown in **figure 22**. The curves compare the changes of the drilling resistance across the profile of each investigated fragment. The curve lines and the average drilling resistance for the same fragment are fairly corresponding.

The abrasion of the drill bit causes a shifting of the values to higher drilling pressure. Because we wanted to get a direct comparison of the mean drilling resistance of the fragments, the curves were adjusted and the systematic shift was eliminated. The coefficient of correction are given by a summation curve. In this curve the increase of the average drilling resistance in each drillhole of a single fragment is add up. Because all fragments are about two centimetre thick we have for each fragment - according to its hardness- a definite increase of the drilling resistance for each drillhole. For the calculation of the corrected curves the according value of the summation curve was subtracted from the measured values. The summation curve for the correction of the measured values is shown in **figure 21**.

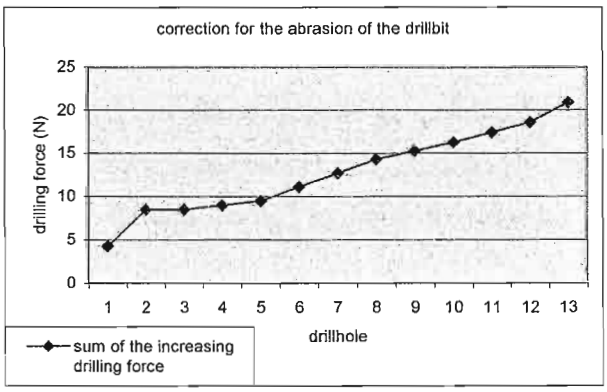



**fig.. 21**:correction curve for the drilling resistance

The proceedings of the Drillmore Workshop are recommending an other correction calculation for the abrasion error. This correction was not used because it is based on a linear abrasion in homogenous material. (SINGER, B., HORNSCHILD, I., SNETHLAGE, R., 2000). In contrast to this, the correction calculation we used in this investigation is considering the specific abrasion of each fragment. In this case the abrasion is not directly proportional with the drilled distance. **(fig. 21)**. The average values**(fig. 22)**, calculated by the corrected values of the curves must not be interpreted as absolute values for the drilling resistance of the fragments. But they are useful for an internal comparison of the drilling resistance of the investigated fragments.

The course of the curves belonging to fragment 03-99, 08-99 and the replica is on the same level for the whole profile. For fragment 02-99 and 05-99 the drilling resistance is declining from the inside to the outside, for fragment 01-99 it is inclining in the same direction. This

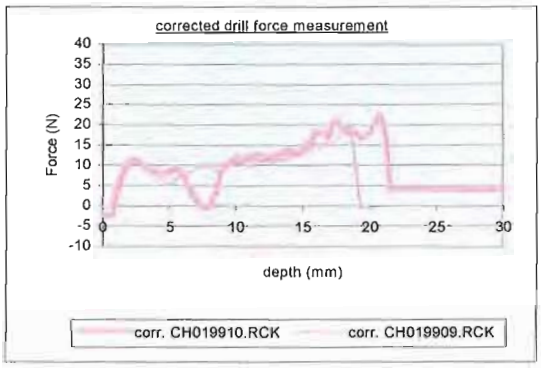
fragment 01-99 is fired from the inside. The sudden increase of the drilling resistance starts at 16mm penetration depth, where the colour of the fragment is changing from red into grey.
Distinct peaks ore bends in the curves are caused by bigger quarz grains ore pores (01-99 and replica). Apart from the significant change in drilling resistance in fragment 01-99 this method could not determine a regularly increase of the hardness from inside to outside ore a weak core ore some other characteristics like this.
The differences concerning the average values of the fragments are high (0N - 22N). The comparison shows no compelling interdependence between the colour of the terracotta and its drilling resistance. The samples 05-99 (grey) and the sample 03-99 (red) are the hardest in this investigation. Their values are comparable with weak sandstones (SINGER, B., HORNSCHILD, I., SNETHLAGE, R., 2000). The samples 02-99 (grey) and 08-99 (red) are very easy to drill. The influence of the content of quarz grains on the result of the drilling resistance measuring is very important for the interpretation of this data. With this method the content of quarz can influences the values much more than other important mechanical strength parameter like bulk density, porosity ore grain linkage. The replica lies with an average drilling resistance of about 7,7N in the under middleclass of the original terracotta.

The drilling resistance method is very sensitive on the quarz grain content and on the porosity of the sample. Besides the matrix porosity and the structural constitution of the matrix are important factors for this method. These parameters are characterising the one axial pressure strength of anorganic porous building materials. An accepted standard parameter for the strength of building materials. The drilling resistance normally can be correlated with the one axial pressure strength (EXADAKTYLOS, G., 2000). But in our investigation the influence of quarz grains obviously is dominating the results. Therefore the correlation of the results of the drilling resistance measuring with other parameters for the strength of the material has to be performed in a very differentiated manner.

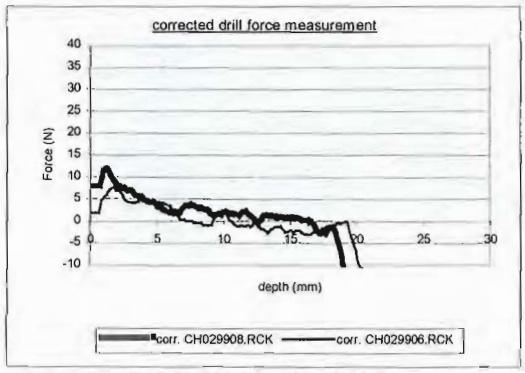
The results of the thin section analysis are important for the assessment of the fragments concerning their drilling resistance values **(compare. appendix 2)**:

**03-99:** high content of quarz grains, big grain size
**01-99:** high content of quarz grains
**08-99:** low content of quarz grains, smaller grain sizes as 03-99
**02-99:** very low content of quarz grains, small grain sizes, the porosity is increasing near to the surface
**05-99:** low content of quarz grains, high share of microscopic porosity but the highest bulk density> very dense matrix (folding structures).
**Replica:** low content of quarz grains, dense matrix. The high number of fissures is not detected with this method.

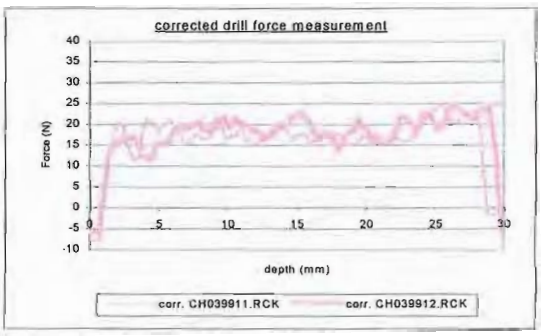
fragment 01-99 average: 11,5



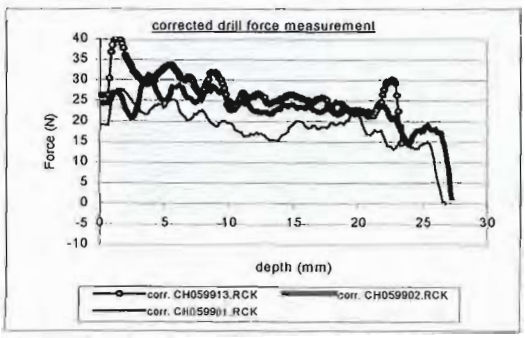

Fragment 02-99 average: 1,3



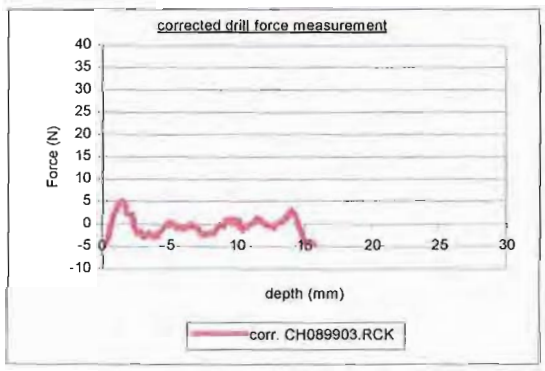

fragment 03-99 average: : 18,8




fragment 05-99 average: 22,4




fragment 08-99 average: 0,0




replica average: 7,7

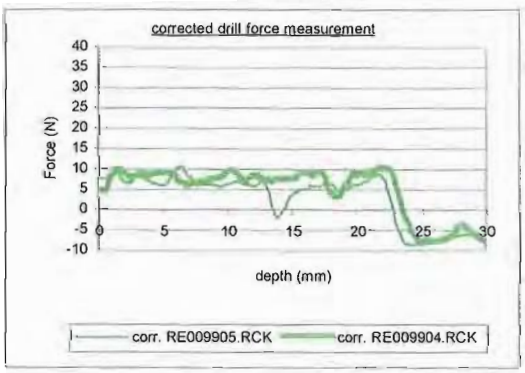



**fig. 22:** The corrected curves of the drilling resistance measuring for each fragment are plotted in separated diagrams. The penetration of the angular drillbit causes the inclined course on the first 2.5 millimetre. At the end of the profile the curve is kinks down sharply. The values between the first and the last peak of the curve were used for the calculation of the mean drilling resistance value. All fragments are drilled from the inside to the outside.

In case of fragment 01-99 the red terracotta on the inside is obviously weakened by the oxidating firing. The additional firing of the red terracotta can not change the structural character of a terracotta (specially the quarz content, as the most important factor for the drilling resistance method is not influenced. Only the microstructure of the matrix and the quality of the grain linkage could be changed by a second heating of the terracotta to1000°C. The values of the fragments 01-99 and 08-99 point at the conclusion, that the oxidativ firing has weakened the grain linkage of the mineral phases in the matrix. Theoretically with this, ore higher temperatures a hardening of the matrix by melting phases could be possible too.

**6.6** Results of the tensile strength measurements

The tensile strength is characterising the quality of the internal grain linkage in porous anorganic materials. It is the sum of all cohesive bindings of the mineral phases. The tensile strength differes from the compressive strength that is mainly influenced by the density of the material and the compressive strength of the components. For the matrix dominated structural constitution of the investigated terracotta the linkage of the mineral phases in the matrix are particularly responsible for the tensile strength of the bulk material.

The protocoll of the tensile strength measuring is added in **appendix 4**. The most important value of the tensile strength test is the maximal tensile strength $\sigma_{max}$, that is measured at the fraction point of the sample. It is calculated by the maximal tensile force $F_{max}$ that is taken from the peak of the loading curve and by the area of the fracture plane A ($\sigma_{max} = F_{max}/A$ ($N/mm^2$)). The maximal tensile strength values of the successful tested samples are shown in **figure 23**.

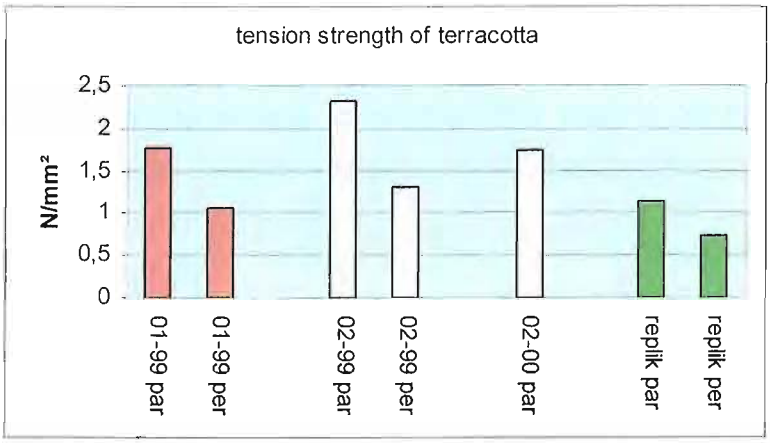



**fig. 23:** The tension strength of the terracotta is depending on the orientation of the sample. Fragment 01-99 is red and grey, 02-99 and 02-00 are grey.

The maximal tensile strength of the terracotta perpendicular to the surface (per) is only 60% of the tensile stress that can be hold by the normal fracture plane parallel to the surface of the fragment (par) (frag. 01-99 60 %, frag 02-99 57% and replica 63%. The fracture of 01-99 per is within the red part of the sample. The fracture plane of sample 01-99 par is cutting the grey and the red part of the fragment. The maximal tensile strength of this fragment is less than the strength of the grey fragments 02-99 and 02-00. This result is amazing in case of sample 02-99 because the other investigations have suggested this sample as more porous and less hard than sample 01-99 (see: **fig. 13** - porosity and **fig. 22** drilling resistance).

It is a reasonable explanation that the cohesive forces within the mineral structure are weakened by the thermal stress while the additional firing. Maybe mani grain linkages in the matrix are broken by this stress. But because of the limited number of tested samples it is not allowed to draw the generalised conclusion that the red, fired terracotta fragments have a

lower tensile strength than the grey, undamaged fragments. The small values of the replica easily can be explained by its numerous micro fissures.

## 7) Summary and conclusion

This investigations on the mechanical and structural properties of the qin terracotta resulted in a more detailed and more differentiated idea of the material. The differences of the hygric and mechanic properties of the excavated terracotta fragments are based in the micro texture of its matrix. The investigations have shown that the colour and the superficial appearance of a fragment are insecure indicators for a differentiation of the distinguishing marks -like porosity ore tensile strength-, that are important for the restoration and reconstruction of the figures. The results of our material tests have shown a distinct interdependence between raw material, manufacturing technique and the material properties of today. Material faults that are caused by the bedding in the ground for more than 2000 years have not been observed.
Factors for the modern properties of this old terracotta are the ancient composition and preparation of the raw material, the manufacturing technique of the figures, the drying process and the burning process. Even after 2000 years in the earth the qin terracotta keeps higher quality standards than the terracotta of the modern replica.

### 7.1 Raw material

The terracotta of the qin warriors owns an amazingly homogenous composed raw material. The high quality of the raw mass was the basis for the high-technical and artistic grade in the outward appearance of the finished terracotta figure. The microscopic investigations with fragments of different figures proved a high correspondence of the fragments according to the sizes, shape, type and number of the components and according to the structural composition of the matrix. The matrix porosity in all fragments shares 80%-85% of the bulk porosity. The volume and the structure of the matrix porosity is also corresponding in all the original fragments. If we compare the composition of the raw material for the qin warriors with the composition of the loess material in the partition walls of pit one and two, it seems convincing that the regional loess -ore a derived sediment of it- was used as raw material for the production of the warriors. This raw clay was mixed with precisely defined amounts of sieved fluvial sands.
The results of the thin section analysis in combination with the results of the density determination prove an uniform manufacturing process for the production of the raw material

of the qin warriors. Additionally it seems reasonable that also the preparation processes for the raw clay (milling, flooding, drying... ) have been performed in a uniform process for all the investigated fragments. Besides the material itself this procedures are highly influencing the properties and the quality of the fired terracotta (particularly the matrix porosity). Comparable analysis with other fragments, that were published in the excavation report are confirming this thesis. (SHAANXI SHENG..., 1988).

The excavation report and other publications, that are basing on that report describe the number and the various habits of the master craftsman and their teams, that were producing the terracotta warriors. The figures of the different craftsman teams got totally mixed up when they were positioned in the pits (SHAANXI SHENG..., 1988, SCHLOMBS, A., 1990, LEDDEROSE, L., 1998). Concerning to this, the fragments of this investigation are likely to belong to different craftsman teams. The observations of the art historians say that the whole production process for the raw figures -beginning with the forming of the single parts, going on with the forming of the body and ending with the detailed finishing of the surface- was performed within one team. The techniques for building up the figures and the artistically form of the finished figure are characteristic features for each team of craftsman. The finished figures of all craftsman teams were burned in central furnaces (LEDDEROSE, L., 1998).

**In contrast to this state of knowledge** the results of our investigations demand the conclusion that the mixing processes and the preparation processes for the plastic raw material were performed in one central production place. After this uniform preparation, the homogenous plastic mass was distributed to the craftsman teams. The optimised mixture of clay with sand and the homogenous preparation of the plastic mass was the basic prerequisite for a successful burning of this oversized figures. If the single master craftsman would have been in charge for the raw material, the differences in the structural composition of the investigated terracotta fragments would be much higher- like the difference between the original fragments and the fragments of the modern replica.

### 7.2 **production technique - plastic forming**

The detailed manufacturing technique of the terracotta figures is documented in the excavation report of Prof. Yuen and his archaeologists (SHAANXI SHENG ...,1988). The figures were formed of a plastic mass. Three different methods were used for the plastic forming.. The heads, the hands, the legs and in some cases also the forearms were formed in wooden moulds. The torso and the arms were build up by coils **(fig. 24)**. Alternatively to this technique particularly for creating the arms and the legs they used clay slabs **(fig. 24).** When

the clay has dried to a leather-hard consistence they formed the surface by striking it with wooden paddels. Shrink pores and shrinking fissures were closed by this treatment. The legs and the arms were applied to the torso by various techniques. Mostly fine clay suspensions were used in the mechanic connections as adhesive agent. The burning temperature in reducing atmosphere was between 950°C and 1050° (SHAANXI SHENG ...,1988). The heads and the hands were burnt separately.

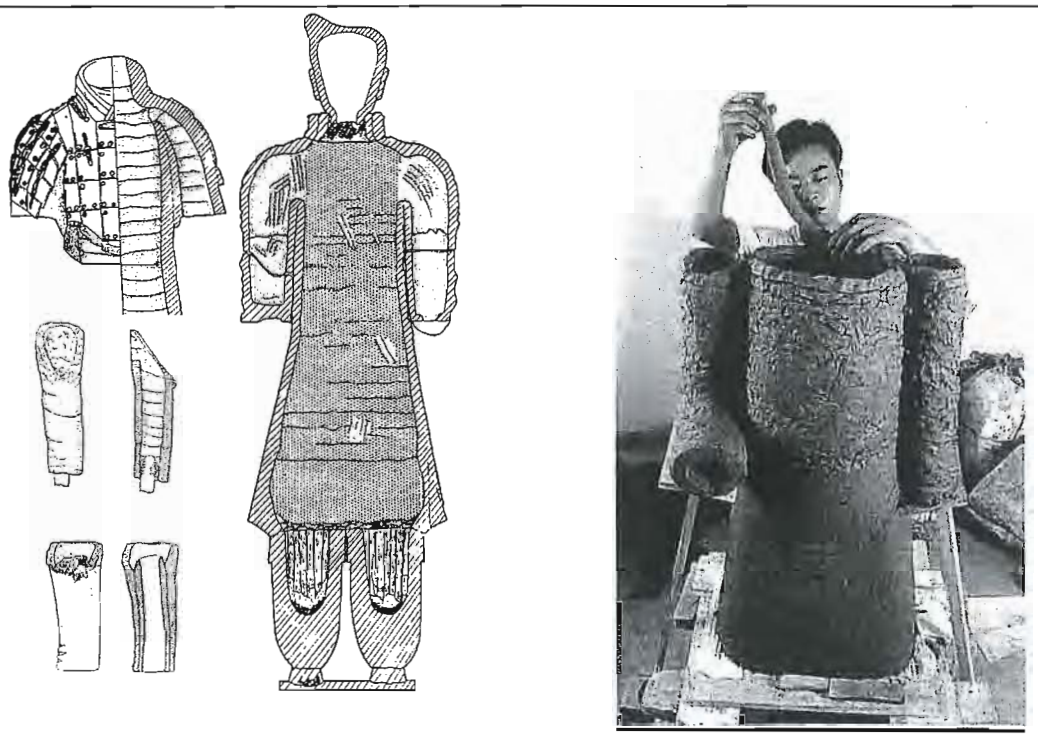


**Fig. 24**: The base, the legs and the head of the painted figure are formed in moulds. The rest of the figure is built up by the coil technique. The type of the forming technique often can be reconstructed by typical prints in the inside of the torso walls. An example of the clay slab technique is shown in the scetch of a forearm.
The right picture shows the building up of a figure for a modern reconstruction. On the skirt the coils already are overformed by striking the surface with wooden paddels.

The clay slab technique was used for the production of tube shaped figure elements like forearms ore legs. For this technique the plastic mass was rolled to a thin sheet. The sheet was folded and again rolled to a slab with about 2,5cm thickness. The finished slab was cut up to size and rolled to a cylindrical tube, ore applied on other parts of the figure. The big terracotta horses were predominantly built up by this technique.

By the coil technique the plastic mass was either rolled to long sticks with about 4cm diameter ore thick stripes were cut of a clay panel produced b the clay slab technique. The body ore the arms were build up by putting the stripe, ore the stick one on top of the other in the form of a coil (**fig. 24**). The joints between the coils were overformed on the outside by banging the figure with wooden sticks. On the inside the joints remained visible (**fig. 24**).

parallel directions, because for this copy also the torso was manufactured in clay slab technique.

The **microscopic investigations, the porosity measuring** and the measuring of the material density on all original fragments have determined a bulk porosity of about 30%, similar distribution of the pore sizes and a uniform mineral composition. Because of this corresponding data it is very likely that also the **capillary water uptake**, which is measured only for two original fragments up to now, has w-values from 1 (per) to 4 (par) for all original fragments. The textured matrix porosity shares more than 80% of the bulk porosity in the original fragments. The laminated character of the matrix porosity causes the anisotropy of the capillary water uptake.

The results of the **drilling resistance** measuring have to be read in a very differentiated manner, because, concerning the homogenity in density and matrix structure, the content of quarz components is an highly influencing factor for the resulting data. The curve lines of the drilling resistance measuring show no weak core which could be expected with unsufficient burning times. The drill could recognise only few bigger pores ore quarz grains. The methode is not sensible enough for micro fissures that are reducing the tensile strength of the terracotta. Because of its high sensibility for the content of quarz grains this methode can not recognise a relationship between colour and drilling resistance. Nevertheless the data of the fragments 01-99 and 08-99 point to the idear, that the second firing of the terracotta has reduced the linkage of the mineral phases in the red terracotta. Comparing the different methods, the drilling resistance measuring is less useful for the comparing the fragments of the terracotta army because the correlation of the drilling resistance data with the data of the other investigations (tensile strength, ultrasonic velocity) is only possible, if the individual composition of the fragment is already known (thinsection).

Concerning the question of the fragility of the figures and the jointing technique in restoration the **tensile strength** of the terracotta is the most important factor. The tensile strength characterises the quality of the internal linkage in mineralic materials. For the matrix dominated structure of the terracotta particularly the linkage of the matrix structure determines the tensile strength of the material.

The tensile strength of the terracotta perpendicular to the surface (per) is only 60% of the tensile strength that the usual fracture planes (par) can stand.

Up to now the measuring indicate a lower tensile strength for the red fragments as for the grey fragments. It seems reasonable that the cohesive forces of the mineral linkages are reduced by

the thermal stress of the second firing. The average tensile strength of the copy is only half of the original. The results are based on very few tests of the tensile strength. They have to be confirmed by more measuring of the tensile strength.

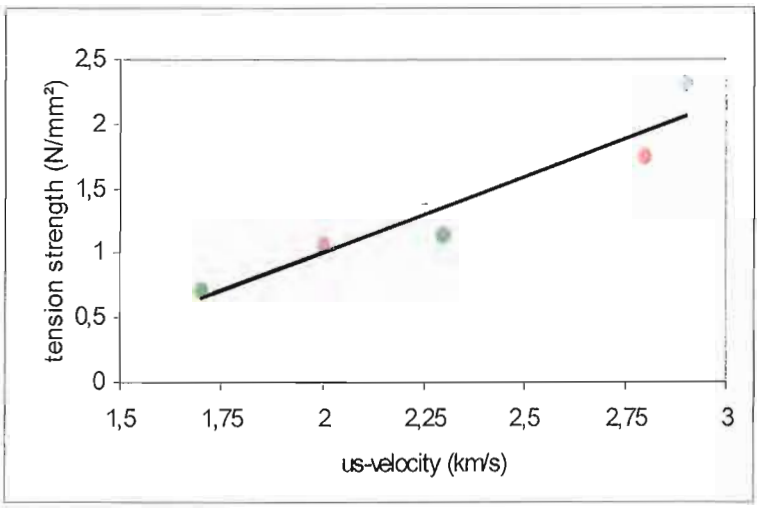



**fig. 26**: The tensile strength of the terracotta has a linear interdependence with its ultrasonic velocity. The samples 01-99 (red), 02-99 (grey) and replica (green) were measured in perpendicular and parallel direction refering to the surface of the fragment.

But even if the tensile strength was only tested for few samples, it is possible to show a very clear linear interdependence between the oriented tensile strength and the oriented ultrasonic velocity of the same fragment. **(fig. 26)**.

If this interdependence will be confirmed in further test series, it will be easy to derive the important factor of the tensile strength directly from the ultrasonic measuring. A method that is non destructive and easy to perform.

### 7.4 Conclusion

The original terracotta fragments of the terracotta army of Qin Shishuangdi have a uniform mineral composition and a uniform pore size distribution. All investigated original fragments can be classified as high quality terracotta. The results point to a centralised preparation of the plastic mass as raw material for the forming of the figures and a centralised burning procedure after their forming.

Concerning the homogenous composition and the uniform burning of the terracotta the variation of the manufacturing technique and the plastic forming of the figure has the most influence on possible differences according the mechanical properties of the terracotta. A microscopic texture of the matrix has been determined. It is caused by the plastic forming of the figure. The microscopic texture is the reason for a distinct mechanic and hygric anisotropy of the terracotta. Therefore all reasonable investigations concerning the hygric and mechanic properties of the material have to be performed with oriented samples. Former investigations

that have not taken the orientation of the samples into consideration need new assessing (SHAANXI SHENG..., 1988).

The grain linkages of the red fragments seem to be reduced by the fire in the pits. The bulk strength of this red fragments is lower than the strength of the grey terracotta fragments that were not affected by the fire. The terracotta of the replica is very different from the original according to the composition and the hygric and mechanic properties. The terracotta of the replica has a lower quality and can replace the original fragments only in some types of further experiments.

The microscopic investigations were the key for the understanding of the hygric and mechanic properties of the terracotta. The results of the non destructive ultrasonic measuring are highly corresponding with the values of the tensile strength tests. The ultrasonic measuring seems to be the best method for a mechanical classification of the original fragments before ore after the restoration of the warriors.

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## 9)Appendix

**Appendix 1 Documentation of the fragments**

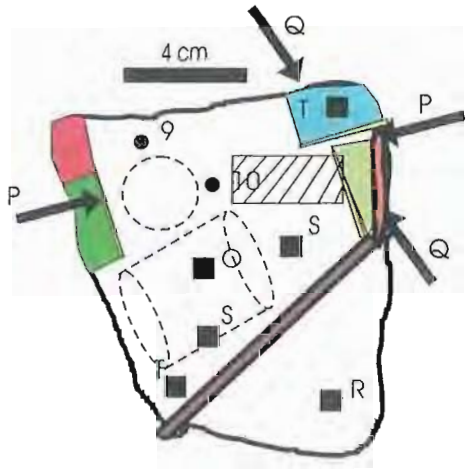
**Appendix 2 Photolist**

**Appendix 3 US measurements**

**Appendix 4 Protocol of the tensile strength measuring**

Appendix 1

# Sample: Frag.: 01-99




## Description:

Grey and red terracotta ;
thickness: 2-3,5cm; grey surface (0,5cm thick);
backside is burnt (red colour)


Drillcore (19mm diameter)
Drillcores, taken perpendicular (per) ore parallel (par) to the surface of the fragment

Sample for porosity and density No.: 01/P 02

| porosity | saturation | pure-density | bulk density |
|---|---|---|---|
| Vol.% | Vol.% | g/cm³ | g/cm³ |
| 29,11 | 88,00 | 2,70 | 1,91 |

Samples for microscopic thinsection  No.: 01/C 02

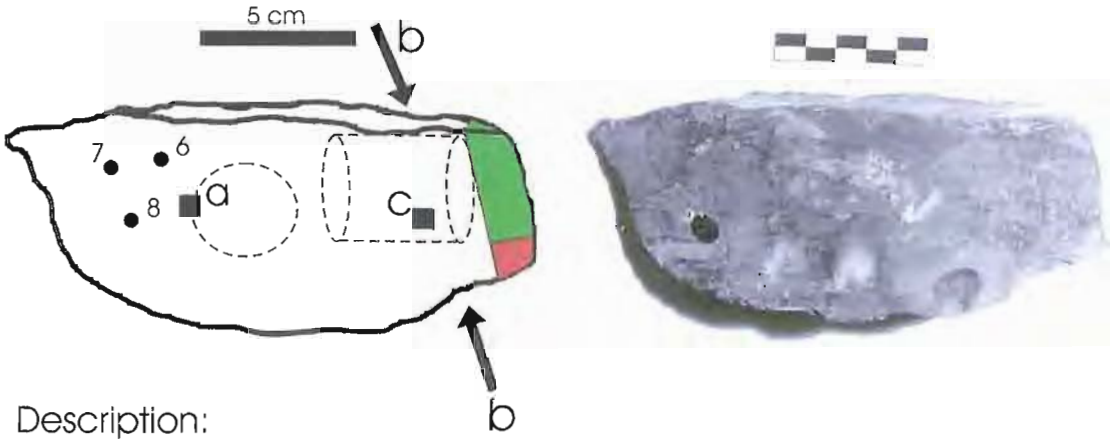
 No.: 01/C10  No.: 01/C 09  N0.: 01/C 08

- Drill force measuring ( 3,5 mm diameter )
  drilled from backside.
  Corrected mean value: 11,5 N

Ultrasonic measurements
Values are listed in "Anhang 3". The surface measurement S-S is measured on the front side, the surface measurement T-T is measured on the backside of the fragment

Appendix 1

# Sample: Frag.: 02-99




## Description:

Grey terracotta; thickness: 2cm; roughly formed surface
part of trousers


Drillcore (19mm diameter)

Drillcores, taken perpendicular (per) ore parallel (par) to the surface of the fragment

Sample for porosity and density No.: 02/P 03

| porosity | saturation | pure-density | bulk density |
|---|---|---|---|
| Vol.% | Vol.% | g/cm³ | g/cm³ |
| 31,87 | 88,43 | 2,70 | 1,84 |

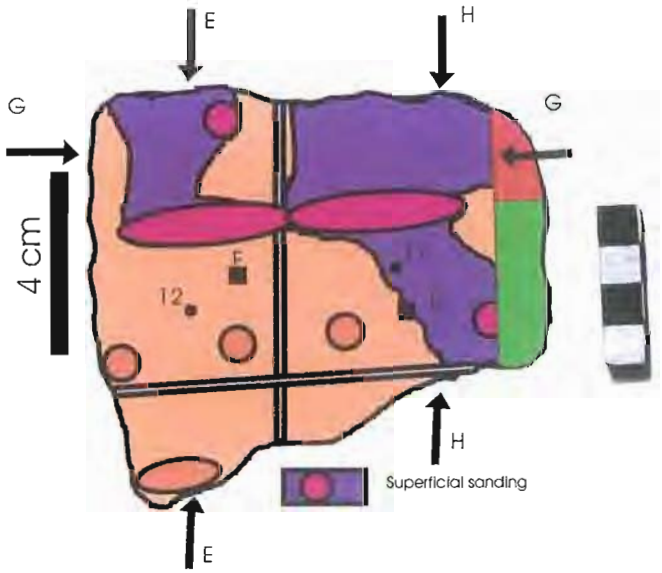
Sample for microscopic thinsection No.: 02/C 03

- Drill force measuring ( 3,5 mm diameter )
  drilled from backside
  drill no. 07 failed.
  corrected mean value: 1,3 N

Ultrasonic measurements
Values are listed in "Anhang 3".

Appendix 1

# Sample: Frag.: 03-99




99—1Pit—03

## Description:

Red terracotta highly burnt; partly sandy surface;

Sample for porosity and density No.: 03/P 01

| porosity | saturation | pure-density | bulk density |
|---|---|---|---|
| Vol.% | Vol.% | g/cm³ | g/cm³ |
| 29,69 | 94,74 | 2,70 | 1,90 |

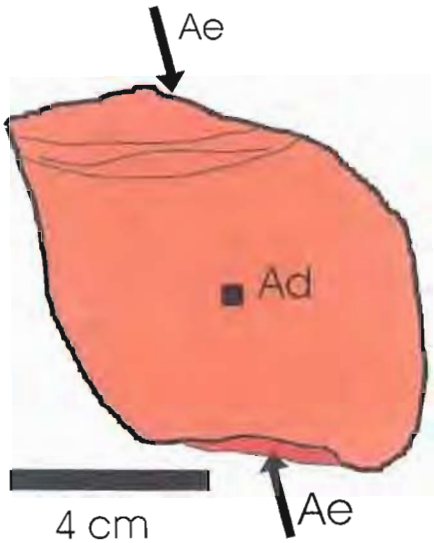
Sample for microscopic thinsection No.: 03/C 01

- Drill force measuring ( 3,5 mm diameter ) drilled from backside. Corrected mean value: 18,8 N

Ultrasonic measurements
Values are listed in "Anhang 3".

Appendix 1

# Sample: Frag.: 04-99



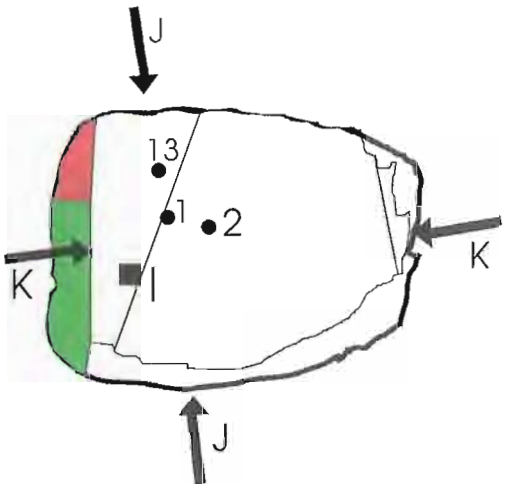

## Description:

Red terracotta highly burnt; convex shape (part of a leg?)
thickness up to 5cm;

■ Ultrasonic measurements
→ Values are listed in "Anhang 3"

Appendix 1

# Sample: Frag.: 05-99




9 cm

## Description:

Grey terracotta
thickness: 2-3,5cm; shiny surface (laquer?)

Shiny surface with two linear carving marks

Sample for porosity and density No.: 05/P 05

| porosity | saturation | pure-density | bulk density |
|---|---|---|---|
| Vol.% | Vol.% | g/cm³ | g/cm³ |
| 27,99 | 93,77 | 2,68 | 1,93 |

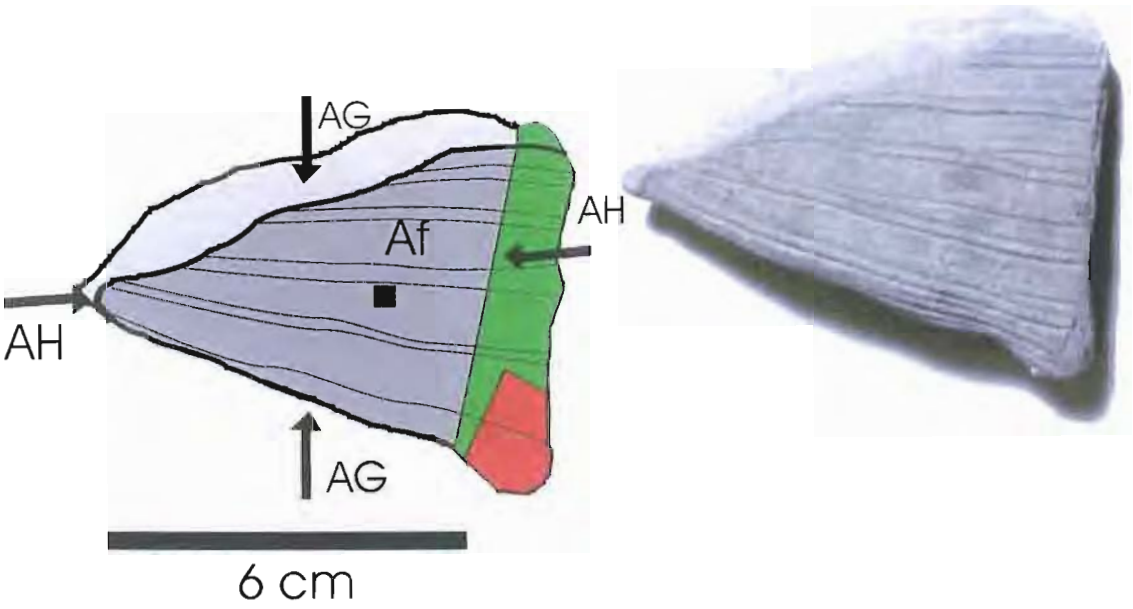
Sample for microscopic thinsection No.: 05/C 05

• Drill force measuring ( 3,5 mm diameter )
drilled from backside.
corrected mean value: 22,4 N

■ Ultrasonic measurements
Values are listed in "Anhang 3"

Appendix 1

# Sample: Frag.: 06-99




## Description:

Grey terracotta; part of hair
thickness: 2 cm; surface seems to be covered with a thin modelled layer of fine clay (cream of clay ;carbotine)

Sample for porosity and density No.: 06/P 04

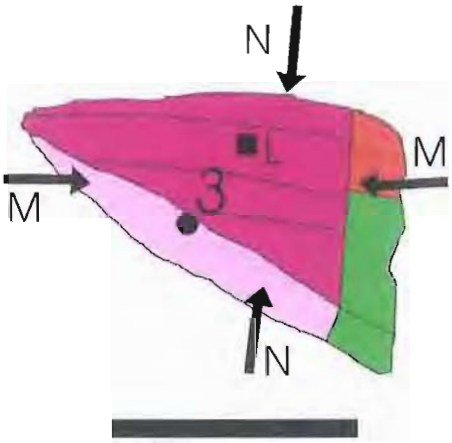
| porosity | saturation | pure-density | bulk density |
|---|---|---|---|
| Vol.% | Vol.% | g/cm³ | g/cm³ |
| 31,71 | 90,21 | 2,69 | 1,84 |

Sample for microscopic thinsection No.: 06/C 04

Ultrasonic measurements
Values are listed in "Anhang 3"

Appendix 1

# Sample: Frag.: 08-99




4 cm

## Description:

Red terracotta, highly burnt, more red than sample 03-99
thickness: 2 cm; modeled surface;
traces of dark brown laquer ?

Sample for porosity and density No.: 08/P 06

| porosity | saturation | pure-density | bulk density |
|---|---|---|---|
| Vol.% | Vol.% | g/cm³ | g/cm³ |
| 31,19 | 88,50 | 2,71 | 1,87 |

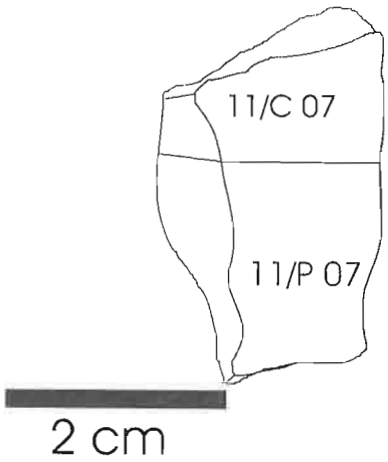
Sample for microscopic thinsection No.: 08/C 06

● Drill force measuring ( 3,5 mm diameter )
drilled from backside.
Corrected mean value: 0,0 N

■→ Ultrasonic measurements
Values are listed in "Anhang3"

Appendix 1

# Sample: Frag.: 11-99




## Description:

Grey terracotta;
thickness: 2 cm;

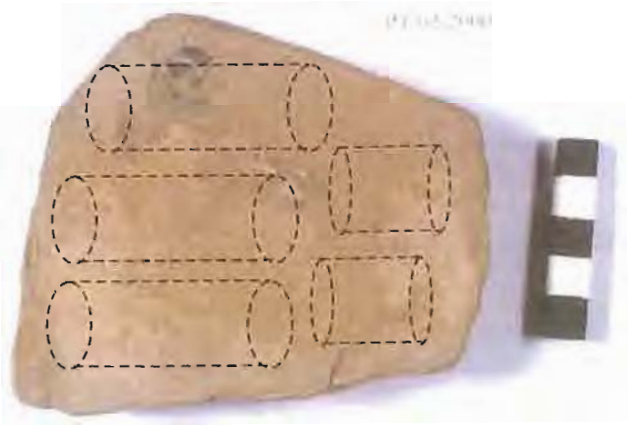
Sample for porosity and density No.: 11/P 07

| | |
|---|---|
| Porosity: | 26,26 Vol. % |
| saturation: | 90,87 Vol. % |
| pure-density | 2,68 g/cm$^2$ |
| bulk density | 1,97 g/cm$^2$ |

Sample for microscopic thinsection No.: 11/C 07

Appendix 1

# Sample: Frag.: 02-00



## Description:

Grey terracotta ; part of a skirt?; Thikness 2,8cm;


Drillcore (19mm diameter)
Drillcores, taken parallel (par) to the surface of the fragment

# Sample: replica


## Description:

Red terracotta; Grey on inner and outer surface; part of the replica; typical shell-shaped fracturing; Thikness 2,9cm;

# Appendix 2: Photolist

| No | Sample | Nicols/objektiv | description |
|---|---|---|---|
| 1 | 03/C 01 | Wild 6,3 | Oberfläche ist oben. Hoher Quarzanteil, Korn kantig nicht gerundet; leicht schichtige Einregelung parallel zur Oberfläche; gleichmäßige Verteilung; hellrote Matrix , dichtes Gefüge wenige, aber relativ große Grobporen diese sind sphärisch, nicht orientiert.<br>*Leitz: entspricht 01/C 02* |
| 2 | 03/C 01 | Wild 6,3 | Oberfl. liegt rechts |
| 3 | 08/C 06 | Wild 6,3 | Oberfläche liegt rechts. Geringerer Quarzanteil, Korngröße(kleiner als bei 03☹), kantig nicht gerundet; im Zentrum zentrierte Einregelung ("kneten"), Poren sphärisch. |
| 4 | 08/C 06 | Wild 6,3 | Rückseite ist links |
| 1 | 01/C 02 parallel | Wild 6,3 | Oberfläche rechts. Hoher Komponentenanteil ca. 20%?, Korngröße(s.u.) kantig nicht gerundet; leicht schichtige Einregelung parallel zur Oberfläche; gleichmäßige Verteilung. Matrix hellrot wird zur Oberfl. hin ockerblass bis grau, keine strukturelle Änderung, nur Farbwechsel. sphärische Poren und schichtorientierte Mikrorisse.<br>*Leitz:*<br>Verdunklung der Matrix von der Oberfläche her (< 1mm Tiefe) (Verfärbung durch Qui lack?)<br>Struktur: Matrixgestützt; Komponenten/ Matrix ca.: 20/ 80 (visuelle (Abschätzung nach Flügel 1982)<br>Haupt-Komponenten: gut sortiert, Eckig meist leistenförmig leicht kantengerundet, horizontal eingeregelt: Quarz, Plagioklase, Mikroklin; Quarzit. Gesteinsbruchstücke Korngröße: GK.: 1,2mm, Hauptanteil ca. 0.3mm, Kleinanteil: 0.1mm.<br>Zusätzlich: Biotit, mikrit. Kalk.(randlich angelöst), Chlorit, Muskovit und opake Bestandteile: Kohle, Erzminerale)<br>Matrix: rote Matrix aus 70% Schichtsilikat und Eisenhydrate? und 30% Quarz, bzw. Feldspat u. Gesteinsbr. Korngröße: <0.03mm, deutliche parallele Einregelung der Matrixminerale.<br><br>Vergleich mit Soil: Größtkorn entnommen; starke Anreicherung an Komponenten, Komponententypen entsprechend der Erde, jedoch starke Reduktion d. mikr. Kalke und großer Schichtsilikate.<br><br>Porenraum: sphärische, unregelmäßige Poren besonders im Zentrum der Terrakotta; leicht oberflächenparallel ausgerichtet, Schwundporen! Maximaldurchmesser: 0.08-0.6mm Porenanteil: ca.: 5-7%<br>Zwei durchlaufende oberflächenparallele Rissporen Spaltweite: 0,05mm. Beim Brand der Terrakotta entstanden.<br>Matrixporosität: entsprechend der Matrixminerale < 0.03mm.Sichtbarer Porenanteil: <5% der Matrix<br>Hauptanteil der Porosität im untermikroskopischen Bereich<0.03mm (3µm) |
| 6 | 01/C 02 | Wild 6,3 | Oberfläche rechts. |
| 7 | 06/C 04 | Wild 6,3 | Oberfläche rechts. Gravierte Oberfläche; geringer Quarzanteil, kleine Korngröße, Einregelung an Oberfläche angeglichen, z.T. angerundete Körner und Kohleeinschlüsse. Hellgraue Matrix an der Oberfläche rötlich braun. Porenraum; oft längsgerichtet linsenförmig parallel zur Einregelung (Wasserblasen beim verarbeiten). Zusätzlich querdurchlaufende Scherrisse. Kohleeinschlüsse. |

| | | | |
|---|---|---|---|
| 8 | 06/C 04 | Wild 6,3 | Wie 7 grüner Hintergrund |
| 9 | 06/C 04 | Wild 6,3 | Helle, porenreiche Zone im Innern der Probe schwache . Quarzgehalt nimmt von Innen nach Außen ab, leichter Anstieg an der Oberfläche.(vgl. Bohrhärte) |
| 10 | 06/C 04 | Wild 6,3 | Oberfläche oben; Hoher Porenanteil im Zentralbereich der Probe |
| 11 | 02/C 06 schnitt | Wild 6,3 | Oberfläche oben. Sehr geringer Quarzanteil, kleine Korngrößen der Quarze. Keine erkennbare Einregelung ( in diesem bereich der probe) hellgraue Matrix, inhomogene Matrixfärbung, viele blasenförmige und verzweigte Grobporen: Durchmesser: 0.3-1.6mm.<br>*Leitz:*<br>Struktur: Matrixgestützt; Komponenten/ Matrix ca.: 5 / 95 (visuelle (Abschätzung nach Flügel 1982)<br>Haupt-Komponenten: mäßig sortiert, Eckig meist leistenförmig leicht kantengerundet, nicht eingeregelt: Quarz, Plagioklase, Mikroklin; Quarzit. Gesteinsbruchstücke Korngröße: GK.: 0.8mm, hauptanteil ca. 0.3mm, Kleinanteil: 0.1mm.<br>Zusätzlich: Biotit, mikrit. Kalk.(randlich angelöst), Chlorit, Muskovit und opake Bestandteile: Kohle, Erzminerale)<br><br>Matrix: graue Matrix aus 70% Schichtsilikat und 30% Quarz, bzw. Feldspat u. Gesteinsbr. Korngröße: <0.03mm, Matrixminerale nicht gerichtet. Dunkelgraue Matrixbereiche enthalten weniger Matrixminerale im sichtbaren Bereich.<br><br>Porenraum: sphärische, unregelmäßige Poren besonders in Oerflächennahen Bereich; leicht oberflächenparallel ausgerichtet, Schwundporen! Maximaldurchmesser: Durchmesser: 0.3-1.6mm<br>Porenanteil: ca.: 5-7%<br>Wenige kurze oberflächenparallele Rissporen<br>Matrixporosität: entsprechend der Matrixminerale < 0.03mm.Sichtbarer Porenanteil: <5% der Matrix<br>Hauptanteil der Porosität im untermikroskopischen Bereich<0.03mm (3µm) |
| 12/13 | 02/C 06 | Wild 6,3 | Mit grünem Hintergrund |
| 14 | 02/C 06 | Wild 2,0 | Oberflächenparallel und einregelungsparallel verlaufende Mikrorisse .Biotit, Quarz und Poren |
| 15 | 02/C 06 | Wild 1,6 | Dunkle Einfärbung an der Oberfläche mit darunter liegender Eisenhydroxidschicht. Reste der Lackbehandlung? |
| 16 | 05/C 05 | Wild 6,3 | Oberfläche ist links. Dunkelfärbung der Oberfläche (Lack?); geringer Quarzgehalt, viel Porenraum, Porenraum ist schichtig eingeregelt;<br>*Leitz:*<br>Struktur: Matrixgestützt; Komponenten/ Matrix ca.: 5 / 95 (visuelle (Abschätzung nach Flügel 1982)<br>Haupt-Komponenten: mäßig sortiert, Eckig meist leistenförmig leicht kantengerundet, nicht eingeregelt: Quarz, Plagioklase, Mikroklin; Quarzit. Gesteinsbruchstücke Korngröße: GK.: 0.6mm, Hauptanteil ca. 0.3mm, Kleinanteil: 0.1mm.<br>Zusätzlich: Biotit, mikrit. Kalk.(randlich angelöst), Chlorit, Muskovit und opake Bestandteile: Kohle, Erzminerale)<br><br>Porenraum: sphärische, unregelmäßige Porenschichtig ausgerichtet, Schwundporen! Maximaldurchmesser: Durchmesser: 0.3-1.2mm<br>Porenanteil: ca.: 7-10 %<br><br>Matrixporosität: entsprechend der Matrixminerale < 0.03mm.Sichtbarer Porenanteil: <5% der Matrix<br>Hauptanteil der Porosität im untermikroskopischen Bereich<0.03mm |

| | | | |
|---|---|---|---|
| | | | (3µm) |
| 17 | 05/C 05 | Wild 6,3 | Faltenstruktur der geknickten Terrakotta Poren ist deutlich schichtgebunden. |
| 18 | 05/C 05 | Wild 6,3 | Helle porenreiche Zone im Inneren der Terrakotta (Faltenschenkel |
| 19 | 11/C 07 | Wild 6,3 | Oberfläche rechts; sehr großer Anteil an eckigen Quarzkörnern; homogene Verteilung und gute Sortierung. Hellorange Matrix, keine Einregelung erkennbar. |
| 20 | 11/C 07 | Wild 3,2 | Nahaufnahme; gute Sortierung |
| 21 | Replik | Wild 6,3 | Oberfläche rechts; geringe Grobquarzanteile, homogene ziegelrote Matrix; Viele sphärische Großporen Schrumpfporen eckig langgezogen langdurchgehende Haarrisse> splittriges Bruchverhalten. Oberfläche ist dunkel eingefärbt.<br>*Leitz:*<br>Struktur: Matrixgestützt; Komponenten<<5%(visuelle (Abschätzung nach Flügel 1982)<br>Haupt-Komponenten: mäßig sortiert, kantengerundet, nicht eingeregelt: Quarz, Plagioklase, Gesteinsbruchstücke Korngröße: GK.: 0.3mm, Hauptanteil ca. 0.3mm, Kleinanteil: 0.1mm.<br>Zusätzlich: Biotit, , Chlorit, Muskovit und opake Bestandteile: Kohle, Erzminerale)<br><br>Matrix: dunkelrote undefinierbare Matrix aus ca. 15% Quarz, und Schichtsilikat : <0.03mm, Matrixminerale nicht gerichtet. Rest ist nicht erkennbar<br><br>Porenraum: langgezogene Poren<br>oberflächenparallel ausgerichtet, Schwundporen!<br>Maximaldurchmesser: Abmaßung: 0.3x1.6mm und kleiner<br>Porenanteil: ca. 10%<br>Viele lange Rissporen (Öffnungsweite ca.:0,03mm)<br>Matrixporosität: entsprechend der Matrixminerale < 0.03mm. Kein sichtbarer Porenanteil:<br>Bereich<0.03mm (3µm) |
| 22 | Replik | Wild 6,3 | Rückseite mit Haarrissen; grüner Hintergrund |
| 23 | Replik | Wild 2,0 | Matrix mit typischem Poren und Rissgefüge |
| Neuer Film 10.08.00 | | | |
| 16 | 01/C 02 | Leitz 2.5 par | Struktur Textur ( Schliff liegt diagonal) |
| 17 | 01/C 02 | Leitz 2.5 gekr. | Komponenten Porosität, Kalkmikrit angelöst (Schliff liegt diagonal) |
| 18 | 01/C 02 | Leitz 2.5 gekr. | Komponenten Porosität, Kalkmikrit angelöst (Schliff liegt diagonal) |
| 19 | 01/C 02 | Leitz 16 gekr. | Matrixtextur (Schliff liegt diagonal) |
| 20 | 01/C 02 | Leitz 6.3 gekr. | Matrixtextur (Schliff liegt diagonal) |
| 21 | 01/C 10 | Leitz 6.3 par | Matrixtextur parallel zur Oberfläche ungerichtet |
| 22 | 01/C 10 | Leitz 16 par | Matrixtextur parallel zur Oberfläche ungerichtet |
| 23 | 01/C 10 | Leitz 6.3 gekr. | Matrixtextur parallel zur Oberfläche ungerichtet |

Appendix 3: US measurements

| Meas | Sample | Colour | md | md | Orien-tation | Tech-nique | d (cm) | t (µs) | v (km/s) |
|---|---|---|---|---|---|---|---|---|---|
| a | 02\99 | grey | - | per | | Trans | 2,15 | 15,6 | 2,4 |
| b | 02\99 | grey | ¦ | par | ? | Trans | 4,05 | 20,8 | 2,9 |
| c | 02\99 | grey | - | per | | Trans | 2,65 | 19,2 | 2,1 |
| d | 03\99 | brown-reddish | - | per | | Trans | 3 | 21,2 | 2,1 |
| e | 03\99 | brown-reddish | ¦ | par | hor | Trans | 7,2 | 31,2 | 2,9 |
| f | 03\99 | brown-reddish | - | per | | Trans | 3,05 | 21,6 | 2,0 |
| g | 03\99 | brown-reddish | ¦ | par | vert | Trans | 8,5 | 48 | 2,1 |
| h | 03\99 | brown-reddish | ¦ | par | hor | Trans | 6,4 | 30 | 2,7 |
| i | 05\99 | grey | - | per | | Trans | 2,6 | 15,8 | 2,8 |
| j | 05\99 | grey | ¦ | par | hor | Trans | 6,2 | 28,3 | 2,9 |
| k | 05\99 | grey | ¦ | par | vert | Trans | 7,3 | 34 | 2,7 |
| l | 08\99 | red | - | per | | Trans | 1,7 | 15,8 | 1,8 |
| m | 08\99 | red | ¦ | par | hor | Trans | 3,9 | 22,4 | 2,5 |
| n | 08\99 | red | ¦ | par | vert | Trans | 2,9 | 21,4 | 2,0 |
| o | 01\99 | grey (outside) - red (inside) | - | per | | Trans | 2,7 | 19,6 | 2,1 |
| p | 01\99 | grey (outside) - red (inside) | ¦ | par | vert | Trans | 9,3 | 39,6 | 2,8 |
| q | 01\99 | grey (outside) - red (inside) | ¦ | par | hor | Trans | 6 | 27,6 | 2,9 |
| r | 01\99 | grey (outside) - red (inside) | - | per | | Trans | 2,2 | 18,2 | 1,9 |
| s | 01\99 | grey (outside) - red (inside) | outs | | | Surf | 5 | 36,8 | 1,7 |
| t | 01\99 | grey (outside) - red (inside) | ins | | | Surf | 5 | 41,6 | 1,4 |
| u | Replic 00/99 | | ¦ | par | | Trans | 6,4 | 33,2 | 2,4 |
| v | Replic 00/99 | | ¦ | par | | Trans | 4,1 | 24 | 2,4 |
| w | Replic 00/99 | | - | per | | Trans | 2,3 | 21,4 | 1,6 |
| x | Replic 2/99 | | - | per | | Trans | 2,5 | 21 | 1,7 |
| y | Replic 2/99 | | ¦ | par | | Trans | 6,1 | 32,8 | 2,3 |
| z | Replic 2/99 | | ¦ | par | | Trans | 11,5 | 57,2 | 2,3 |
| aa | Replic 3/99 | | - | per | | Trans | 4,3 | 30,8 | 1,8 |
| ab | Replic 3/99 | | ¦ | par | | Trans | 8,1 | 39,2 | 2,5 |
| ac | Replic 3/99 | | ¦ | par | | Trans | 13,3 | 60,8 | 2,5 |
| ad | 04\99 | red | - | per | | Trans | 4,5 | 23,8 | 2,6 |
| ae | 04\99 | red | ¦ | par | | Trans | 7,4 | 38,4 | 2,3 |
| af | 06\99 | grey | - | per | | Trans | 2,1 | 16 | 2,2 |
| ag | 06\99 | grey | ¦ | par | | Trans | 3,3 | 16,2 | 3,4 |
| ah | 06\99 | grey | ¦ | par | | Trans | 5,3 | 24,4 | 3,0 |

# Appendix 4: Protocol of the tensile strength measuring

Zwick

**Zugversuch** **09.07.2001**

## Parameterlist:

Material : terracotta
Dateiname: quin-terracotta2.ZSE

Prüfer : utz

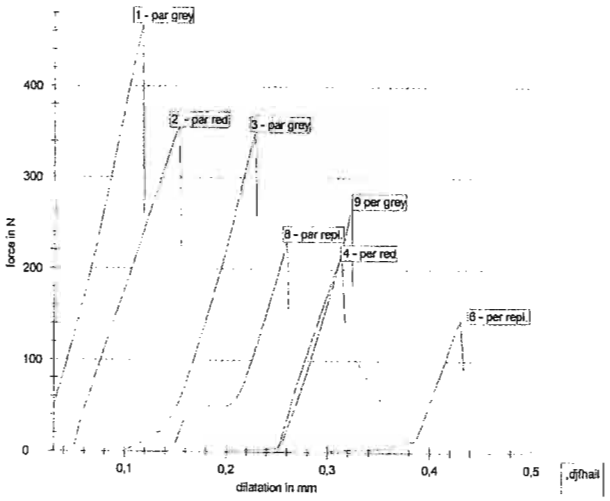
v Stufen : 1 mm/min

Vorkraft : 0,5 N

## Results:

| Nr | S0 mm² | F max N | σ max N/mm² | E-Modul kN/mm² | L-Fmax mm | t-F max s | L-Beginn mm | L-Ende mm | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 201 | 467 | 2,32 | 3,64 | 0,12 | 7,50 | 0,046 | 0,081 | 02/99 par |
| 2 | 201 | 355 | 1,76 | 2,60 | 0,10 | 6,64 | 0,020 | 0,059 | 01/99 par |
| 3 | 201 | 348 | 1,73 | 2,90 | 0,13 | 8,14 | 0,062 | 0,096 | 01/00 par |
| 8 | 201 | 230 | 1,14 | 2,81 | 0,11 | 7,00 | 0,069 | 0,097 | repl. / par |
| 9 | 201 | 266 | 1,32 | 3,04 | 0,12 | 7,90 | 0,081 | 0,111 | 02/99 per |
| 4 | 201 | 213 | 1,06 | 2,77 | 0,06 | 4,32 | 0,013 | 0,035 | 01/99 per |
| 6 | 201 | 144 | 0,72 | 2,47 | 0,13 | 8,30 | 0,100 | 0,119 | repl. / per |

## Seriengrafik:

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# Test series for the assembling of terracotta figures carried out on a replica of a warrior (work stay in Munich, November and December 1999)

Fig. 1. Replica of a warrior, body

Fig. 2. Replica after washing. The three levels of the body are visible.

The main subject of the work during the stay of Mr. Guo Baofa, Mr. Lan Desheng and Mr. Xia Yin in Munich in October and November 1999 was the assembling of broken terracotta figures. After discussions about problems and possible alternatives on both sides, the decision was made to perform practical tests. The idea was to test materials and methods on an object that corresponds in weight and shape to the terracotta warriors. As replicas of every size are produced around the museum, for obvious reasons a replica was chosen for the tests.
The replica should be made from the same material and with the same method as the original ones and also should have the same size. Before the work stay the replica was sent to Germany. After long discussions with the German customs it arrived in Munich.

The replica represents a standing warrior. It has same size as the original figures and is made of clay from the area around the museum. The method of production and the firing conditions do not correspond to the original ones. The replica consists of several parts, e.g. base slab, legs, three parts of body, hands and head. Base slab, feet and body have been produced and fired separately. The body was cut horizontally into three parts before firing. The technique of production of the replica is not known: Probably it was not modelled by hand, but pressed into a mould. The arms are attached to the

body in their full length - a situation that does not occur on the originals. In contrast to the original ones, the replica was not fired under reducing but oxidising conditions: The terracotta is red, not grey. Afterwards the figure was put together again, using plaster to attach the parts to each other. The hollow legs were totally filled with plaster. To produce a visual impression similar to the originals the surface was stained with a dark grey colour (probably ink). Afterwards soil dust mixed with water was applied with sponges. That way, the figure looked as if it was coming “directly out of the pit” (fig. 1).

The figure has cracks that have developed during firing: The lower part of the body had been broken into three pieces, the had shows bid cracks. The cracks were filled with plaster. During the tests to assemble the figures, it was a problem to connect parts that either did not have real connection zones at all because they had been made separately or did not fit because the pieces had deformed during firing.

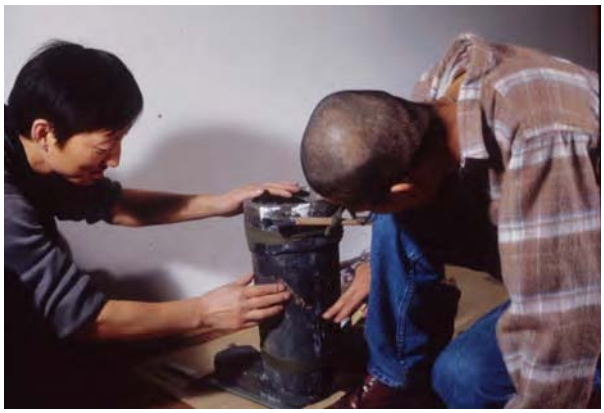
During unpacking the figure, the legs broke off. The head was taken off. For the assembling tests, the replica had to been broken into pieces. On Friday, October 29, Mr. Wu, director of the Museum of the Terracotta Army, was in Munich. He met with Mr. Petzet, General director of the Bavarian State Department for Historical Monuments. Together they smashed the figure by hitting it with a big hammer. It was the last day of work for Mr. Petzet before he retired.

The figure broke at the joints, i. e. three levels of the body, and into small fragments where the hammer hit the figure, i.e. the left arm and the lower and middle part of the body.
Before the tests for assembling the figure could start, the plaster had to be removed. This was a tiring and time-consuming work. Fortunately the plaster could be removed relatively easy after heating the pieces in an oven for some time. Before the work had been started, the whole figure had been washed to remove the “patina”. Still, remnants of organic materials, probably from the grey colour remained. If heated too hot or too long, it burnt with an unpleasant smell. Finally the bigger part of the fragments had been cleaned, so the tests could start (fig. 2).

Besides the German and Chinese colleagues, also Mr. Köhler from the Department for Archaeological Restoration[1], specialised on terracotta restoration, participated in the practical work.
Mrs. Stephanie Wallner, who has compiled the following description of the method and the results of the tests. had just started her internship at the restoration workshops before this work stay.

The aim of the experiments was to test different adhesives and mechanical constructions, as alternatives and also in combination with each other. Dowels and screw cramps were used. Besides the epoxy resin also other materials were tested which are used in the terracotta restoration, as acrylates, polyvinyl acetate. A method was tested to make joints glued with epoxy resins reversible: A “primer” was applied as separation and contact layer, before the epoxy resin was used. In tests on smaller fragments it was possible to open the joints again. Obviously this method to reach a reversibility for joints glued with epoxy resin could work successfully. This method now is used on the new excavated figures in the Museum of the Terracotta Army (Paraloid B 72 as primer).
The figure was not totally reassembled during the work stay. The base slab was glued with epoxy resin, also using dowels. The lower part of the body was connected only with mechanical solutions. The middle part was glued, mainly with polyvinyl acetate. Other methods were tested on the legs and parts of the arms. No tests were made to connect the parts that had been fired separately. The lower part of the body could be assembled, but the cracks form firing of course could not be closed.
There still are a lot of isolated fragments left for further tests. It is planned to continue the practical tests after basic research work on the properties of the terracotta and some adhesives is done.

[1] Department of the Bavarian State Department for Historical Monuments



Working in Munich, November and December1999

Through Mr. Köhler, a contact to Mr. Corrado Pedelì was possible, who works in the field of archaelogical restoration at the Servizio Beni Archeologici e Diagnostica of the Direzione tutela partimonio culturale in Aosta. During his visit in Munich a long discussion on the problem of assembling the terracotta warriors took place. He also helped with information on adhesives and experience on restoration of big terracotta objects. Further contacts were made by visits: to Mrs. Pluntke, restorer for ceramics in the workshops of the Roman Germanic Central Museum, Mrs. Strnischtie and Mr. Buhl from the workshop of the Antikensammlung Munich, Elisabetta Brunaf, restorer for ceramics in Rome, Elena Agnini, restorer, specialised on glass and ceramics in Munich, Mr. Gabriel Schneck in his workshop for technique and design. Other persons were contacted by telephone calls: Mr. Hans-Jürgen Ranz, restorer from the Münchner Werkstätten, specialised on metal support systems for metal figures and Mr. Klaus von Woysky who had worked in Athens as restorer of antique archaeological objects for 27 years.

(C. Blaensdorf)

# VERSUCHE ZUM ZUSAMMENSETZEN VON TERRAKOTTAFRAGMENTEN AN DER KOPIE EINES KRIEGERS

Stephanie Wallner

Verschiedene Methoden zum Zusammenfügen wurden von Oktober 1999 bis Januar 2000 in München an der Kopie eines Kriegers getestet. Als Versuchsmaterial diente eine in China angefertigte Kopie eines Terrakottasoldaten. Beim Zerschlagen wurde darauf geachtet, daß die Anzahl der Bruchfragmente und die Art der Brüche möglichst der Fundsituation der Originale entsprechen. Die einzelnen Fragmente wurden numeriert; ihre genaue Position ist in Skizzen eingetragen (s. Anhang zu diesem Text). Es wurden Versuche mit verschiedenen mechanischen Verbindungen (Dübel und auf der Innenseite angebrachte Spannklammern) mit und ohne Kleben ausgeführt. Außerdem wurden mehrere Klebemittel, flächig oder nur in Punkten aufgetragen, und die Verwendung von Primern getestet. Durch das Zusammensetzen einzelner Abschnitte der Figur mit jeweils einem Verfahren, wurde die Funktionsweise der verschiedenen Verbindungsarten an größeren Teilstücken untersucht. Dabei konnten auch die einzelnen Methoden miteinander verglichen werden. Die bis Januar 2000 durchgeführten Versuche sind im folgenden zusammengestellt. Weitere Untersuchungen sind geplant.

## 1. Dübel

Die Fragmente wurden durch quer zur Bruchfläche eingesetzte Dübel (mit und ohne Klebemittel) verbunden. Dazu wurden Schrauben oder Gewindestangen (∅3 mm) verwendet, da sich diese mit ihrer gekerbten Oberflächenstruktur gut in der Terrakotta verhaken.

### *1.1. Vorversuch zum Bohren der Dübellöcher und zum Einsetzen der Dübel*

Senkrecht zur Bruchfläche von **U5** wurde eine Schraube mit einem Nylondübel (Firma Fischer) in einem passend gebohrten Loch befestigt. Der Schraubenkopf wurde in einem zuvor in **U4** gebohrtem Loch nur leicht verhakt. Beim Bohren der Dübellöcher erwies es sich als äußerst schwierig, diese exakt parallel zu bohren. Es mußte nachkorrigiert werden. Dabei entstand im Fragment U4 ein nach innen etwas erweitertes Loch, in das sich der Schraubenkopf einhaken ließ. Auf diese Weise wurde noch keine feste und stabile Verbindung hergestellt. Die beiden Fragmente konnten aber bereits bei waagrechter Position des Dübels durch das Verzahnen der Bruchkanten aneinander gehängt werden. Nach mehrmaligen Auseinandernehmen und Zusammensetzen der beiden Fragmente weitete sich das Bohrloch in U4 aus, so daß der Schraubenkopf nicht mehr genügend verhakt werden konnte.

*1.2. Versuch zum Vergleich eines mit Epoxidharz eingeklebten und eines mechanisch befestigten Dübelendes*

In die Bruchfläche der Fragmente **P3** und **P4** wurden zwei Schrauben eingesetzt, die in P3 mit Nylondübeln befestigt wurden. In P4 wurden die Schraubenköpfe mit Epoxidharz eingeklebt. Nach 24 Stunden wurde versucht, die Verbindung gewaltsam wieder auseinander zu ziehen. Der Nylondübel wurde dabei rausgezogen und die Bohrlöcher brachen aus. Außerdem platzte beim Auseinanderbrechen ein Stück der Terrakotta ab. Die Epoxidharzklebung hielt dagegen problemlos. Ihre Verbindung ist stärker als die des Nylondübels.

*1.3. Versuch zum Vergleich eines mit Moltofill eingeklebten und eines mechanisch befestigten Dübelendes*

Ähnlich wie im vorhergehenden Versuch wurden zwei weitere Fragmente **P1** und **P2** miteinander verbunden. Dazu wurde auf der einen Seite eine Gewindestange mit einem Nylondübel eingesetzt. Auf der gegenüberliegenden Seite wurde die Gewindestange mit Moltofill eingeklebt. Nach 24 Stunden war das Moltofill im Dübelloch nur teilweise getrocknet. Die beiden Fragmente ließen sich daher ohne Beschädigung der Terrakotta auseinanderziehen.

*1.4. Versuch zur Verbindung kleinerer Bruchstücke mit einem Dübel*

**S13** und **S14** wurden provisorisch zusammengesetzt, um ein Loch quer durch das kleine Fragment S14 hindurch zu bohren und bis in S13 zu verlängern. Im Bohrloch von S13 wurde eine Gewindestange mit einem Nylondübel befestigt. Diese wurde durch S14 durchgesteckt und mit einer Schraubenmutter dort fixiert. Bei einem Transport ist S14 entlang des Bohrlochs in zwei Teile (S14 und S14') zerbrochen. Diese wurden für spätere Versuche mit einer 15%igen Lösung von Mowilith 50 geklebt.

*Beobachtungen und Anmerkungen*

Das Bohren der Löcher in den Bruchflächen ist immer mit einem Verlust an originaler Terrakotta verbunden. Die Oberflächen der Außen- und Innenseite werden aber durch das Einsetzten der Dübel nicht beschädigt und bleiben somit vollständig erhalten.

Durch das Anbringen der Löcher ist die Terrakotta an diesen Stellen dünnwandiger und daher auch sensibler. Bei einer stärkeren Belastung kann es entlang der Bohrung leichter zu einem neuen Bruch kommen, wie bei Fragment S14. Zum Brechen dieses Fragments trug zusätzlich die splittrige Beschaffenheit der Terrakotta der Kopie bei. Daher ist besonders bei dieser Figur, aber auch bei den stabileren Originalen von einer Verbindung kleinerer Bruchstück mit Dübeln abzuraten (siehe Versuch 1.4.).

Eine Verbindung mit Dübeln ist nicht reversibel und kann nicht nachträglich korrigiert werden. Sie kann nur unter Beschädigung der Terrakotta wieder gelöst werden (siehe Versuch 1.2).

**2. Spannklammern ohne Klebung**

Bereits in der griechischen Antike wurden gebrochene Gefäße mit Bleispangen verbunden[1]. Diese wurden auf der Außenseite der Krümmung angesetzt, da bei gebogenen Scherben nur so eine optimale Kräfteverteilung erreicht werden kann. In den folgenden Versuchen wurden davon ausgehend Verbindungen mit zuvor gebauten Spangen oder Klammern geprüft. Diese wurden aber auf der Innenseite angebracht, da bei den Terrakottafiguren die damit verbundenen Beschädigung der Oberflächen auf der Außenseite aus konservatorischen Gründen nicht vertretbar ist. Anders als bei den antiken Spangen sollte die Möglichkeit bestehen, die Verbindungen noch nachträglich zu korrigieren und sie zum Einsetzen weiterer Bruchstücke wieder öffnen zu können.
Abgesehen von 2.1. wurden die in den folgenden Versuchen verwendeten Klammern aus kurzen und dickeren Spannschlössern mit einem Rechts-Links-Gewinde (Länge: 3 cm; aus dem Werkzeugbedarf) mit gebogenen Gewindestangen (∅ 5 mm) als Haken oder aus längeren, aber dünneren Wantenspannern (Länge: 7 cm; aus dem Segelbedarf) und deren aufgebogenen Ringen als Haken hergestellt.

*2.1. Versuch zur Konstruktion eines Spannsystems*
**S5** und **S13** sollten mit einem Spannsystem miteinander verbunden werden. Auf der Innenseite der beiden Fragmente wurde jeweils mit einem Nylondübel eine Ringschraube in einem zuvor gebohrten Loch befestigt. Durch die Ösen wurde eine Gewindestange gelegt. Sie wurde auf jeder Seite mit einer Beilagscheibe und zwei Muttern befestigt, mit deren Hilfe die Bruchstücke zusammengezogen wurden.
Diese Art der Verbindung erwies sich jedoch als nicht stabil, da durch das Anziehen der Muttern die Fragmente nicht fest genug miteinander verbunden werden konnten und die Bruchflächen sich bei stärkerem Anziehen nach außen öffneten.

*2.2. Versuch zur Konstruktion einer Spannklammer*
Aus einem Spannschloß (Länge: 3 cm) und gebogenen Gewindestangen als Haken (∅ 6 mm) wurde eine Spannklammer hergestellt. In **S5** und **S13** wurden parallel zu der Konstruktion mit Gewindestange (siehe Versuch 2.1.) Löcher gebohrt, in die die Klammer eingesetzt wurde. Mit Hilfe des Spannschloß konnte die nötige Spannung erzeugt werden, um die Klammer zu befestigen und die beiden Fragmente fest und exakt passend miteinander zu verbinden. Einige Wochen später wurde ein Riß quer durch das Fragment entdeckt. Dieser kann sich sowohl bei einem Transport der Fragmente, aber auch in späteren Versuchen (siehe 3.4.) durch die beim Korrigieren entstandenen Spannungen oder mechanischen Belastungen, gebildet haben.

*2.3. Versuch zum Anbringen einer Spannklammer an gekrümmten Fragmenten*

[1] siehe Gesprächsnotiz zum Besuch in der Antikensammlung in München; antike Restaurierungsmethode

Die im vorangehenden Versuch verwendete Spannklammer sollte an etwas stärker gekrümmten Fragmenten getestet werden, um ihre Funktionsweise auch bei einer ungünstigen Kräfteverteilung zu untersuchen. Dazu wurden **S9** und **S16** mit dem gleichen Typ Spannklammer wie in Versuch 2.2. verbunden. Da die Klammer nicht paßte, mußten die Löcher ein zweites Mal gebohrt werden. Danach konnten die beiden Bruchstücke mit der durch den Wattenspanner erzeugten Spannung fest miteinander verbunden werden, ohne daß der Bruch sich nach außen öffnete.

*Beobachtungen und Anmerkungen*
Mit den in 2.2. und 2.3. auf der Innenseite angebrachten Spannklammern können zwei Fragmente exakt miteinander verbunden werden, ohne daß die Bruchfugen sich nach außen öffneten wie beim Spannsystem in Versuch 2.1. Durch die Bohrlöcher zum Einsetzen der Klammern wird die Oberfläche der Innenseite und damit auch Informationen zur Herstellung der Terrakottasoldaten geringfügig beschädigt. Außerdem wird der optische Eindruck in diesem Bereich durch die Klammern gestört.
Im Gegensatz zu eingesetzten Dübeln kann bereits mit diesem einfachen Typ einer Spannklammer eine Verbindung von zwei Fragmenten leicht und schnell wieder geöffnet und geschlossen werden. Auch ein exaktes Ausrichten der Fragmente ist jederzeit möglich.
Die Terrakotta ist jedoch ständig einer durch die Klammer erzeugten Spannung und einer mechanischen Belastung ausgesetzt, die auf längere Sicht zu neuen Schäden führen könnten.

## 3. Spannklammer mit Klebung

Es wurde versucht, die durch die Klammern hervorgerufene Spannung und die mechanische Belastung zu reduzieren, um die Bildung neuer Schäden an der Terrakotta möglichst zu vermeiden. Zu diesem Zweck wurde weiterhin der in den Versuchen 2.2. und 2.3. bereits eingesetzte Typ von Spannklammer verwendet. Die Haken wurden aber eingeklebt, so daß die Klammern nicht mehr durch die mit dem Spannschloß erzeugte Spannung in den Bohrlöchern gehalten wurden. Als Klebemittel dienten sowohl Epoxidharze und Heißkleber mit einer großen Klebekraft, als auch ein schwächeres und reversibles Polyacrylat. Außerdem wurde das Spannklammersystem sowohl in Hohlräumen mit kleinem Durchmesser, als auch zum Zusammensetzen einer größeren Einheit getestet.

### *3.1. Versuch zum Einkleben der Spannklammern*
Aus Wantenspannern (Länge: 7cm) und ihren aufgebogenen Ringschrauben bzw. einer Gewindestange wurden drei Spannklammern gefertigt. Möglichst rechtwinklig zur Innenseite der Fragmente **S1**, **S2** und **S3** wurden passende Löcher gebohrt und mit Druckluft von Staub befreit. Danach wurden die Haken der Klammern den Löchern entsprechend gebogen und eingesetzt. Die beiden unteren Klammern, die S1 und S3 miteinander verbinden, wurden mit Araldit 2011 eingeklebt und bis zum Aushärten des Epoxidharzes mit Tesakrepp fixiert.[2] Für die obere Klammer (S1/S2) wurde "Proxxon Schmelzklebstoff" verwendet. Da dieser jedoch sehr schnell erkaltete und fest wurde, wurde sein Aushärten mit einem Heißfön etwas hinausgezögert, um die Klammer exakt einsetzen zu können.
Nach dem Aushärten beider Klebstoffe (24 Stunden) konnte die Position der Fragmente noch korrigiert werden, in dem die Spannschloß leicht geöffnet und die somit etwas beweglichen Fragmente genau zueinander ausgerichtet wurden.
Die mittlere Klammer verbindet S1 mit S3 und überspringt dabei S2. Dies ist eine Möglichkeit, Fehlstellen oder kleinere, schmalere und daher empfindlichere Fragmente zu überbrücken.

### *3.2. Versuch zum Einkleben der Spannklammern mit einem reversiblen Klebemittel*
Mit Epoxidharz eingeklebte Klammern können nicht wieder entfernt werden, ohne die Terrakotta zu beschädigen. Aus diesem Grund wurde versucht, die Klammern mit einem reversiblen, aber auch schwächeren Klebemittel zu befestigen. Es wurde eine 40%ige Lösung von Paraloid B72 in Ethanol hergestellt. Da dieses jedoch keine füllenden Eigenschaften besitzt, die zum Einkleben der Klammern notwendig sind, mußte ein Füllstoff (3% Aerosil) zugesetzt werden. Mit dieser Mischung wurde eine Spannklammer, die die Fragmente **S7** und **S9** verbindet, eingeklebt.

[2] Die Eigenschaften der verwendeten Klebemittel sind in einer Tabelle im Anhang aufgeführt.

Nach 24 Stunden war das Paraloid noch nicht völlig ausgehärtet. Es hatte eine gummiartige Konsistenz angenommen und zeigte nur geringe Klebekraft. Die Klammern konnten herausgezogen werden. Dieses Ergebnis könnte auf das Ethanol zurückzuführen sein, da dieses das Paraloid anquillt.[3]

*3.3. Versuch zum Einkleben der Spannklammer mit einem Schmelzklebstoff*

Da im vorausgehenden Versuch die Klammer zur Verbindung von **S7** und **S9** nicht fest eingeklebt werden konnte, wurde sie mit einem Heißklebstoff erneut eingesetzt. Es wird angenommen, daß dieser Klebstoffe durch Erhitzen wieder weich wird und daher die Klammer entfernt werden könnte. Dies wurde aber noch nicht überprüft. Statt dem in Versuch 3.1. verwendeten „Proxxon Schmelzklebstoff" wurde diesmal „Pattex Schmelzklebstoff" verwendet, da er etwas elastischer ist. Auch mit diesem Klebstoff erhielt man eine stabile Fixierung der Klammer in ihren Löchern.

*3.4. Versuch zum Zusammensetzen eines größeren Abschnitts mit Spannklammern*

Um die Funktionsweise und das Zusammenwirken der Spannklammern an einer größeren Einheit zu untersuchen, wurde der gesamte Rockteil (S) mit diesem Verfahren zusammengesetzt.
Das Fragment **S11** wurde nacheinander mit den Fragmenten **S8**, **S16** und **S12** durch Klammern verbunden, die mit Araldit 2011 eingeklebt wurden. Auf die gleiche Weise wurden **S5** und **S6**, **S6** und **S4**, **S10** und **S16** zusammengesetzt. Die Bohrlöcher für diese Klammern wurden aber zuvor mit einer 20%igen Paraloid B72-Lösung eingestrichen (siehe Kapitel 6: Primer).
Bei der Verbindung von S11 und S12 bzw. S5 und S6 mußte die enorme Krümmung (>90°) im unteren Bereich des Rocks zwischen der horizontalen Unterseite und dem daran anschließenden, weitgehend vertikalen Abschnitt überbrückt werden. Bei den hier eingesetzten Spannklammern wurde deshalb jeweils eine Gewindestange nicht hakenförmig gebogen (S12 bzw. S6).
Mit diesen Verbindungen wurde der Rockteil zu drei großen Stücken zusammengesetzt, die aus (S1/S2/S3), (S7/S8/S9/S10/S11/S12) und (S4/S5/S6/S13/S14/S14‘/S15) bestehen. Durch Klammern zwischen **S1** und **S12**, **S6** und **S8**, **S5** und **S7** und zwischen **S3** und **S4** (zwei Klammern) wurden diese schließlich zu einem Stück zusammengefügt.
Nach dem Aushärten des Araldit 2011 wurde mit den kleineren Fragmenten **S17** und **S18** das nachträgliche Einfügen von Bruchstücken getestet. S17 wurde durch nochmaliges Aufschrauben der Klammern lose eingesetzt. Beim Zusammenschrauben ließ sich das Bruchstück gut in der richtigen Position fixieren. Allerdings brach durch den Druck der umliegenden Fragmente die schmale rechte Spitze von S17 ab.
Das Fragment S18 konnte am oberen Rand des Rockteils ohne das Öffnen der Klammern eingesetzt werden. Es wurde zusätzlich durch Kleben mit Mowilith 50/60 nur mit S5 verbunden, um ein späteres Öffnen und Schließen der Spannklammern nicht zu behindern.
Danach wurde versucht, mit Hilfe der Spannschlösser die einzelnen Fragmente möglichst exakt zueinander auszurichten, was teilweise gut funktionierte. Allerdings blieben alle Bruchfugen durch die auf der Innenseite angebrachten Klammern leicht nach außen geöffnet. An mehreren Punkten trat dabei eine große Spannung auf, die bei S5 zu einem Riß quer durch das Fragment führte. In der oberen Hälfte der Fragmente S3 und S4 platzten außerdem an der Oberfläche dünne Teile der Terrakotta ab. Größere Ungenauigkeiten ergaben sich beim Zusammensetzen der drei großen Teilstücke, (S1/S2/S3), (S7/S8/S9/S10/S11/S12), (S4/S5/S6/S13/S14/ S14‘/S15). Selbst durch starkes Druckausüben konnte keine exakte Paßgenauigkeit erzielt werden. Aufgrund ihres großen Gewichts konnten diese Teile mit den wenigen angebrachten Spannklammern (2 pro langer Bruch) nicht in die exakte Position gebracht werden. Ihre Bruchfugen blieben einige Millimeter geöffnet und zueinander versetzt. Zusätzlich erschwert wurde das Ausrichten an diesen Stellen durch Bruchfugen, die sich nicht ineinander verzahnen. Sie hatten sich aus bereits vor dem Brand entstandenen Rissen gebildet.

*3.5. Versuch zum Einsetzen von Klammern in einem engen Hohlraum*

Nachdem das linke Bein zu einer rechten und einer linken Hälfte aus kleineren Fragmenten zusammengeklebt war (siehe 4.3.), wurden diese im oberen Bereich durch Klammern zwischen den größten Teilstücken **R3** und **R4** auf beiden Seiten miteinander verbunden. Dabei erwies sich bereits das Bohren der Löcher aufgrund der stark gebogenen Form der Fragmente als kompliziert. Um die

[3] laut mündlicher Information von Stephanie Schäuffelhut

Klammern einsetzen zu können, mußten ihre Länge passend gewählt und ihre Haken entsprechend ausgerichtet werden. Während für die Bruchfugen an der Vorderseite eine sehr kurze Klammer aus einem 3cm langen Spannschloß angefertigt wurde, wurde für die Herstellung der Klammer auf der hinteren Seite ein 7 cm langer Wantenspanner auf beiden Seiten um je 1 cm gekürzt. Vor dem Einkleben der Klammern mit Araldit 2011 wurden die Löcher in R4 mit Druckluft und die Löcher in R3 mit Watte und Aceton gereinigt. Alle vier Bohrlöcher wurden mit Paraloid B72 (20% in Ethylacetat) eingestrichen, das ca. 10 Minuten trocknen konnte, bevor die Klammern eingesetzt wurden.

*3.6. Versuch zum Einsetzen eines Spannklammer quer über einen Hohlraum mit kleinem Durchmesser*
Aufgrund der Schwierigkeiten in Versuch 3.5. beim Bohren der Löcher und dem Einsetzen der Spannklammern wurde im unteren Bereich der Fragmente **R3** bzw. **R4** eine Klammer quer über den engen Innenraum gespannt. Für ihre Verankerung wurde diesmal nicht in der Nähe der Bruchkante, sondern in der Mitte der beiden Fragmente jeweils ein Loch gebohrt und mit Paraloid B72 (20% in Ethylacetat) eingestrichen. Danach wurde ein Spannschloß (M3-Modellbau) mit einer Gabelschraube und zwei Bolzen quer über den Innenraum eingesetzt und mit Araldit 2011 eingeklebt.

*Beobachtungen und Anmerkungen*
Die Versuche zeigten, daß es grundsätzlich möglich ist, größere Einheiten und auch Bereiche mit engen Innenräumen fest mit Spannklammern zu verbinden. Allerdings sind durch den Druck der auf der Innenseite angebrachten Klammern, alle Bruchfugen leicht nach außen geöffnet. Vor allen beim Zusammensetzen größerer Abschnitte ist es auch durch starkes Druckausüben nicht möglich, die Klammern soweit zu zuziehen, daß alle Fugen perfekt passen. Statt dessen kommt es zum Abplatzen von Terrakottastücken und der Bildung von Rissen (siehe Versuch 3.4.). Die Spannschlösser sollten daher nur sehr vorsichtig und möglichst wenig angezogen werden. Auch wiederholtes Öffnen und Schließen sollte vermieden werden, da dabei die Bruchflächen aneinander reiben und abgenützt werden.
Beim Zusammenfügen großer und schwerer Teilstücke reichten die eingesetzten Klammern (1-2 pro Bruch, d.h. 3-4 pro Fragment) noch nicht aus, um alle Fragmente in der richtigen Position zu fixieren (siehe Versuch 3.4.). Der optische Eindruck der Oberfläche wurde aber bereits durch die verwendeten Klammern stark gestört. Außerdem nimmt mit steigender Anzahl der zum befestigen der Klammern nötigen Bohrlöcher auch die Beschädigung der Innenseite und damit der Verlust an Spuren der Herstellung der Terrakottasoldaten zu.
Generell wird durch das Anbringen der Klammern das Gewicht der Figur zusätzlich erhöht. Tragende Teile, wie Bein und Füße werden dadurch stärker belasten und es kann zur Bildung neue Risse und Brüche kommen.

## 4. Vollflächige Klebungen mit unterschiedlichen Klebemitteln

Neben den in den vorangegangenen Kapiteln aufgeführten mechanischen Methoden, wurden einige Möglichkeiten zur Klebung der Fragmente getestet. Dabei wurden außer den in Lintong seit 1976

verwendeten Epoxidharz auch reversible und schwächere Klebemittel als Alternativen getestet und ihre unterschiedlichen Eigenschaften und das Verhalten gegenüber der Terrakotta untersucht.
Im Gegensatz zu den Spannklammern kann beim Kleben der Bruchflächen die Oberfläche der Innenseite vollständig erhalten werden. Wird das Klebemittel, wie in den folgenden Versuchen, auf die gesamte Bruchfuge aufgetragen, so werden eventuell auftretende Belastungen über diese Fläche verteilt. Schrumpfungen des Klebemittels und Schwachstellen der Klebung wirken sich mit dieser Methode in geringerem Maße aus, als bei Punktklebungen und eventuell auch bei den eingeklebten Haken der Spannklammern.

*4.1. Versuch zur Beurteilung der Stärke einer Klebung mit einem Polyvinylacrylat (Paraloid B 72) im Verhältnis zur Terrakotta*
Die Fragmente **A4** und **A7** wurden flächig mit einer 20%igen Lösung von Paraloid B 72 (in Ethylacetat) geklebt. Nach dem Aushärten (24h) wurden die Klebungen wieder aufgebrochen. Dabei wurden auf beiden Seiten Terrakottastückchen parallel zur Bruchfläche abgerissen. Es brachen zwei größere Stücke (ca. 1 x 1 cm; 1,5 x 2 cm) und einige kleinere Fragmente ab und blieben am Klebefilm auf der gegenüberliegenden Bruchflächen kleben. Dazwischen sind kleinere Bereiche entlang der Klebefuge gebrochen. Dort könnte möglicherweise der Klebstoff bereits vor dem Zusammensetzen getrocknet sein.
Es scheint außerdem, daß die Paraloidlösung nicht tiefer als ca. 1 mm in die Terrakotta eingedrungen ist, da die Fragmente nur sehr dünn abgerissen sind.

*4.2. Versuch zur Beurteilung der Stärke einer Klebung mit einem Polyvinylacetat (Mowilith 50) im Verhältnis zur Terrakotta*
Die Fragmente **D4** und **D8** wurden mit einer ca. 15% Lösung von Mowilith 50 (in Ethylacetat) geklebt. Beim ersten Versuch, die geklebte Bruchstelle aufzubrechen (durch Guo Baofa), hielt die Klebung und D4 bracht in zwei Teile (D4/D4‘). Beim zweiten Versuch (Rupert Utz) brach die Klebestelle. Auch hier rissen auf beiden Seiten parallel zur Oberfläche mehrere dünnere Stücke der Terrakotta ab und blieben auf der gegenüberliegenden Bruchkante kleben.

*4.3. Versuch zur Klebung mit einem 1:1-Gemisch aus Mowilith 50 und Mowilith 60 in Aceton* Zuerst wurde eine niedrig konzentrierte Lösung als Haftvermittler und darauf sofort eine höher konzentrierte Lösung desselben Klebemittels aufgetragen.[4]
Die Bruchflächen von **D4** und **D4‘** wurden von Staub gereinigt. Darauf wurde eine 5%ige Lösung von Mowilith 50/60, anschließend eine 30%ige Lösung aufgetragen und die beiden Fragmente fest zusammengepreßt. Es mußte dabei schnell gearbeitet werden, da vor allem die 5%ige Lösung sofort antrocknete. Auf die gleiche Weise wurden nacheinander **R4** und **R9**, sowie **R3**, **R12**, **R13**, **R14**, **R1**, **R2** und **R11** zusammengeklebt.
Beim späteren Versuch, die auf diese Weise zusammengesetzten Hälften des linken Beins mit Klammern zu verbinden, brach R12 entlang der Klebefläche mit R3, sowie ein größerer Teil des mit R12 verbundenen Fragments R2 ab (R2‘ ist der Bruchteil, der am Bein kleben blieb). Obwohl beide Fugen (R12/R3, R12/R2) mit Mowilith 50/60 und demselben Verfahren geklebt wurden, hatte die Klebung zwischen R3 und R12 bereits einer geringen mechanischen Belastung nicht standgehalten. Zwischen den beiden Fragmenten konnte sich vermutlich kein ausreichender Klebefilm bilden. Gründe dafür können sowohl das Antrocknen des Klebemittels vor dem Zusammenfügen der Bruchflächen (zu schnelles Verdunsten des Lösemittels), als auch ein zu schnelles und tiefes Eindringen der Lösung unter die Klebefläche aufgrund der großer Porosität der Terrakotta sein. Auch ein zu geringer Druck auf die Klebefuge beim Aushärten des Klebemittels kann dazu beigetragen haben.

*4.4. Versuch zum Kleben eines größeren Abschnitts mit Mowilith 50/60*
Der gesamte mittlere Rumpfteil (D) wurde durch Kleben mit Mowilith 50/60 zusammengesetzt, um Vorteile und Probleme dieser Methode auch an einer größeren Einheit zu untersuchen. Dadurch wurde auch ein besserer Vergleich mit dem mechanischen Spannklammerverfahren möglich.

[4] Methode von Frau Agnini vorgeschlagen; siehe Gesprächsnotiz

Zunächst wurden mehrere Fragmente zu größeren Stücken zusammengesetzt. Dabei wurden **D1, D13, D14, D15** mit **D16** und **D8, D9** mit **D11** sowie **D6** mit **D7** und **D2** mit **D3** und **D2, D10** mit **D12** und **D4, D5** mit **D17** sowie **D18** mit **D19** und **B6** mit **B7** miteinander verbunden. Die einzelnen Bruchstücke wurden bis zum Aushärten des Mowiliths mit Tesakrepp fixiert. Bei der Klebung von D4, D5 und D17 wurde außerdem mit einer Holzschraubzwinge Druck auf die Klebung ausgeübt. Danach wurden die Stücke **(D2/D3/D10/D12)** mit **(D4/D5/D17)** sowie **(D2/D3/D4/D5/D10/D12/D17)** mit **(D8/D9/D11)** und **(D18/D19)** mit **(B6/B7)** zusammengeklebt und mit Teaskrepp fixiert. Bei dem Versuch, (D1/D13/D14/D15/D16) zwischen D9 und D12 einzusetzen, brach die Klebung zwischen D1 und D13 durch den Druck auf die frischen Klebefugen auf. Außerdem erwies es sich aufgrund von abgetragenen Bruchflächen schwierig, die genaue Position von D16 mit D9 zu bestimmen.
Um die weitere Vorgehensweise zu bestimmen, wurde ein Trockenaufbau durchgeführt. Dabei konnte das Fragment (D6/D7) nicht mehr exakt eingesetzt werden. Bei den vorausgehenden Klebungen müssen sich Ungenauigkeiten ergeben haben. Diese sind vermutlich auch darauf zurückzuführen, daß während des Aushärtens des Klebemittels nur durch das Eigengewicht der Fragmente Druck auf die Klebefugen ausgeübt wurde. Durch ein vorsichtiges Nach-Innen-Drücken des ca. 30 min. zuvor geklebten Teilstücks (D8/D9/D11) konnte noch weitgehend korrigiert werden. Allerdings wurden dabei die Klebefugen zwischen diesem Teilstück und D4 sowie D17 ziemlich belastet. Um weitere Ungenauigkeiten einzuschränken, wurde bei den Klebungen während des Aushärtens immer zusätzlich Druck mit Hilfe von Zwingen und Schnüren ausgeübt. Außerdem wurden die Stücke **(D6/D7)** und **(D18/D19/B6/B7)** gleichzeitig eingeklebt, da sie so besser in ihrer exakten Position fixiert werden konnten. Zuletzt wurde das Fragment **D1** und das Stück **(D13/D14/D15/D16)** eingesetzt. Auch bei diesen beiden erwies sich ein gleichzeitiges Einkleben als sinnvoll, da so auch die genaue Position von D16 (abgetragene Bruchfläche) leichter ermittelt werden konnte.

*4.5. Versuch mit Mowilith 50/60 zur Infiltration des Klebemittels in die Bruchfuge*

Um Ungenauigkeiten, die sich bei einem schrittweise Zusammensetzen der Fragmente ergeben, zu vermeiden, wurde versucht, die Fragmente zunächst „trocken“, d.h. ohne Klebemittel aufzubauen und sie in dieser Position provisorisch zu fixieren. Die Klebung sollte danach durch Infiltration eines Klebemittels zustande kommen (Vorgehen vergleichbar mit der Klebung von Porzellan und Glas).
Die Fragmente **B4** und **B5** wurden exakt zusammengesetzt und in dieser Position mit Hilfe von Schnüren und einem Holzkeil möglichst fest fixiert. Danach wurde in den Spalt von oben Aceton eingeträufelt, um die Fuge zu reinigen. Das Aceton lief dabei von oben durch die Klebefuge bis an das untere Ende durch. Auf die gleiche Weise wurde zunächst eine 10%ige und später eine 30%ige Lösung von Mowilith 50/60 eingeträufelt. Auf der Innenseite konnte der Weg des Klebemittels entlang der Bruchkante bis an das untere Ende der Bruchstücke verfolgt werden.
Um den Verlauf des Mowilith 50/60 im Inneren der Fuge zu kontrollieren, wurde die Klebung wieder aufgebrochen. Dazu war ein deutlich geringerer Kraftaufwand notwendig, als dies bei einer durch Einstreichen der Fugen ausgeführten Klebung (siehe 4.2.) der Fall war. Die Bruchflächen zeigten eine durch das Mowilith hervorgerufene Verfärbung nur entlang der Innenkante. Das Klebemittel ist also nicht in das Innere der Fuge vorgedrungen. Außerdem sind zwei scharfe Ränder entlang der unteren und der oberen Kante zu beobachten. B4 und B5 konnten also mit dieser Methode nicht genügend miteinander verbunden werden.

*4.6. Versuch mit Mowilith 50/60 zur Verwendung eines Füllstoffs*

Das linke Bein (R1/R2/R3/R4/R9/R11/R13/R14/R15) wurde auf den linken Fuß (R5/R6/R7/R8/R10/R12) gesetzt. Da die Bruchkanten ringsum nicht exakt paßten, wurde das Bein so ausgerichtet, daß sich die Fugen im vorderen Teil schlossen, im hinteren Teil aber leicht geöffnet blieben. Zum Kleben wurde zunächst eine dünne Schicht der 5%igen Lösung von Mowilith 50/60 aufgetragen und darauf im vorderen Bereich eine 30%ige Lösung. Da Mowilith keine fugenfüllenden Eigenschaften besitzt, wurden im Bereich der geöffneten Fuge der 30%ige Lösung Hohlglaskügelchen als Füllstoff zugesetzt. Beim ersten Versuch das Polyvinylacetat mit dem Füllstoff zu vermischen entstand, ähnlich wie bei Versuch 3.2. mit Paraloid B72, eine zäheelastische Masse. Durch Verringerung des Anteils an Hohlglaskügelchen wurde diese jedoch fest. Der Klebemittelfilm blieb noch 1-2 Tage etwas weich, bevor er endgültig aushärtete.

*4.7. Versuch zur Reversibilität des thermoplastischen Epoxidharzes „Uhu plus“* [5]

Die Bruchflächen der Fragmente **U5** und **U7** wurden von Staub befreit und mit dem Fön erwärmt, damit das Klebemittel schneller aushärtet.[6] Danach wurden die Fragmente durch flächiges Auftragen von "Uhu plus" auf die Bruchflächen miteinander verbunden. Nach dem Aushärten des Epoxidharzes (24h) wurde versucht, die Klebung mit einem Heißfön wieder zu öffnen. Nachdem nach 30 min. keine Veränderung zu beobachten war, wurden die geklebten Fragmente im Heizschrank auf 144°C erwärmt. Auch dadurch konnten die beiden Fragmente nicht voneinander getrennt werden. Der Klebefilm ließ sich nur geringfügig mit dem Fingernagel kratzen. Diese Klebung ist also nicht reversibel.

*4.8. Versuch mit einem Klebemittel auf Cellulosenitrat-Basis: Mecosan L-TR*

Auf die Bruchflächen der Fragmente U2 und U3 wurden das Cellulosenitrat Mecosan L-TR in der verkauften Konzentration[7] flächig aufgetragen. Die beiden Fragmente wurde sofort zusammengefügt und einige Minuten aneinander gepreßt. Dabei entstand eine feste Klebung. Es wurden bis jetzt keine weiteren Beobachtungen gemacht oder Versuche durchgeführt.

*Beobachtungen und Anmerkungen*

Um die Stärke von reversiblen aber schwachen Polyvinylacetaten und –acrylaten im Vergleich zur Terrakotta beurteilen zu können wurden in den Versuchen 4.1. und 4.2. Klebungen mit Paraloid B72 bzw. Mowilith 50 wieder aufgebrochen. In beiden Versuchen bildete sich ein neuer Bruch in der Terrakotta und nicht in der alten Bruchfuge. Dieses Ergebnis zeigt, das auch die schwächeren Polyvinylacetate und –acrylate stärker sind als die Terrakotta in der Umgebung des Bruchs. Es kann jedoch nicht daraus geschlossen werden, daß sie generell stärker sind als diese Terrakotta, da bei der Entstehung eines Bruchs sich in der umliegenden Terrakotta immer Mikrorisse bilden.
Im Vergleich zur mechanischen Methode mit Spannklammer konnten durch Kleben alle Bruchfugen optimal geschlossen werden. Dazu mußte jedoch während des Aushärtens des Klebemittels mit Zwingen oder Schnüren zusätzlich Druck auf die Fuge ausgeübt werden. Um die Fragmente exakt einzupassen und damit Ungenauigkeiten beim schrittweise Zusammensetzen größerer Einheiten, möglichst zu vermeiden, wurden diese nicht fortschreitend von unten nach oben zusammengesetzt. Stattdessen wurden mehrere größere Teilstücke aufgebaut, die sich später leicht und ohne Probleme durch Untergriffigkeit ineinanderfügen ließen. In einigen Fällen war es außerdem günstiger, mehrere Stücke gleichzeitig einzukleben, um ihre Position exakt fixieren zu können (siehe 4.4.).

## 5. Punktklebungen

Die große Klebekraft der Epoxidharze kann im Laufe der Zeit zu einer erneuten Schädigung der Terrakotta führen, indem bei einer stärkeren Belastung im Bereich der Klebestelle ein neuer Bruch in der schwächeren Terrakotta und nicht in der Klebefuge entsteht. In diesem Fall ist das verwendete Klebemittel „zu stark“. Trägt man das Epoxidharz nicht flächig, sondern nur als einzelne Klebepunkte auf, wird die Klebekraft auf den Bruchflächen reduziert. Außerdem kann durch eine Punktklebung die Fläche, auf der später die eben beschriebenen Schäden auftreten können, reduziert werden. Auch muß nur ein kleiner Teil der Bruchflächen mit dem irreversiblen Epoxidharz bedeckt werden.

*Versuch zur Reduzierung der Klebkraft durch punktuelles Auftragen von Araldit 2011*

Die Bruchflächen der Fragmente **B1** und **B2** wurden von Staub gereinigt und durch eine Punktklebung mit Araldit 2011 miteinander verbunden. Einige Wochen später wurden B1 und B2 mit einem Hammer zerschlagen. Dabei brach B1 in mehrere Teile. Die Punktklebung zwischen B1 und B2 trennte sich aber nicht. B1 brach nur neben dem äußersten Klebepunkt senkrecht zur Klebefuge und nicht zwischen den Klebepunkten. Die Stabilität der Punktklebung beim Zerschlagen von (B1/B2)

[5] Laut Gebrauchsanweisung soll Uhu plus ein thermoplastisches Epoxidharz sein
[6] siehe Gebrauchsanweisung Uhu plus
[7] siehe Lieferschein der Kissel und Wolf GmbH

zeigte, daß die Klebekraft des Araldit 2011 auch bei einer Punktklebung für eine feste Verbindung der Fragmente noch völlig ausreichte.

## 6. Epoxidharzklebung mit Primer

Mit Epoxidharzen können sehr feste Verbindungen erzeugt werden, die allerdings nach dem Aushärten des Klebers nicht mehr reversibel sind. Wird jedoch vor der Klebung auf die Klebeflächen ein schwächeres, aber reversibles Klebemittel als Primer[8] aufgetragen, so kann eine solche Verbindung durch Anlösen oder Erwärmen des Primers wieder geöffnet werden. Der Primer dient dabei als Brücke und Isolierschicht zwischen Terrakotta und Epoxidharzfilm. Die Klebekraft geht jedoch von Epoxidharz aus.
Diese Methode ist bei Keramikrestauratoren bereits bekannt[9] und wird teilweise auch zum Kleben von Terrakotta eingesetzt. In Xi'an wurden zum Beispiel auf diese Weise vom ICR neolithische Vasen geklebt.[10]

### *6.1. Vorversuch zur Verwendung von Polyacrylaten als Primer an Ziegelplättchen mit glatter Oberfläche*

Die Verwendung von Primern wurde zunächst an Tonplättchen getestet. Dabei wurde auch die notwendige Auftragsdicke des Primers untersucht und die Verwendung eines gelösten Acrylats (Paraloid B72) mit einer Acrylatdispersion (Primal AC 33) verglichen.
Aus einem Ziegel wurden zylinderförmige Tonplättchen in zwei verschiedenen Größen gesägt (∅ ca. 2 cm, Stärke: 1 cm bzw. ∅ 4,5 cm, Stärke: 0,5 cm). Auf die zu klebenden Seiten wurde als Primer eine 17%ige Lösung von Paraloid B72 in Ethylacetat bzw. die Primal AC 33 unverdünnt aufgetragen. Dabei wurden auf die größeren Plättchen drei Schichten und auf die kleinen drei bzw. eine Schicht aufgetragen, um den Einfluß der Schichtdicke auf das Ergebnis zu untersuchen.
Nach dem Trocknen der Acrylatschicht wurden die Tonplättchen flächig mit Araldit 2011 verklebt. Außerdem wurden als Blindprobe ein kleines und ein großes Plättchen ohne Primer mit dem Epoxidharz geklebt. Nach dem Aushärten des Epoxidharzes (~100h) wurde versucht, die Klebung mit Aceton zu lösen; dazu wurden Wattekompressen verwendet. Die Proben wurden mit Hostafan umwickelt und in ein verschließbares Gefäß gestellt, um die Verdunstung des Lösemittels zu verlangsamen. In regelmäßigen Abständen wurden die Proben kontrolliert.
Nach ca.15 min. lösten sich bereits alle mit Primal AC 33 behandelten Plättchen. Beim Trennen bildeten sich lange, transparente Fäden; auf der Oberfläche blieb eine transparente, gequollene, zähe, und etwas klebrige Masse aus Epoxidharz und Primer zurück. Diese trocknete nach einigen Stunden wieder ein und schrumpfte dabei. Sie blieb aber noch einige Zeit etwas zäh und klebte danach wieder fest auf der Oberfläche auf.
Nach 20 min. ließen sich die kleinen Plättchen mit einem Anstrich Paraloid B72, nach 23 min. die mit drei Anstrichen und nach ca. 40 min. auch die großen Scheiben voneinander lösen. Von der Oberfläche der Plättchen ließ sich ein nicht klebriger, transparenter Klebemittelfilm abnehmen. Auf seiner Oberfläche haftete nur eine geringe Menge Terrakottamehl. Nach dem Trocknen wurde der Film etwas spröde. Das Paraloid schien teils von der Kompresse und teils von der Terrakotta absorbiert worden zu sein. Es blieb eine saubere, jedoch etwas dunklere Oberfläche der Terrakotta zurück. Die Blindprobe löste sich auch nach einer 24 stündigen Behandlung mit Aceton nicht.
Mit beiden Polyacrylaten konnten die ansonsten irreversiblen Epoxidharzklebungen wieder gelöst werden. Obwohl die Dispersion (Primal AC 33) sich schneller löste, konnten die Klebemittelreste jedoch schlechter von der Terrakottaoberfläche entfernt werden. Dagegen ließ sich bei Verwendung der Acrylatlösung (Paraloid B72) das Epoxidharz in Form eines Films einfacher abnehmen. Auf der Terrakotta haftete anschließend nur sehr wenig Klebemittelfilm, der problemlos mit Aceton beseitigt werden konnte. Das unterschiedliche Verhalten beim Anlösen der beiden Acrylate könnte sich darauf

[8] siehe auch Stephen P. Koob, „The use of Paraloid B72 as an adhesive: its application for archeological ceramics and other materials", Studies in Conservation 31 (1986), S.11
[9] siehe Gesprächsnotizen Elena Agnini, Sandra Pesso und Elisabetta Brunaf
[10] siehe Gesprächsnotizen Sandra Pesso und Elisabetta Brunaf

zurückführen lassen, daß das Epoxidharz beim Aushärten möglicherweise mit Wasser oder anderen in der Dispersion enthaltenen Stoffen reagiert hat.
Die Auftragsdicke des Primers beeinflußte lediglich in geringen Maß die zum Anlösen benötigte Zeitspanne, nicht aber das Ergebnis. Es ist jedoch zu vermuten, daß bei einem dickeren Film das Acrylat nicht mehr als reiner Isolator dient, sondern auch als Klebemittel. Die Klebekraft der Verbindung würde in diesem Fall wesentlich geringer sein, da sie nicht mehr vom Epoxidharz ausgehen würde.

*6.2. Versuch zum vollflächigen Kleben mit Primern und dem Wiederöffnen der Verbindung an der Kopie*

Auf die unebenen Bruchflächen der Fragmente **U6** und **U7** wurde eine dünne Schicht einer 20%igen Lösung von Paraloid B72 aufgetragen, die man ca. 30 min. trocknen ließ. Danach wurden die beiden Fragmente durch flächiges Auftragen von Araldit 2011 geklebt. Nach dem Aushärten des Epoxidharzes (ca. 4 Tage) wurde versucht, die Klebung wieder zu öffnen. Dabei wurde die Klebung nur von der Außenseite her angelöst, da bei einer originalen, bereits vollständig geklebten Figur nur diese Vorgehensweise möglich wäre. Als Lösemittel wurde Ethylacetat verwendet, das zunächst mit einer Pipette direkt in die Klebefuge geträufelt wurde. Es wurde von der porösen Terrakotta sofort aufgesaugt. Danach wurde eine Wattekompresse mit Ethylacetat entlang der Klebefuge angebracht und mit Hostafan abgedeckt, um die Verdunstung des Lösungsmittels zu verlangsamen.
Nach drei Stunden ließen sich die Fragmente noch nicht trennen. Deshalb wurde an der Innenseite eine zweite Kompresse angebracht, um prinzipiell die Möglichkeit des Öffnens der Klebung einer unebenen Bruchfläche zu testen. Nach 30 min. konnten die Fragmente mit etwas Kraftanwendung getrennt werden. Dabei sind auf der Innenseite parallel zur Bruchfläche einige Terrakottastückchen, die mit der Klebeschicht noch fest verbunden waren, abgerissen. An diesen Stellen war das Paraloid B72 noch nicht genügend angelöst, d.h. die Verbindung wurde zu früh geöffnet. Um eine solche Beschädigung der Terrakotta zu vermeiden, sollte man daher prinzipiell mit dem Öffnen einer Primerverbindung warten, bis sich die Bruchstücke von selbst, also ohne jeglichen Kraftaufwand trennen.
Durch das zu frühe Aufbrechen der Klebung ist der Verlauf des Lösevorgangs an den Klebeflächen der Fragmente zu beobachten. In der Nähe der Außenseite hat sich das Epoxidharz bereits in kleineren, eher opak-gelblichen Stücken von beiden Bruchflächen gelöst oder kann relativ leicht abgezogen werden. Zur Innenseite hin haften noch größere zusammenhängende Flächen des glänzenden Epoxidharzfilms und damit vermutlich auch noch nicht gelöstes Paraloid B 72 auf der Terrakotta. An diesen Stellen befinden sich die dünnen abgebrochenen Terrakottastückchen.
Während auf der Innenseite der Bruchflächen die Verdunklung der Terrakottaoberfläche – hervorgerufen durch den aufgetragenen Primer - noch unverändert ist, nimmt diese zur Außenseite ab und ist am äußeren Rand nur noch sehr gering. Auf Innen- wie Außenseite der Fragmente sind weder Ränder noch Verdunklungen des in die Terrakotta abgewanderten Acrylats zu sehen.

*6.3. Versuch zur Anwendung von Primer beim Kleben eines größeren Teilstücks*

Die Bruchflächen von **L1** bis **L9** (rechter Fuß und rechtes Bein) wurden mit einer dünnen Schicht einer 20%igen Lösung von Paraloid B72 bestrichen. Nach ihrem Trocknen wurden die einzelnen Fragmente durch flächiges Auftragen von Araldit 2011 miteinander geklebt. Bis zum Aushärten des Epoxidharzes wurden die Fragmente mit Bändern und Zwingen fixiert.
Auf die gleiche Weise wurden die Fragmente **A5** und **A6** geklebt. Statt des Araldit 2011 wurde als Epoxidharz allerdings UHU plus verwendet.

*6.4. Versuch zur Anwendung eines Primers bei einer Punktklebung*

Auf die zu klebenden Bruchflächen der Fragmente **R5, R6, R7, R8** und **R10** (linker Fuß) wurde zunächst eine dünne Schicht einer 20%igen Lösung von Paraloid B72 als Primer aufgetragen. Nach dem Trocknen des Paraloids wurden die einzelnen Stücke durch eine Punktklebung mit Araldit 2011 verbunden. Bis zum Aushärten des Epoxidharzes wurden die Teile mit Tesakrepp fixiert.

*6.5. Versuch zur Verwendung eines Primers beim Einkleben von Dübeln und zum Wiederöffnen der Verbindung*

In die Bruchflächen der Fragmente **A1** und **A2** wurden zwei gegenüberliegende Löcher für einen Stahldübel gebohrt. Danach wurden die Löcher mit einer Luftdruckpistole von Terra-kottastaub gereinigt, um eine möglichst gute Haftung des Klebers zu erzielen. Die Dübellöcher und ein ca. 5 mm dicker Rand wurden mit einer 20%igen Lösung von Paraloid B 72 eingestrichen, die man ca. 30 Minuten trocknen ließ. Danach wurden die Löcher mit Araldit 2011 aufgefüllt und der Stahldübel (Gewindestange: Länge: 4 cm lang / ∅ 3mm) eingesetzt. Auf der Innenseite der Fragmente wurde zuvor die Position des Dübels markiert.
Nach dem Aushärten der Klebung (10 Tage)[11] wurde versucht, die Klebung nur von der Außenseite her anzulösen. Dazu wurde zunächst auf Höhe des Dübels in die Bruchkanten Aceton geträufelt. Danach wurde eine Wattekompresse mit Aceton auf der Außenseite angebracht und mit Hostafanfolie abgedeckt, um die Verdunstung zu verlangsamen.
Nach 3h 15 min. ließen sich die beiden Terrakottafragmente etwas verschieben, die Fragmente konnten noch nicht getrennt werden. Nach weiteren 3h 15 min. war keine weitere Veränderung zu beobachten. Die Klebung wurde daher auseinandergebrochen, um den Grund für das Verhaken der beiden Teile herauszufinden.
Dabei ist am Fragment A2 das Dübelloch zur Außenseite ausgebrochen und kleine Terrakottastücke sind abgebrochen. Das Bohrloch und die Bruchfläche zeigten keine Verdunklung mehr, d.h. der Primer hatte sich bereits vollständig gelöst. Das Epoxidharz klebte auf dem freien Dübelende und ließ sich von diesem leicht abziehen. Das zweite Ende klebte noch fest in A1 und ließ sich auch durch weitere Lösemittelzugabe nicht herausnehmen. Die Bruchfläche um den Dübel zeigte ebenfalls keine Verfärbung durch den Primer. Allerdings klebte an einer kleinen Stelle das Epoxidharz fest auf der Bruchfläche.
Der Dübel in A1 löste sich aufgrund einer mechanischen Verankerung des Epoxidharzes nicht. Beim Bohren gelingt es meistens nicht, die beiden Dübellöcher exakt in einer Linie zu bohren. Auch in diesem Fall wurde das Loch in A1 nach unten weiter ausgebohrt, um den Dübel einsetzen zu können. Dabei wurde jedoch nicht bedacht, daß das Epoxidharz beim Einkleben das Loch ausfüllte und sich nach dem Härten im Loch verhakte. Auch bei A2 lag eine solche Verankerung in den Poren oder Unregelmäßigkeiten des Bohrlochs vor. Die Verbindung der beiden Fragmente konnte daher nicht getrennt werden, ohne die Terrakotta zu beschädigen.

*Beobachtungen und Anmerkungen*
Die Versuche bestätigten, daß prinzipiell das Anlösen einer flächigen Epoxidharzklebung durch vorausgehendes Auftragen eines Primers möglich ist. Beide im Versuch 6.1. als Primer verwendeten Acrylate (Paraloid B72 und Primal AC 33) waren dafür geeignet. Eine Acrylatlösung ist jedoch zu bevorzugen, da sich das Epoxidharz einfach als nicht klebriger Film abnehmen läßt. Beim Gebrauch einer Acrylatdispersion ist es dagegen etwas schwieriger, die Klebereste zu entfernen, da einige ihrer Bestandteile mit dem Epoxidharz zu einer klebrigen Masse reagieren.
Beim Anlösen des Primers wandern Teile des Acrylats, transportiert vom Lösemittel, in die Terrakotta ab. Diese können zu Verfärbungen der Terrakotta und zu Rändern parallel zur Bruchfläche führen. Bei den durchgeführten Versuchen wurde eine solche Veränderung der Terrakotta allerdings nicht beobachtet.
Wird der Primer wie in den Versuchen 6.1., 6.2. und 6.5. mit Hilfe von Lösemittelkompressen angelöst, so hängt die zum Öffnen der Klebung benötigte Zeit stark von der Größe der Klebefläche ab. In Versuch 6.1. ließen sich daher auch die Plättchen mit einem kleineren Durchmesser bedeutend schneller trennen als die größeren. Bei einem vollständig zusammengesetzten Terrakottasoldaten können die Kompressen außerdem nur auf der Außenseite der Figuren angebracht werden. Dadurch wird die zum Öffnen der Klebung benötigte Zeit zusätzlich bedeutend verlängert (siehe Versuch 6.2.).
Vom ICR gab es Überlegungen, die in Xi'an unter Verwendung eines Primers geklebten neolithischen Vasen gegebenenfalls zum Öffnen der Verbindungen in Lösemittel zu baden. Dieses Vorgehen wurde dort jedoch nicht getestet. Außerdem ist es für die Terrakottarmee ungeeignet. Selbst wenn das Baden der Terrakottasoldaten eine schnellere und rückstandsfreiere (Ränder und Verdunkelungen durch den

[11] Obwohl von der Herstellerfirma zum völligen Aushärten des Epoxidharzes 4 Tage als ausreichend angegeben werden, wurde mit dem Öffnen der Klebung 10 Tage gewartet, um ein möglichst sicheres Versuchsergebnis zu erhalten.

Primer) Möglichkeit wäre, ist es nicht nur aufgrund der Größe der Terrakottasoldaten undenkbar. Es würden auch jegliche Reste von Farbfassungen mit auflösen.
Praktiziert wird bereits eine andere Möglichkeit des Öffnens einer solchen Verbindung. Mit Hilfe eines Heißföns werden dabei mit der Primermethode geklebte Fragmente erwärmt. Diese sollen sich aufgrund der thermoplastischen Eigenschaften der Acrylate bereits nach wenigen Minuten trennen. Die Klebemittelreste müssen später mit einem Lösemittel entfernt werden.[12]
Verbindungen mit eingeklebten Dübeln können dagegen auch durch die Verwendung eines Primers nicht wieder gelöst werden (siehe Versuch 6.5.). Das Epoxidharz füllt beim Einbringen in die Bohrlöcher Unregelmäßigkeiten und kleineren Löchern der Terrakotta aus und ist nach dem Aushärten an diesen Stellen zusätzlich mechanisch verankert.

## 7. Zusammensetzen größerer Abschnitte

Nach Versuchen mit einzelnen Fragmenten wurden größere Abschnitte mit ausgewählten Verfahren zusammengesetzt, wobei für jedes Teilstück nur eine Methode zur Anwendung kam. Die Abschnitte orientieren sich an den durch die Herstellung bedingten Einheiten (Bodenplatte, Beine und Füße, Rock, mittlerer Rumpfteil, Oberkörper, Arme, Hände, Kopf). Dabei sollte die Funktionsweise der einzelnen Methoden an einer größeren Einheit getestet und soweit wie möglich die Verbindungen miteinander verglichen werden.
Die Bodenplatte (P) wurde von den chinesischen Kollegen mit der im folgenden beschriebenen Idee zusammengefügt: Zur Verbindung der Fragmente **P1**, **P2**, **P3**, **P4** und **P5** wurden aus einer Gewindestange (∅ 3 mm) vier Dübel angefertigt. In die Bruchflächen der Fragmente wurden entsprechende Löcher gebohrt, in die die Dübel möglichst genau paßten. Die Bruchflächen wurden mit Paraloid B72 (20%ige Lösung in Ethylacetat) als Primer vorbehandelt, um diese Klebung später wieder öffnen zu können. Dabei wurden die Dübellöcher ausgespart, da angenommen wurde, daß Primer bei Dübeln prinzipiell wirkungslos seien.[13] Die Dübel wurden mit Araldit 2011 eingesetzt und die Bruchflächen durch flächiges und großzügiges Auftragen desselben Epoxidharzes geklebt. Die chinesischen Kollegen wollten mit dieser Methode die bisher in Xi'an angewendete Epoxidharzklebung durch das Anbringen von Dübeln unterstützen. Vor allem stark belastete Teile, wie in diesem Fall die Bodenplatte, würden auf diese Weise mehr Stabilität erhalten. Mit dieser doppelten Verbindung wollten sie außerdem eine Absicherung gegen ein alterungsbedingtes Versagen einer der beiden Verbindungen erhalten. Das später gefundene Bruchstück **P6** konnte nachträglich nicht mehr eingesetzt werden, da diese Methode des Zusammenfügens nicht reversibel ist.
Als nächstes wurden die Füße und Beine zusammengefügt. Da die Füße der Kopie nicht wie die originalen massiv und nicht fest mit der Bodenplatte verbunden sind, sind die an ihnen durchgeführten Versuche nur beschränkt aussagekräftig. Der linke Fuß (R5, R6, R7, R8, R10) wurde mit Epoxidharz (Araldit 2011) unter Verwendung eines Primers (Paraloid B72) geklebt. Das Klebemittel wurde dabei in einzelnen Punkten auf den trockenen Primerfilm aufgetragen. Das linke Bein (R1, R2, R3, R4, R9, R11, R12, R13, R14, R15) wurde zunächst durch Kleben mit Mowilith 50/60 der kleinen Fragmente zu zwei großen Hälften zusammengefügt, die dann im oberen Abschnitt mit Klammern bzw. einem über den Hohlraum quergespannten Spannschloß im unteren Abschnitt miteinander verbunden wurden. Dieser Kombination aus mechanischer Verbindung und reversibler Klebung wurde mit dem rechten Bein und dem rechten Fuß (L) eine vollflächige Klebung mit Primer und Epoxidharz gegenübergestellt. Interessant sind in diesem Abschnitt der Figur die Knöchel, die auch bei vielen ausgegrabenen Soldaten gebrochen sind. Dieser Schwachpunkt wurde dazu genutzt, die Epoxidharzklebung am rechten Fuß mit der schwächere Klebung einer Mischung aus Mowilith 50, Mowilith 60 und einem Füllstoff zu vergleichen.
Der gesamte Rockteil wurde mit Spannklammern aufgebaut. Nur zwei kleinere Fragmente wurden lose eingesetzt bzw. an ein größeres Fragment geklebt, ohne die Funktion der Spannklammern zu stören. Dagegen wurde der gesamte mittlere Rumpf (D) mit dem reversiblen, aber auch schwachen Polyvinylacetat (Mowilith 50/60) geklebt. Besonders bei diesen beiden Abschnitten ist ein Vergleich der Methoden gut möglich, da sie sich in Dimension, Form und Anzahl der Bruchstücke ähnlich sind.

[12] Siehe Gesprächsnotiz Sandra Pesso
[13] laut Herrn Guo Baofa

Weitere Abschnitte wurden noch nicht zusammengesetzt und werden für weitere Tests bereit gehalten.

## 8. Diskussion der Ergebnisse

In den Versuchen bis Januar 2000 wurden sowohl mechanische Verbindungen als auch Klebungen einzeln oder in Kombination getestet. Dabei wurden verschiedene Klebemittel eingesetzt, wobei für Epoxidharze unterschiedliche Auftragsarten und die Verwendung von Primern erprobt wurden. Da diese organischen Klebemittel eine sehr begrenzte und nicht voraussehbare Beständigkeit besitzen, wurde bei den Versuchen zu mechanischen Verbindungen nach Möglichkeiten ihrer weitgehenden Reduktion gesucht. Eine „rein mechanische“ Methode konnte allerdings dabei nicht entwickelt werden, da immer ein Minimum an Klebemittel notwendig war.
So können Dübel zwar auf einer Seite mit einem Nylondübel mechanisch verankert werden, zumindest die zweite Seite muß aber eingeklebt werden. Das Bohren von exakt passenden Dübellöcher erwies sich als schwierig. Besonders beim Einsetzen von mehreren Dübeln in eine Bruchfläche, wie bei größeren Fragmenten, konnten die entsprechenden Teilstücke überhaupt nicht oder zumindest nicht exakt zusammengesetzt werden. Es mußte immer nachträglich korrigiert werden, indem mindestens ein Loch vergrößert wurde. Das Anbringen der Löcher bedeutet einen Verlust an originaler Terrakotta. Nach dem Zusammensetzen bleiben aber keinen sichtbaren Beeinträchtigungen. Entlang der Bohrung ist die Terrakotta dünnwandiger und daher empfindlicher. Bei einer stärkeren Belastung kann dort leichter ein neuer Bruch entstehen. Zur Verbindung kleinerer Fragmente sind Dübel daher nicht geeignet. Sowohl mechanisch verankerte, wie geklebte Dübeln sind in jedem Fall nicht reversibel, d.h. sie können nicht ohne Beschädigung der Terrakotta entfernt werden. Auch die Verwendung eines Primers beim Einkleben blieb wirkungslos.
Spannklammern sind im Gegensatz zu Dübeln nach ihrem Einsetzen noch erreichbar, da sie auf der Oberfläche der Figuren angebracht werden. Somit ist ein nachträgliches Korrigieren und Einsetzen von Fragmenten jederzeit möglich, so lange die Klammern beim Eingreifen in den Innenraum noch mit Händen oder entsprechenden Werkzeugen erreicht werden können. Zu ihrer Befestigung müssen Löcher in die Oberfläche der Figur gebohrt werden, weshalb die Klammern nur auf der Innenseite angebracht werden können. Dies bedeuten einen stellenweise Verlust von Spuren des Herstellungsprozesses. Durch die erforderliche Anzahl und Größe der Klammern wird der optische Eindruck der Oberfläche stark gestört.
Problematisch zu sehen, ist die mit den Klammern erzeugte Spannung, durch die die Terrakotta ständig einer mechanischen Belastung ausgesetzt ist. Um diese zu reduzieren, wurde auf eine „rein mechanische“ Methode der Verbindung verzichtet. Die Haken der Klammern wurden eingeklebt, damit sie nicht mehr durch die von ihnen erzeugte Spannung in den Löcher gehalten wurden. Spätere Versuche zeigten jedoch, das auch auf diese Weise eine erneute Schädigung der Terrakotta nicht verhindert werden konnte.
Um die Klammern gegebenenfalls wieder entfernen zu können, wurde zum Einkleben neben Epoxidharz auch ein reversibles Polyacrylat getestet. Durch einen Fehler bei der Durchführung kam jedoch keine feste Klebung und daher auch kein aussagekräftiges Ergebnis zustande. Außerdem wurden Schmelzklebstoffe verwendet, die vermutlich durch Erhitzen reversibel sind. Tests zur Bestätigung dieser Annahme wurden jedoch noch nicht durchgeführt.
Beim Zusammensetzen eines Teilstücks mit engen Hohlraum erwies sich das Bohren der Löcher und das Einsetzen der Spannklammern aufgrund der starken Krümmungen als schwierig. Diese Probleme konnten aber umgangen werden, indem die Spannklammer nicht über den Bruchfugen eingesetzt, sondern quer über den Hohlraum gespannt wurde.
Grundsätzlich konnten mit den Klammern zwei gerade, aber auch gebogene Fragmente fest und exakt verbunden werden. Beim Zusammensetzen eines größeren Abschnitts stieß man aber auf Schwierigkeiten, da beim Anbringen der Klammern auf der Innenseite der Krümmung ungünstigere Kräftewirkungen auftreten, als beim Aufsetzen auf der Außenseite. Alle Fugen zwischen den Fragmenten blieben leicht nach außen geöffnet und einige Kanten sogar zueinander versetzt. Auch durch starkes Anziehen der Klammern konnten diese Ungenauigkeiten nicht ausgeglichen werden. Statt dessen bildeten sich durch die starke mechanische Belastung Risse und kleine Teile der Terrakotta platzten entlang der Bruchfuge an der Außenseite ab. Auch auf längere Sicht ist die Bildung weiterer Schäden zu erwarten.

Bei Klebungen wurden als Alternativen zu dem in Lintong verwendeten Epoxidharz in der Terrakottarestaurierung übliche Cellulosenitrate, Polyvinyacetate und –acrylate getestet. Diese wurden dazu in vollflächigen Klebungen an der Kopie eingesetzt.
Um die Stärke der im Gegensatz zum Epoxidharz reversiblen, aber auch schwächeren Klebemittel zu testen, wurden Klebungen mit Mowilith 50 bzw. Paraloid B72 gewaltsam wiedergeöffnet. Interessanterweise brach dabei nicht die Klebefuge, sondern es bildeten sich daneben mehrere kleinere und neue Brüche in der Terrakotta. Selbst diese schwachen Klebemittel waren also stärker als die durch den ersten Bruch bereits strapazierte Terrakotta.
Beim Zusammensetzen einer größeren Einheit durch Kleben erwies es sich günstiger, nicht fortschreitend von unten nach oben aufzubauen, sondern zunächst mehrere große Teilstücke zusammenzusetzen, die sich ohne Probleme durch Untergriffigkeit ineinander fügen ließen. In einigen Fällen wurden auch mehrere Fragmente gleichzeitig eingesetzt, da sie so leichter in der richtigen Position fixiert werden konnten. Wurde während des Aushärtens des Klebemittels nicht zusätzlich Druck mit Schnüren oder Zwingen auf die Klebefuge ausgeübt, war ein exaktes Einpassen der Fragmente nicht möglich. So konnten bereits nach dem Zusammenbau eines Teilstücks in der Größe von ca. einem Drittel des Rumpfs einige Fragmente nicht mehr genau eingesetzt werden.
Während die Spannklammern zunächst angefertigt und eingesetzt werden mußten, und noch anschließend ein Ausrichten der Fragmente nötig war, konnte ein entsprechender Abschnitt durch Kleben der Bruchfugen wesentlich schneller und einfacher zusammengesetzt werden. Generell konnten durch Kleben alle Fugen enger geschlossen und alle Fragmente exakt passend eingesetzt werden. Das nachträgliche Einfügen von Fragmenten und Korrigieren von Ungenauigkeiten war bei den Klebungen zwar komplizierter und langwieriger, da die Verbindungen mehrerer Bruchkanten angelöst und später wieder erneuert werden mußten. Bei Verbindungen mit Spannklammern wuchsen dagegen mit zunehmender Größe des zusammengesetzten Abschnitts auch die Schwierigkeiten, Fragmente überhaupt exakt positionieren zu können.
Kleinere Fragmente konnten generell nur geklebt werden, da daß Anbringen von Dübeln oder Spannklammern aufgrund ihrer Dimensionen nicht möglich ist bzw. zu starken Schäden bis zu ihrem Durchbrechen führt. Beim Zusammensetzen von tragenden Teilen der Figuren (Füße und Beine, Arme) besonders bei der Verwendung von Klebemitteln mit geringerer Klebekraft, kann dagegen das Anbringen von Dübeln oder Spannklammern als Stütze an stark belasteten Punkten sinnvoll sein.
Um ein möglichst exaktes Einpassen von Fragmenten zu erzielen, wurde auch versucht wie beim Kleben von Porzellan und Glas, die Terrakottafragmente zuerst „trocken“ exakt zusammenzusetzen, um danach das Klebemittel in die Bruchfuge zu infiltrieren. Aufgrund der großen Porosität der Kopie konnte sich mit dabei weder das Klebemittel in der Fuge verteilen, noch bildete sich ein ausreichend starker Klebefilm. Vermutlich ist diese Methode für das Kleben von Terrakotta mit den gängigen Klebemitteln nicht geeignet.
Bei den Epoxidharzen wurden neben dem flächigen Auftragen auch Punktklebungen getestet. Der Versuch, zwei so zusammengefügte Fragmente zu zerschlagen, zeigt, daß eine solche Klebung trotz reduzierter Klebefläche und -kraft noch sehr stabil ist und größeren Belastungen standhält.
Tests zur Verwendung von Primern bei Epoxidharzklebungen bestätigten, daß Epoxidharzklebungen durch vorausgehendes Auftragen eines Polyacrylats (in Lösung bzw. als Dispersion) wieder geöffnet werden können. Dabei ist eine Acrylatlösung im Gegensatz zur Dispersion zu bevorzugen, da sich nach den Trennen der Fragmente das Epoxidharz als Film einfach abnehmen läßt. Zum Öffnen der Verbindungen wurden Lösemittelkompressen verwendet, die nur auf der Außenseite der Fragmente angebracht wurden, da bei einer vollständigen Figur nur dieses Vorgehen möglich ist. Allerdings benötigte man mit dieser Methode mehrere Stunden pro Bruchfuge.
Nicht funktioniert hat die Anwendung von Primern beim Einkleben von Dübeln, da sich hier das Epoxidharz nach dem Aushärten mechanisch in Unregelmäßigkeiten des Bohrlochs verhakt. Ein ähnliches, negatives Ergebnis ist auch bei den mit Primer eingeklebten Spannklammern zu erwarten.

## 9. Ausblick

In den bis Januar 2000 an der Kopie durchgeführten Versuche zum Zusammenfügen von Fragmenten konnten noch keine ausgearbeiteten und endgültigen Lösungen entwickelt werden. Sie dienten viel mehr einem ersten Abwägen von Vorteilen und Problemen verschiedener Methoden. Diese sollten noch ausgearbeitet und speziell auf die Eigenschaften der Terrakotta der originalen Soldaten ausgerichtet werden. Zu diesem Zweck können noch weitere Information gesammelt werden. Allerdings wird es auch notwendig sein, zusätzlich Versuche durchzuführen. Im folgenden werden noch einige Anregungen und Ideen zur weiteren Arbeit gegeben:

- Verbesserung des Systems und Modells der *Spannklammer*
Sie sollten kleiner und schmaler sein, und vielleicht aus einem leichten Material angefertigt werden. An Stelle des Spannschlosses sollte eine ausgefeiltere und flexiblere Technik entwickelt werden, um das exakte Ausrichten der Fragmente zu ermöglichen. Unbedingt sollte eine Methode gefunden werden, um die Spannung auf die Terrakotta möglichst gering zuhalten.
Probleme der Alterung können bei den Klammern durch die Verwendung eines entsprechenden Materials (rostfreier Stahl, Glasfaser, Karbon etc.) zu weiten Teilen ausgeschlossen werden. Belastungen, die durch eine von der Terrakotta verschiedene thermische Ausdehnung zustande kommen, können auch durch das Einsetzen einer Art *Puffer* z.B. aus Teflon oder Nylon aufgefangen werden.
Da für das Zusammensetzten der Soldaten eine große Anzahl an Klammern notwendig ist und ihr individuelles Anfertigen und Anpassen zu zeitraubend wäre, ist ihre Verwendung nur dann praktikabel, wenn eine serielle Herstellung möglich ist. Die so produzierten Klammern sollten trotzdem flexibel genug sein, um sich der jeweiligen Situation an zu passen. Zu diesen Zweck wäre auch die Herstellung einiger weniger Typen denkbar.

- Weitere Untersuchung zu den *Eigenschaften der originalen Terrakotta*, wie Härte, Porosität und Saugfähigkeit sollten als Basis für die Wahl oder Entwicklung eines geeigneten *Klebemittels* und der entsprechenden *Klebemethode* (flächiges oder punktuelles Auftragen, Verwendung von Primer) durchgeführt werden.

- Weitere Versuch zur Anwendung von *Primern:*
In Bezug auf Konzentration, Schichtdicke und Auftragsart von Primern sollten noch einige Versuch durchgeführt werden. Ihre Verwendung ist nur dann sinnvoll, wenn die Klebekraft allein vom Epoxidharz ausgeht und das Acrylat nur als Brücke und Isolierschicht zwischen Terrakotta und Epoxydharz dient.
Auch getestet werden sollten Kombinationen aus Primer und Punktklebung mit Epoxidharz. Man kann dadurch nicht nur die Menge und die Klebekraft des eingebrachten Epoxidharzes beeinflussen, sondern vermutlich auch die Zeit zum Wiederöffnen verkürzen.
Da das Öffnen von Klebungen mit Primern mit Hilfe von Lösemittelkompressen mehrere Stunden Zeit benötigt, sollten schnellere Möglichkeiten, wie z.B. die Verwendung eines Heizföns, getestet werden.

- *Alterung* organischer Klebemittel:
Durch starke Schwankungen der Temperatur und der Luftfeuchtigkeit in den Gruben sind die Terrakottafiguren, aber auch die neu eingebrachten Materialien, dort extremen Bedingungen ausgesetzt. Besonders davon betroffen sind die organischen Klebemittel, deren Eigenschaften sich unter diesen Vorraussetzungen im Laufe der Zeit stark ändern können. Daher sollten nur solche Produkte ausgewählt werden, die in Bezug auf die Klebekraft, die Zug- und Scherfestigkeit, das Quell- und Schwundverhalten, die Farbe und Reversibilität eine geringe Alterung besitzen. Bisher gesammelte Informationen über verschiedene Klebemittel[14] geben allerdings nur sehr ungenaue (6 Monate – 100 Jahre Stabilität), kaum detaillierte und nur schwer vergleichbare Daten. Zusätzlich sind fast alle Produkte nicht für restauratorische Zwecke entwickelt und ausgerichtet worden. Unter den wenigen wissenschaftlichen Untersuchungen, die speziell zur Alterung der von Restauratoren verwendeten Klebemitteln durchgeführt wurden, ist ein Projekt des CCI (Canadian Conservation

[14] siehe Tabellen in der Klebemittelkartei in diesem Arbeitsbericht.

Institute) [15] besonders interessant. Verschiedene Polyvinylacetate und -acrylate, die von amerikanischen Restaura-toren häufig verwendet werden, wurden auf verschiedene Alterungserscheinungen (Emmision gefährlicher Inhaltsstoffe, Vergilbung, Veränderung des pH-Werts, der Festigkeit und Flexibilität) untersucht und miteinander verglichen.[16] Eine genaue, speziell auf die Probleme der Terrakottasoldaten bezogene Aussage läßt sich jedoch mit diesen Informationen nicht treffen, da die Untersuchungen auf die Gruppe der Polyvinylacetate und –acrylate und auf wenige Alterungserscheinungen beschränkt ist. Aufgrund der einmaligen Situation der Terrakottarmee (Klima in der Gruben, Wandstärke, Größe und Anzahl der Figuren) ist, neben weiterem Sammeln von Literatur und Erfahrungen, das Durchführen von speziell auf die Terrakottarmee ausgerichteten Tests notwendig.

- Methoden zur *Fixierung der Fragmente* während des Zusammenbaus und zum Druckausüben auf die Klebefugen: Arbeitsrahmen,[17] Plastikspangen aus halbiertem Plastikstab mit einem Gewinde[18], Vakuumkissen[19]

- Tests mit *anorganischen Klebemittel*
Da die organischen Klebemittel nur eine bedingte Langzeitstabilität aufweisen, entstand die Idee, statt dessen anorganische Kleber oder Kombination aus beiden zu verwenden. Bisher wurden dazu noch keine Informationen gesammelt oder Untersuchungen durchgeführt. Verschiedene Produkte sollten in Hinblick auf Klebekraft, Reversibilität, Alterung und dem Einbringen schädlicher Substanzen (z.B. Salze) getestet werden.

- Verträglichkeit der Materialien und Methoden zum Zusammenfügen der Terrakottasoldaten und zum Festigen der *Farbfassung*:
Nicht berücksichtigt wurde bis jetzt die Farbfassung der Terrakottakrieger. Diese ist auch nach ihrer Festigung noch empfindlich gegen mechanische Belastung (z.B. Anfassen) und Kontakt mit Klebe- und Lösemittel. Klebemittel, Lösemittel und Möglichkeiten zum Öffnen der Terrakottaverbindungen sollten mit der Methode zur Stabilisierung der Farbfassung gut abgestimmt werden. Sie dürfen ihre Stabilität und das Aussehen der Farbfassung nicht beeinträchtigen.

- Verträglichkeit der Materialien und Methoden zum Zusammenfügen mit Kittmaterialien zum Ergänzen von Fehlstellen in der Terrakotta

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[15] Jane L. Down, Maureen A. MacDonald, Jean Tétreault, R. Scott Williams, „Adhesives testing at the Canadian Conservation Institute - an evaluation of selected Poly(vinylacetate) and Acrylic Adhesives“, Studies in Conservation 41 (1996), S.19-44;

[16] Mit guten bis akzeptablen Ergebnissen schlossen dabei Paraloid B72 (= Acryloid B72 der Firma Rohm & Haas, USA), sowie Mowilith 50 (= AYAT) und Mowilith 60 (= AYAF der Union Carbide Canada) ab.

[17] Bereits in China zum Zusammenbau der Bronzekutschen verwendet

[18] Siehe Gesprächsnotiz zum Besuch der Antikensammlung, Buhl

[19] siehe Gespräch mit Fr. Agnini

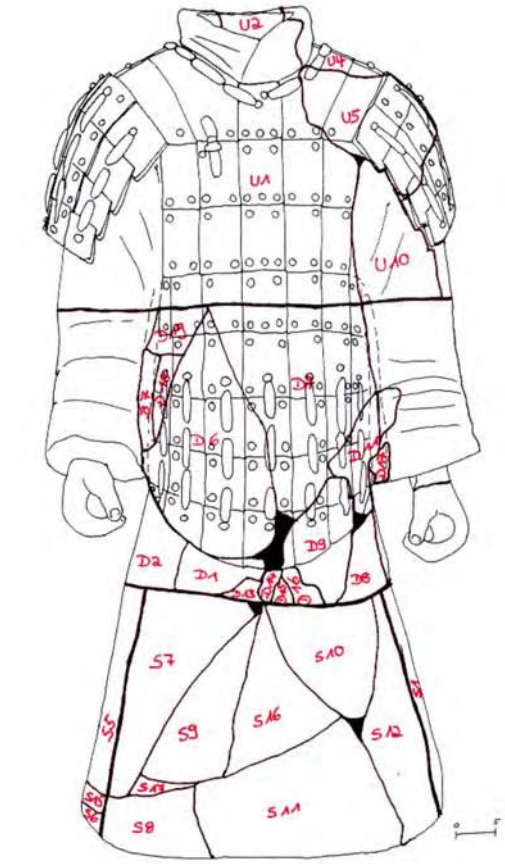
# Übersicht über die Versuche

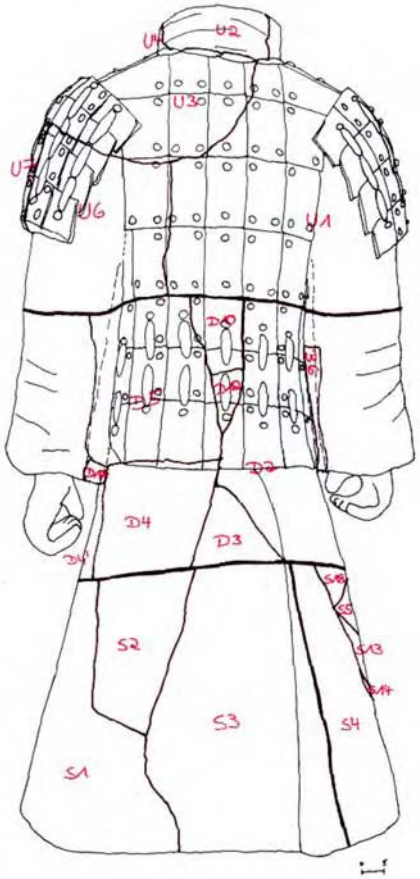
| Versuch | Fragmente | Methode zum Zusammensetzen |
|---|---|---|
| 1.1. | U4,U5 | Dübel (Schraube[1]), Nylondübel[2], Schraubenkopf lose eingesetzt |
| 1.2. | P3, P4 | Dübel (Schraube[1]), Nylondübel[2], Schraubenkopf mit Araldit 2011 eingeklebt |
| 1.3. | P1, P2 | Dübel (Gewindestange[3]) mit einem Nylondübel[2] verankert, freies Ende mit Moltofill eingeklebt |
| 1.4. | S13, S14 | Kleines Fragment durchbohrt, Dübel (Gewindestange[3]), Nylondübel[2], Mutter |
| 2.1. | S5, S13 | Spannsystem (Ringschrauben[4], Nylondübel[5], Gewindestange[3], Muttern) |
| 2.2. | S5, S13 | Spannklammer[6] ohne Klebung, gerade Fragmente |
| 2.3. | S9, S16 | Spannklammer[6] ohne Klebung, gebogene Fragmente |
| 3.1. | S1, S2, S3 | Spannklammer[7], mit Araldit 2011[8] bzw. Proxxon Schmelzklebstoff eingeklebt |
| 3.2. | S7, S9 | Spannklammer[6], eingeklebt mit Paraloid B72 und Aerosil (Füllstoff) |
| 3.3. | S7, S9 | Spannklammer[6], eingeklebt mit Pattex Schmelzklebstoff |
| 3.4. | S1-S18 | Zusammensetzen des gesamten Rockteils<br>Spannklammer[7], mit Araldit 2011 eingeklebt, einige mit Primer[9] |
| 3.5. | R3, R4 | Anbringen einer Spannklammer[10], in engem Hohlraum; eingeklebt mit Primer[9] und Araldit 2011 |
| 3.6. | R3, R4 | Wantenspanner[11] quer über Hohlraum mit engem Radius eingeklebt, mit Primer[9] und Araldit 2011 |
| 4.1. | A4, A7 | Flächiges Kleben mit Paraloid B72;<br>Wieder aufgebrochen |
| 4.2. | D4, D8 | Flächiges Kleben, Mowilith 50 (15% in Ethylacetat); wieder aufgebrochen |
| 4.3. | D4, D4‘; R4, R9;<br>R1, R2, R3, R11, R12, R13, R14 | Flächiges Kleben, Mowilith 50/60, Primer: 5%ige Lösung, Klebstoff: 30%igen Lösung |
| 4.4. | D1- D19,<br>B6, B7 | Zusammensetzen des mittleren Rumpfteils; flächiges Kleben, Mowilith 50/60, Primer: 5%ige Lsg., Klebstoff: 30%ige Lsg. |
| 4.5. | B4, B5 | Kleben durch Infiltration von Mowilith 50/60 |
| 4.6. | (R1/R2/R3/R4/R9/R11/R13/R14/R15)<br>(R5/R6/R7/R8/R10/R12) | Flächiges Kleben, Mowilith 50/60, Primer: 5%ige Lösung, Klebstoff: 30%igen Lösung + Hohlglaskügelchen (Füllstoff) |
| 4.7. | U5, U7 | Flächiges Kleben mit „Uhu plus“, Öffnen (?) |
| 4.8. | U2, U3 | flächiges Kleben mit Mecosan L-TR |
| 5. | B1, B2 | Punktklebung mit Araldit 2011, zerschlagen |
| 6.1. | aus einem Ziegel gesägte Tonplättchen | kleben mit Paraloid B72 bzw. Primal AC33 (Primer) und Araldit 2011, anlösen mit Aceton |
| 6.2. | U6, U7 | flächiges Kleben mit Primer[9] und Araldit 2011 |
| 6.3. | L1-L9 | flächiges Kleben mit Primer[9] und Araldit 2011 |
| 6.4. | R5, R6, R7, R8, R10<br>A5, A6 | Punktklebung mit Primer[9] und Araldit 2011<br>Bzw. Uhu plus |
| 6.5. | A1, A2 | Dübel (Gewindestange)[12] eingeklebt mit Primer[9] und Araldit 2011 |
| 7 | P1, P2, P3, P4, P5 | Dübel (Gewindestange)[13] eingeklebt mit Araldit 2011, Bruchflächen geklebt mit Primer[9] und Araldit 2011 |

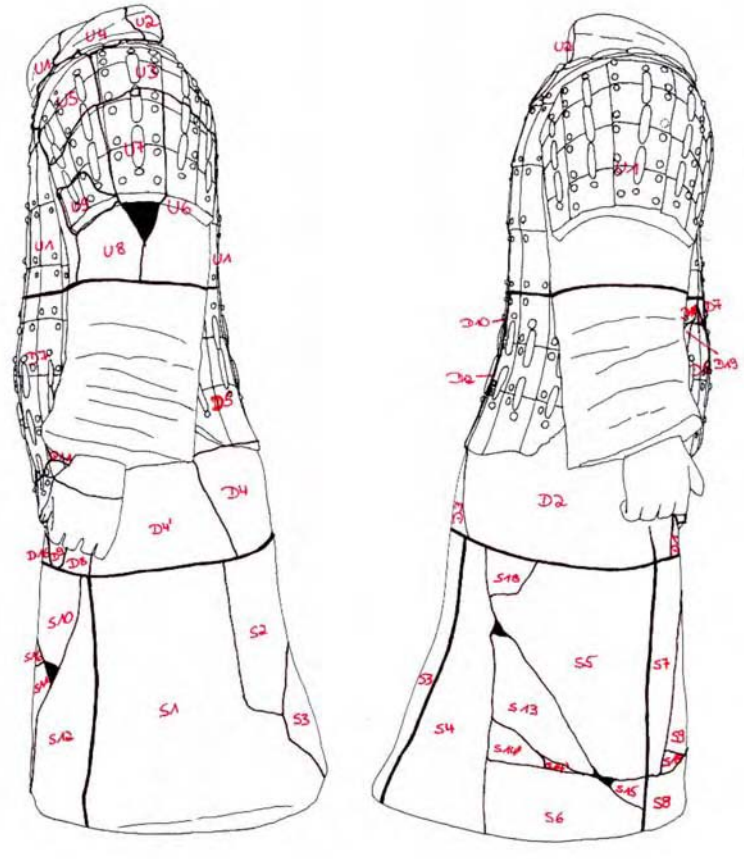
Anmerkungen zu der Tabelle:

[1] Stahlschraube, ∅ 4 mm
[2] Fischer Nylondübel, S6
[3] Gewindestange, ∅ 4 mm
[4] Ringschrauben ∅ 3 mm
[5] Fischer Nylondübel, S4
[6] Spannklammer konstruiert aus einem Spannschloß in Form eines Sechskantzylinder mit rechts-links Gewinde (∅ max. 11,5 / Länge: 3cm) und zwei Stifte aus einer Gewindestange (5 mm; rechts- bzw. linksdrehend)
[7] Spannklammer aus Wantenspanner (∅ max. 10,5 / Länge: 7cm) und zwei Stifte aus aufgebogenen Ösen bzw. aus Gewindestange (∅ 4 mm; rechts- bzw. linksdrehend)
[8] Angaben zu Klebemitteln siehe Übersicht über Klebemittel für die Restaurierung von Terrakotta
[9] 20%ige Lösung von Paraloid B72 in Ethylacetat
[10] (∅ max. 11,5 / Länge: 3cm; ∅ max. 10,5 / Länge: 5 cm)
[11] Wantenspanner (M3-Modellbau) mit einer Gabelschraube und zwei Bolzen
[12] Gewindestange, ∅ 3 mm, Länge: 4 cm
[13] Gewindestange, ∅ 3 mm

**Anhang: Skizzen der Kopie mit Nummern der Fragmente (rot)**

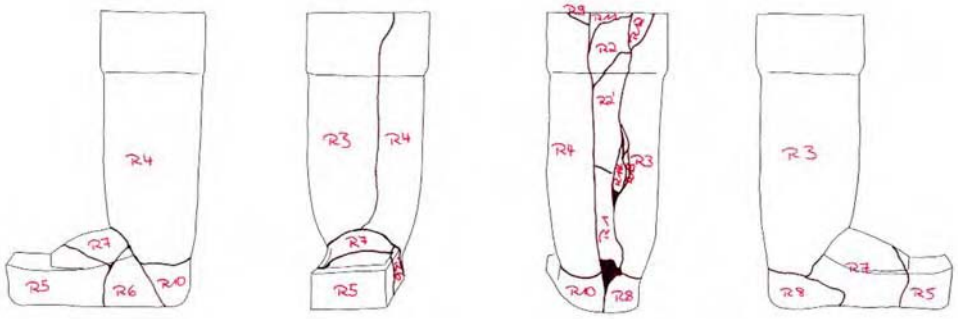




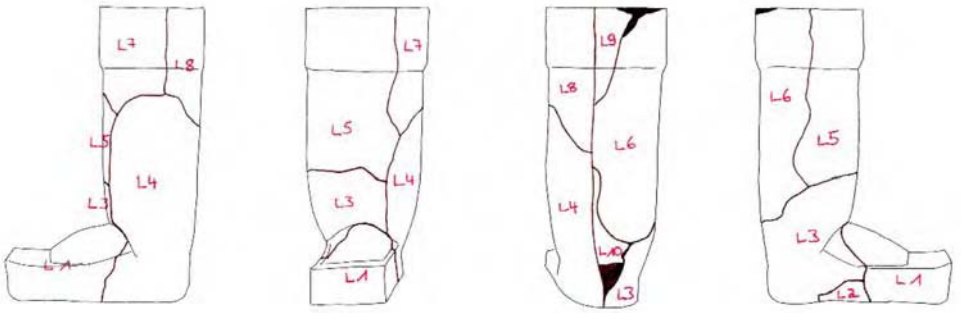


Körper der Kopie
Vorderseite, Rückseite und Seitenansichten

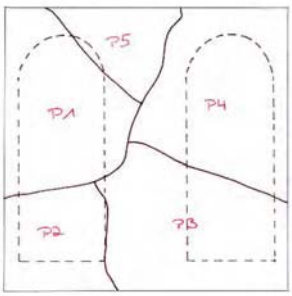
Buchstabenbezeichnungen bei den Nummern der Fragmente
u = upper body
d =
s = skirt




Linkes Bein




Rechtes Bein




Bodenplatte

**Experiments for assembing terracotta fragments on pieces of a replica**

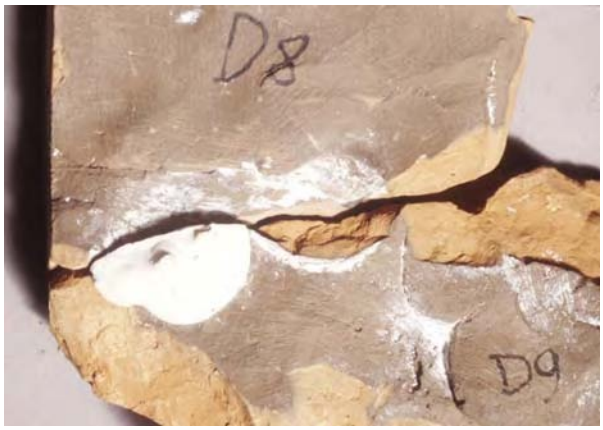

Connection between S 13 and 14 with dowels. The small fragment S 14' has broken apart at the hole drilled through for the dowel during transport.


Screw cramp made for the assembling of the fragments.


Two fragments connected with mechanical constructions only (S9 and S 14)


Reverse of the same fragments (S 9 and S 14)

Fragments U 6 and U 7, glued with epoxy resin and a primer, after opening the joint again.




Test to remove a temporary fixation made with plaster

## Übersicht über Klebemittel für die Restaurierung von Terrakotta

In den folgenden Tabellen sind für die Terrakottarestaurierung gebräuchliche Klebemittel zusammengestellt. Sie sind nach ihrer Zusammensetzung in Cellulosenitrate, Polyvinylacetate, Acrylate, Epoxidharze und sonstige Klebemittel eingeteilt. Zu den hier aufgelisteten Klebmitteln wurden Einzelinformationen gesammelt und die hier genante Literatur in Kopien zusammengestellt. Die hier abgedruckten Tabellen stellen eine Zusammenfassung zu dieser Dokumentation dar. Die Dokumentation entstand während des Arbeitsaufenthalt chinesischer Kollegen im November und Dezember 1999. Es ist geplant, sie weiter auszubauen.

**Cellulosenitrate**

| Handelsname | Hersteller | Chemische Gruppe | Handelsform | Thermoplast | Literatur |
|---|---|---|---|---|---|
| Archäocoll 2000N | Fa. Dr. Georg Kremer, 88317 Aichstett Tel.: 07565-1011/1604 | Cellulosenitrat | Gelöst in Aceton und Ethylacetat | nein | Arbeitsblätter für Restauratoren Heft 2,1997 Gruppe 4 Keramik S.98-105<br><br>Studies in Conservation 37 (1992) S.113-119 |
| Mecosan L-TR | Kissel u. Wolf GmbH, In den Ziegel-wiesen 6, 69168 Wiesloch Tel.: 06222-5780 | Cellulosenitrat | Gelöst in Ethanol, Methylacetat, Propanol, Naphta und Dibutylphtalat | nein | Sicherheitsdaten-blatt Kissel und Wolf GmbH |
| Mecosan S (wird nicht mehr hergestellt) | Kissel u. Wolf GmbH, In den Ziegelwiesen 6, 69168 Wiesloch Tel.: 06222-5780 | Celluloid (Cellulosenitrat mit Kampfer als Weichmacher) | | nein | Arbeitsblätter für Restauratoren Heft 2,1997 Gruppe 4 Keramik S.99 |
| Duosan (alt) (wird nicht mehr hergestellt) | VEB Filmfabrik DDR | Cellulosenitrat | Vermutlich mit einem geringen Zusatz an Carbonsäureester | nein | Arbeitsblätter für Restauratoren Heft 2,1997 Gruppe 4 Keramik S.99 |
| Duosan (neu) | Uhu-Werke, Bühl/Baden | Cellulosenitrat | Polyvinylacetat beigemengt | nein | Arbeitsblätter für Restauratoren Heft 2,1997 Gruppe 4 Keramik S.99 |
| Uhu hart | Uhu-Werke, Bühl/Baden | Cellulosenitrat | Geringer Zusatz eines Carbon-säureester als Weichmacher | nein | Arbeitsblätter für Restauratoren Heft 2,1997 Gruppe 4 Keramik S.99 |
| Uhu endfest | Uhu-Werke, Bühl/Baden | | | | |
| Schein-Goldkleber | Schein-Orthopädie-Service KG, Postf. 110609, 42866 Remscheid Tel.: 02191-9100 | Celluloid (Cellulosenitrat mit Kampfer als Weichmacher) | | nein | Informationsblatt Schein Ortopädie-service |

## Polyvinylacetate und Polyacrylate

| Handelsname | Hersteller | Chemische Gruppe | Handelsform | Thermoplast | Literatur |
|---|---|---|---|---|---|
| Uhu | Uhu-Werke, Bühl | Polyvinylacetat | Polyvinylacetat-lösung | nein | Arbeitsblätter für Restauratoren Heft 2,1997 Gruppe 4 Keramik S.99 |
| Mowilith 50<br><br>(AYAT) | Hoechst AG Mühlheimerstr. 24-28, 68219 Mannheim<br><br>Union Carbide, Canada | Polyvinylacetat | Granulat | Ja<br>Tg: 24°C | Mowilith Handbook, Hoechst AG<br><br>Studies in Conservation 41 (1996), S.19-44 |
| Mowilith 60<br><br>(AYAF) | Hoechst AG Mühlheimerstr. 24-28, 68219 Mannheim<br><br>Union Carbide, Canada | Polyvinylacetat | Granulat | Ja,<br>Tg:26°C | Mowilith Handbook, Hoechst AG<br><br>Studies in Conservation 41 (1996), S.19-44 |
| Primal AC 33<br><br>(Rhoplex AC33) | Fa. Dr. Georg Kremer, 88317 Aichstett Tel.: 07565-1011/1604<br><br>Rohm & Haas, Canada | Polyacrylat, EA (60), MMA (40), EMA (?) | Reinacrylatdis-persion | | Sicherheitsdate-nblatt Fa. Dr. Georg Kremer |
| Paraloid B72<br><br>(Acryloid B72) | Fa. Dr. Georg Kremer, 88317 Aichstett Tel.: 07565-1011/1604<br><br>Rohm & Haas, Canada | Polyacrylat, EMA (70), MA (30) | Granulat | Ja | Sicherheitsdaten-blatt Fa. Dr. Georg Kremer,<br><br>Studies in conservation 31 (1986), S.7-14<br><br>Studies in Conservation 41 (1996), S.19-44 |
| Paraloid B44 | Fa. Dr. Georg Kremer, 88317 Aichstett Tel.: 07565-1011/1604 | Polyacrylat MMA | Granulat | ja | Sicherheitsdaten-blatt Fa. Dr. Georg Kremer<br><br>Studies in Conservation 41 (1996), S.19-44 |

## Epoxidharze

| Handelsname | Hersteller | Chemische Gruppe | Handelsform | Thermoplast | Literatur |
|---|---|---|---|---|---|
| Fynebond | Fyne Conservation Service, Airds Cottage St Catherin's By Loch Fyne Argyll PA25 8BA Scotland Fax: 0044-141 357 4107 | Harz (Komponente A): Auf Basis von Bisphenol A Härter(Komponent B): Difunktionales primäres Amin | Zweikomponentenkleber | nein | Sicherheitsdatenblatt, Fyne-bond Conservation Sevice; Conservation News, number 65, March 1998, Ceramics and Glass Section |
| Araldite 6030 (AY 103/ XW396) China bzw. Araldite 2011 Europa | Ciba Geigy Öflingerstr.44 79662 Wehr/Baden Tel. 07762/8261 | China: Epoxidharz + „polyamide gum (=Ketimin) | Zwei Komponenten in Dosen (China), in Kartuschen (Europa) | nein | Informationsblatt Araldit, Ciba-Geigy (Pedelì) |
| Araldit 2015 (AV 5308/HV 5309-1) | Ciba Geigy Öflingerstr.44 79662 Wehr/Baden Tel. 07762/8261 | | Zweikomponenten Kleber in Kartuschen | nein | Informationsblatt Araldit, Ciba-Geigy (Pedelì) |
| Araldite SW 419-1<br><br>Härter HV2419 | Ciba Geigy Öflingerstr.44 79662 Wehr/Baden Tel. 07762/8261 | Epoxidharz: Bisphenol A (20-28%) Bisphenol F (6-12%)<br><br>Härter auf Basis eines Amins Trimethylhexamethylendi-amin (15-23%) Triethylentetraamin (10-18%) Benzylalkohol (14-20%) | Flüssig<br><br>Flüssig | nein | Sicherheitsdatenblatt Ciba-Geigy |
| XW 396 Harz (Clemens Standartepoxidharz)<br><br>Versuchsprodukt XW 397 | Ciba Geigy Öflingerstr.44 79662 Wehr/Baden Tel.: 07762/8261 | Epoxidharz: Bisphenol A (49-61%) 1,4- Butandioldiglycid-ether (39-51%)<br><br>Härter auf Basis eines Amins Isophorondiamin (43-55%) Trimethylhexamethylendamin (20-28%) | flüssig | nein | Sicherheitdatenblatt Ciba-Geigy |
| Uhu plus | Uhu-Werke, Bühl | Epoxidharz: Diglycidylether auf Bisphenol A Basis Härter: Triethylentetramin | Zweikomponenten Kleber in Tuben | Ja (laut Gebrauchsanweisung) Nein (laut Versuch) | Datenblatt Uhu plus, Gebrauchsanweisung, Gesprächsnotiz Elisabetta Brunaf |

**Sonstige Klebemittel**

| Handelsname | Hersteller | Chemische Gruppe | Handelsform | Thermoplast | Literatur |
|---|---|---|---|---|---|
| Pattex-Schmelz-klebstoff | Henkel KgaA Düsseldorf | | Patronen für Heißklebepistole | | Angaben auf der Packung |
| Proxxon-Schmelzkleb-stoff | Proxxon | | Patronen für Heißklebepistole | | Angaben auf der Packung |
| AKEMI | J. König GmbH+Co. Dieselstr. 2 76227 Karlsruhe Fax: 0721-4090533 | Steinkitt | | | Bestellschein HGKK Bern |

**Survey and investigations on the distribution of the soil moisture in the earthen construction of pit one and two**

These investigations should help to clear up the present state of the moisture distribution in the pits. They should show the influence of the specific distance to the ground water table and the influence of the annual variation of the groundwater table on the moisture content in the partition walls. The drainage system for the meteoric water was examined to check if there are sources of moisture in addition to the groundwater. The overriding target, in combination with the climate monitoring is to characterise the drying process in the pits concerning the interdependence between the time of the excavation, the distance to the groundwater table and the climate in the halls.

**Investigation program:**

In Mai 1999 -and 17 month later in October 2000 the distribution of the soil moisture in the partition walls in pit 1 and 2 and in the ground of pit 2 was investigated by taking soil samples with a percussion core probe. The probe had a length of 1.1 metre and a inner diameter of 2,5 centimetre. In both years the sampling was performed for a partition wall in pit 1 (excavation sector T20; between the corridors G9 and G10), for one partition wall in pit 2 (excavation sector T21; between G17 and G18) and for the walls in a well in pit 2 (excavation sector T6; corridor G6). The exact positions of the sampling are shown in **figure 4 and 5**. The moisture content of the soil samples was determined by gravimetric comparison of the fresh sample with the sample after drying for 24 hours in 105°C. For the visualisation of the results the moisture distribution was plotted in coloured profiles.
The precise altitude of the present excavation level was measured in all corners of the pits. The data were transferred into a digital plan, which was compiled after the original construction plans of the halls (**figure 6**). The real altitude differences between the brick levels in pit No. 1 and pit No. 2 and the main drainage pipes between the pits are plotted in this plans.

**Results:**

**Differences in altitude (the altitudes of the brick level)**
The positions of the brick level in pit 1 and pit 2 are shown in **figure 6**. The average altitude of the brick level in pit 1 is 4 metre higher than the brick level in excavation sector T1 in pit 2. There is a slight decrease of 50 centimetre from west to east on the whole length of the corridors in pit 1. The brick level in pit 2 is falling 1,5 metre from south to north and 0,7 metre from west to east. The highest difference in the altitude of the brick levels in pit 2 is between the south-western corner and the north-eastern corner (The altitude of the brick level in T1 is 2,2 metre higher than in T21) (**fig. 4; 5; 6**).

**The drainage of the meteoric water**
Up to the distance of at least 15 metre the whole ground in the surrounding of the halls of pit 1 and pit 2 is sealed with concrete (pit 1) ore with a pavement of terracotta panels (pit 2). As it seems this could be enough protection for the excavations against the percolation of rainwater. The roof water of pit 1 is drained to the base of the northern and southern walls of the hall. From there it is superficially flowing on the concrete ground cover to the drainage canals (**fig. 7 and 8**) The roof water of pit 2 is drained by eaves to the base of the northern and southern walls. Again the eaves are not connected directly with the drainage canals (**fig. 7 and 8**).
Especially the main drainage canal between the two halls is not sufficient for the simultaneous water drainage of the half roof area of both pits (12600m²). In case of a heavy summer rain

with 15 l/m²h the roof area drains off about 3m³ rainwater per second into this canal. Because the canal has an insufficient drainage capacity the pavement between the hall of pit 2 and the canal is flooded while every heavy rainfall. Particularly at this times much water is percolating into the ground, because the concrete ground sealing has many fissures and gaps. The percolating meteoric water can cause a local elevation of the groundwater table between the two pits (**see fig. 8**). Higher moisture contents in the southern edge of pit 2 and in the northern edge of pit 1 -as they are reported by our Chinese colleagues- are the result of this periodical rainwater infiltration into the ground between the pits.

**Groundwater**

The altitude of the groundwater table was determined by measuring and observations in the well of pit 2. The average altitude of the groundwater is about 7,7m below the top of the partition wall in T1; pit 2 (**fig. 1**). In this position the distance between GW- table and brick level is 6,25m.

The soil profile in the well has a uniform appearance. It seems to be the same type of loess from the top to the bottom of the well. There are no indications for alternating bedding planes ore interstitial layering within the loess. Therefore the water under the pits can be designated as free aquifer.

Because loess is a very fine grained and clay bearing material its water conductivity is low. Conductivity values between $10^{-5}$ m/s and $10^{-7}$ m/s are normal for loose sediments with this grain size distribution (HÖLTING, B., 1996). Because of the low conductivity in combination with a high porosity free aquifers in loess materials are constant water supplies with small changes of the water table. Only small amounts of the rainwater is percolating to the aquifer. The percolation in loess can last many days for 1 ore 2 metre depth. The most rainwater in loess regions is drained by creeks and rivers and does not reach the aquifers. Because of all this reasons the reaction of the groundwater on seasonal and periodic rainfalls is very low.

The observations in the well confirm this character of aquifers in loess for the groundwater under the excavations. Flooding marks on the wall indicate, that the change of the groundwater level has never exceeded one metre. The difference between the measured levels in 1999 and 2000 was 13 cm. Mai belongs to the month of high groundwater and October to low groundwater, but both month usually do not have extreme values. Concerning the seasonal position of the measuring in 1999 and 2000, the data point to a average annual change of the ground water table within 20-25cm. According to these characteristics of the aquifer, the groundwater table under pit one and pit two is supposed to be a more ore less horizontal plane (**see fig. 6**). Considering the assumed infiltration beneath the main drainage canal, the groundwater table can have periodically highs in this position **(see fig. 8).**

The average distances between the brick level and the ground water table are 10,0m-10,5m in pit 1, 6,25m in the south-western corner of pit2 and about 4,0m in the north-eastern corner of pit2.

**The moisture in the ground**

The only possible way to determine the moisture distribution in the deep ground of the pits was the soil sampling in the walls of the well in pit 2. The graded moister distribution in the ground was estimated by the interpolation of the data that were gained by a horizontal sampling with a percussion core probe **(fig. 1).** The results of the interpolation is shown in **figure 2.** Besides, within the sampling on the partition walls in pit 1 and pit 2 the moisture content of the ground up to 1.1 metre under the brick level was determined.

The data of the measuring in the well show moisture contents between 30% directly above the groundwater and 14%-15% under the brick level. The measuring in the well and the measuring

beside the partition walls found no moister change in the ground below the brick level within 17 month (**Fig. 2 and 3**).
The sampling spots were positioned in **figure 6** according to their real altitude. The result is a corresponding distribution of the graded moisture content in the ground between the groundwater and the brick level for all three sampling positions. Beneath the brick level the moisture content of the ground seems to be directly depending on the distance from the ground water. The time of the excavation - T20 in pit 1 between 1979 and 1982; T16 in pit 2 1994-1997; T21 in pit 2 Feb. 1998 - and the different climate in the halls seem to have no influence on the moisture distribution beneath the brick level. In **figure 6** is shown the interpolated line of 16% water content. It is drawn parallel to the groundwater table.

**The moisture in the partition walls**
In contrast to the moisture in the ground the moisture content in the partition walls (**fig. 3**) and the moisture content of the other superficial earth (see: well **fig. 2**) has diminished in the time between the measuring.
In Mai 1999 the partition wall in pit 2 was excavated since 15 month. This time the natural graded moisture profile has dried only in the upper 20 to 30 centimetre and in the upper part of the sides up to 15 centimetre under the surface. Because of the drying air conditioning in pit 2 which has started in the winter 98/99, within the 17 month the water content in this partition wall has reduced to 8-9% in 45 cm depth under the surface. The surface itself on the top of the wall has dried from more than 6% under 4%. Also the sides have dried down to the brick level. In the upper part of the well the changes of the moisture content are very similar **(fig. 2).**
Even the partition wall in pit 1, which is excavated at least since 17 years has lost some moisture. The drying progress to the inner core of the wall is still going on.

**Conclusion**
The water content of the soil under the brick level seems directly influenced by the specific distance to the groundwater table. The brick level seems to hinder the evaporation and the progression of drying. Because altitude of the water table has only very little variations, the moisture content in the ground under the brick level will be constant for long terms.
The excavated surfaces in the pits and particularly the partition walls are exposed to a more ore less rapid drying process in accordance to the climatic conditions in the halls. Even the bigger vicinity of the partition walls in pit 2 wont hinder this process with its destructive consequences.

Positioning plan for the soil sampling in the well of pit No 2 in the years 1999 and 2000

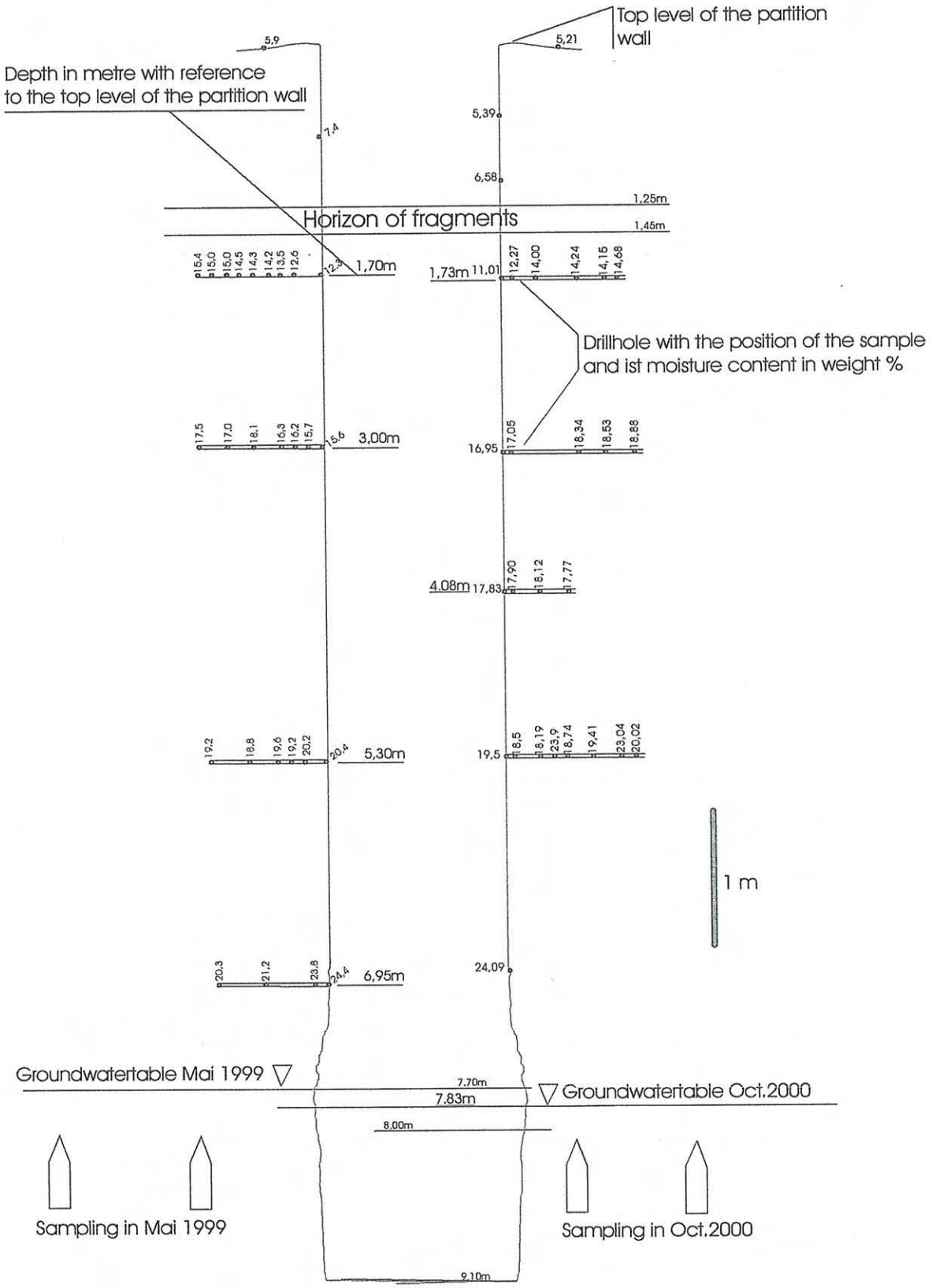



**Fig.1:** plan of the soil sampling in the well in pit 2 (excavation sector T16).

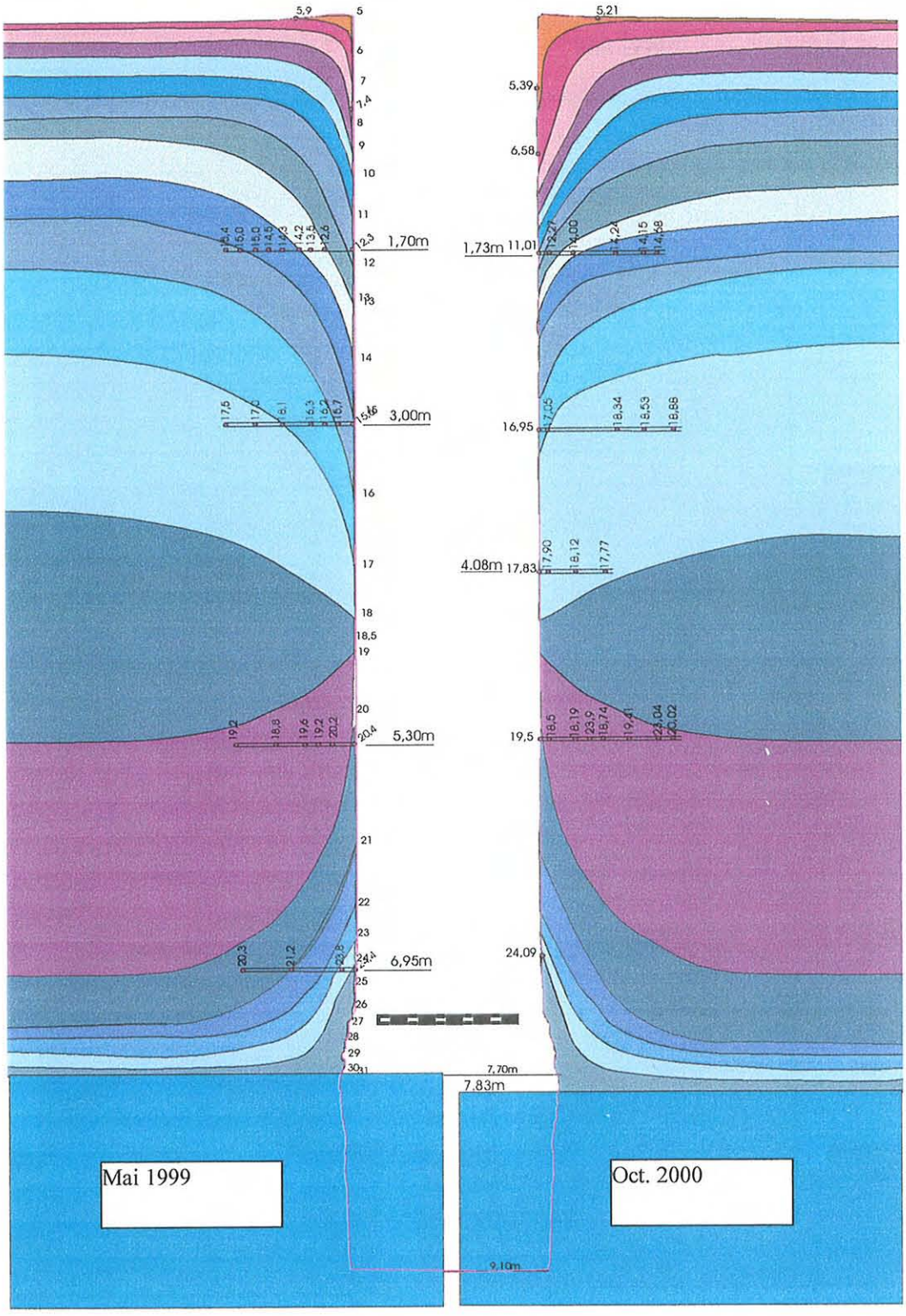



**Fig.2:** Interpolation of the graded moisture content according to the data of the soil sampling. For the ground beneath the brick level is no difference between the two measuring.

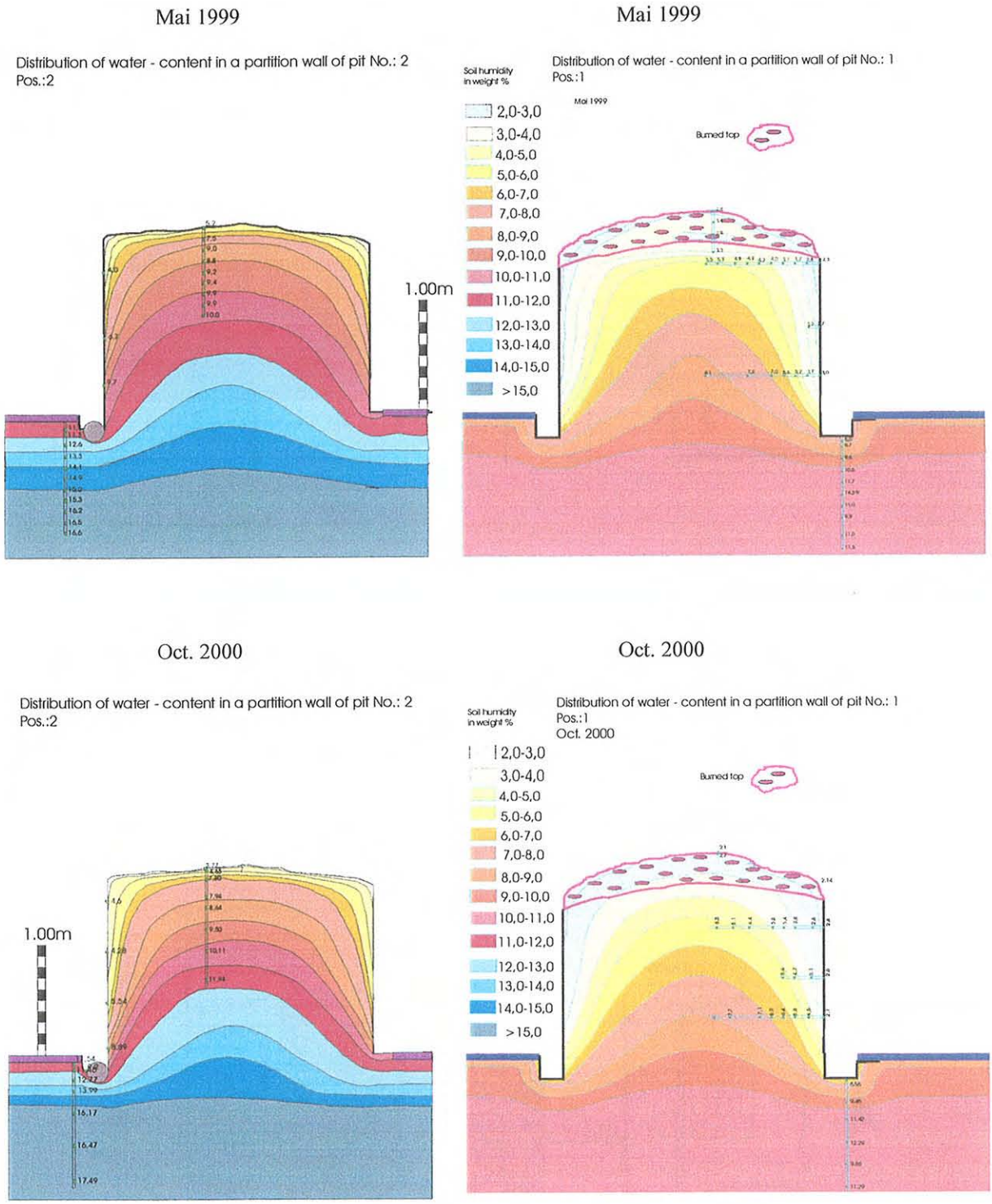



**Fig. 3**: Positions of the soil sampling in the partition walls of pit 2 and pit with the interpolation for the momentary distribution of the moisture content. The moisture content under the brick level did not change in 17 month between the measuring in 1999 and 2000.

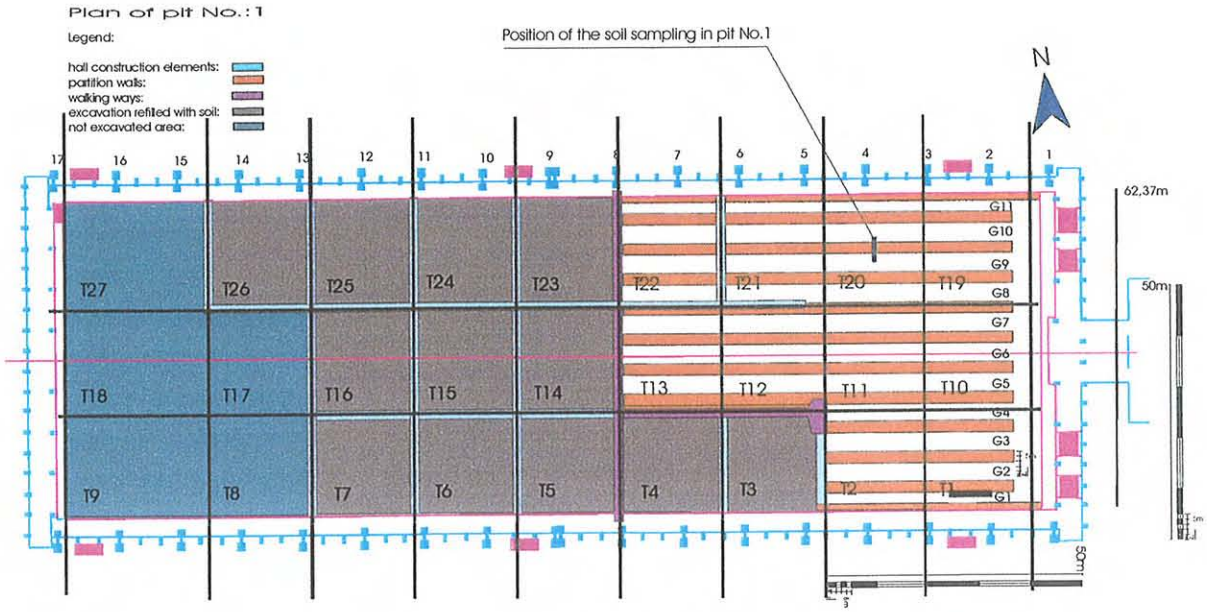



**Fig. 4**: true scaled plan of pit 1

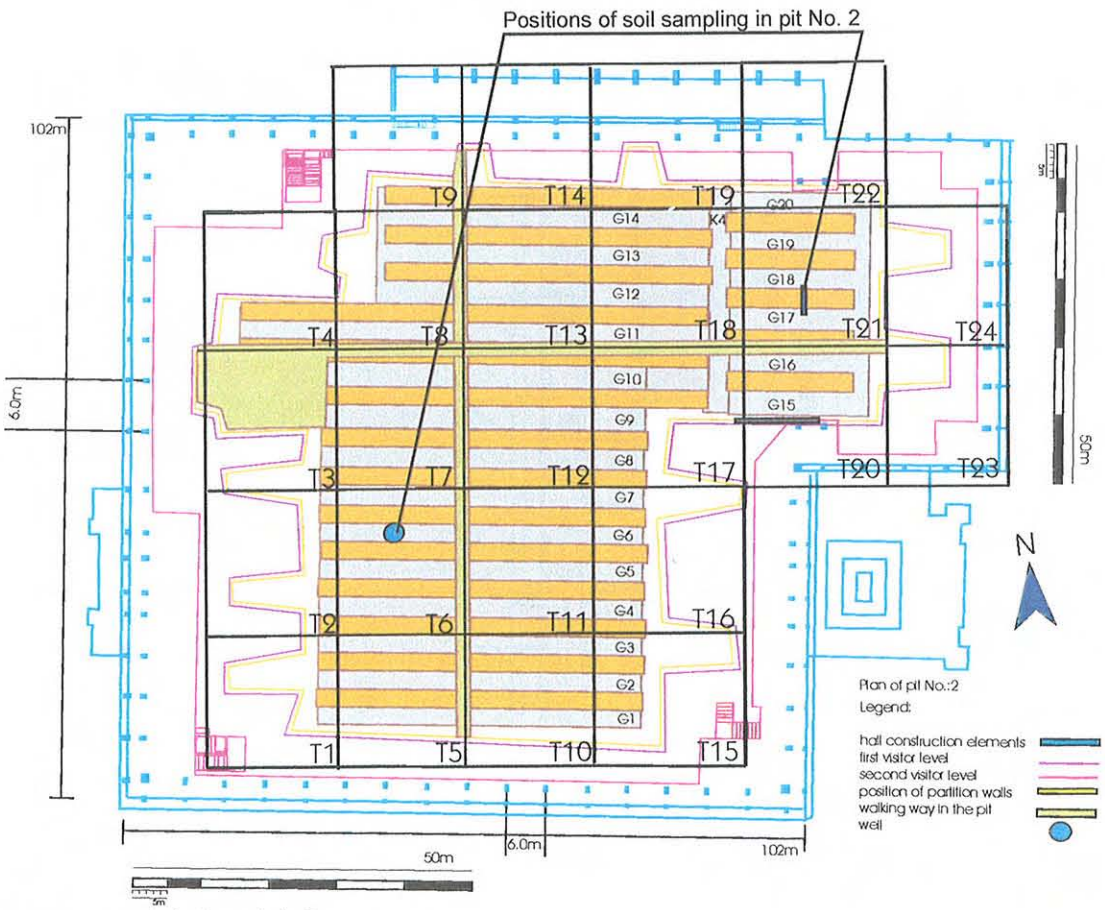



**Fig. 5**: true scaled plan of pit 2

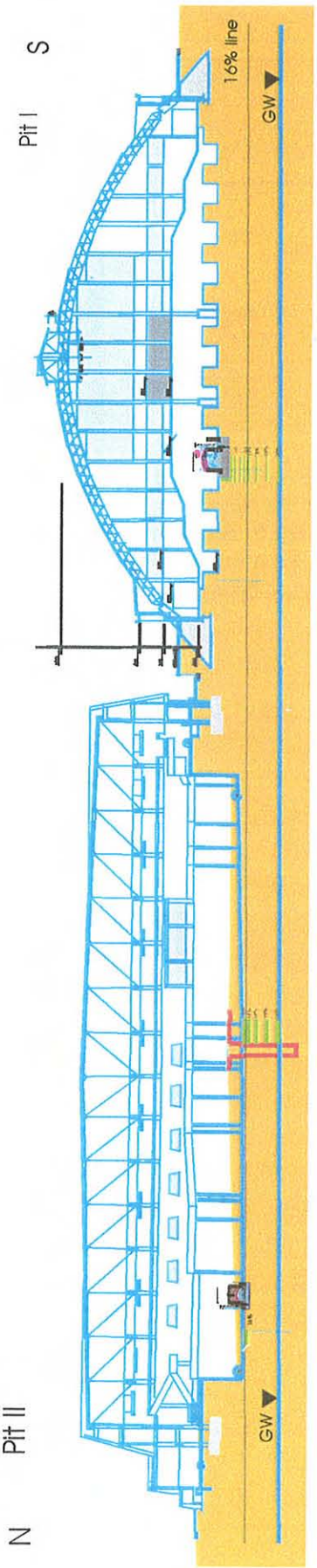



**Fig. 6**: True scale plan of pit 1 and pit 2. The average level of the groundwater table and the line for 16% water content of the ground are parallel. The positions of the sampled well and partition walls are plottet in their precise position.

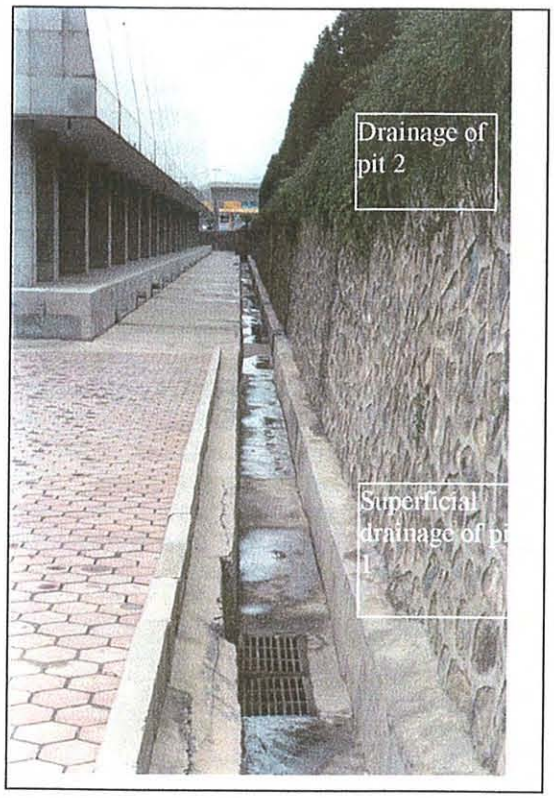



**Fig. 7**: Main drainage canal with the brown tracs of the superficial flows of the roof water of pit 1 and pit 2. The drainage and the sealing of the cround in this position are not sufficient to prevent percolation into the ground.

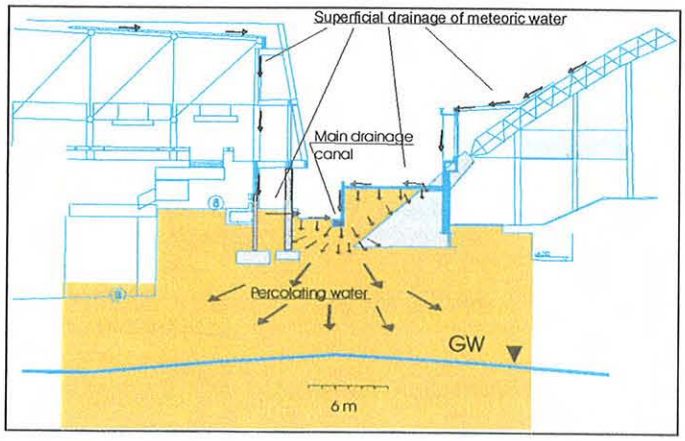



**Fig. 8**: System of the roof water drainage between pit 1 and pit 2. Frequently flooding of the pavement can cause a slight elevation of the groundwater table under the main drainage canal and a rise in the moisture of the earthen constructions in the neighbouring parts of the excavations.

## Klimamessungen in der Grube II

Ergebnisse des climate mappings am 26.oct.99 um 9:30 bzw. am 28.oct.99 um 15:30.

• **Einflussfaktoren für das Raumklima in der Grube II:**
Die wichtigsten Faktoren für das Klima in großen, „ungeheizten“ Räumen, das natürlich grundsätzlich vom Außenklima bestimmt wird sind die thermische und hygrische Sorptionsfähigkeit der raumbegrenzenden Flächen (Außenschale, Boden, Einrichtung ...), die Nutzung des Raumes z.B. durch Besucher, und die Luftströmungen. Zudem kann die Strahlungswärme des durch die Fenster eindringenden Lichtes, die Wärmeeinleitung durch die Außenwände oder die Wärmeentwicklung durch Nutzer und Besucher eine natürliche Raumaufheizung bewirken.

Die bunkerartige Hallenkonstruktion der Grube II verfügt, verglichen mit der Grube I, über gute bauliche Voraussetzungen für ein ausgeglichenes Raumklima (Abb.1).

Die Außenschale des Gebäudes ist zweischichtig aufgebaut. Die betonierten Außenwände sind mit festverfugten Granitplatten verkleidet. Dazwischen liegt eine isolierende Luftschicht (Abb.3) Konstruktion). Das Dach besteht aus einer isolierten Holzverschalung, die mit Blech abgedeckt ist. Es bietet daher vergleichbar wenig Schutz vor dem Außenklima (insbes. Wärmeleitung).
Die stark begrenzte Fensterfläche ist zurückgesetzt und so von der Außenkonstruktion abgeschirmt, daß keine direkte Sonneneinstrahlung auf den Innenraum möglich ist.(Abb.1u.2).


Abb.1: Außenansicht der Grube II. Blick auf den Hauteingang auf der Ostseite der Halle. Die Fassade ist mit Granitplatten verkleidet. Die Fenster sind in zurückgesetzten Nischen versteckt.

Abb.2: Blick nach S-E in der Halle der Grube II (Stand der Ausgrabung 1995). Kleine Fenster spenden nur wenig Licht. Die Aufheizung der Grube durch direkte Sonneneinstrahlung ist gering. Die Belüftung hängt versteckt über den Stahlträgern der Dachkonstruktion.

Die beiden Besuchereingänge auf der Ost und Westseite sind über Vorräume mit doppelten Glastürenfronten innen und außen gut gegen die Außenluft abgeschirmt. Der Luftaustausch in Grube II ist über eine Belüftungsanlage mit vier im Dachbereich über der Halle hängenden, E-W gerichteten Kanälen steuerbar (Abb.2 u. 3). Dabei wird Außenluft in die Halle eingeblasen. Die Abluft soll an Abluftschlitzen, die in Bodennähe an den Außenwänden der unteren Besucherebene angebracht sind abströmen.
Nach Aussagen des Chef-Archäologen Mr. Liu ist die Belüftungsanlage seit Sommer 1998 während der Sommermonate täglich von 9:00 bis 17:00 in Betrieb. Im Winter wird sie nur 2 – 3 mal pro Woche eingeschaltet. Abgesehen von diesem unkontrollierten Einsatz der Belüftungsanlage wird die Möglichkeit für die Steuerung des Raumklimas in der Halle auch durch den Umstand herabgesetzt, daß in den Sommermonaten tagsüber die Fenster geöffnet

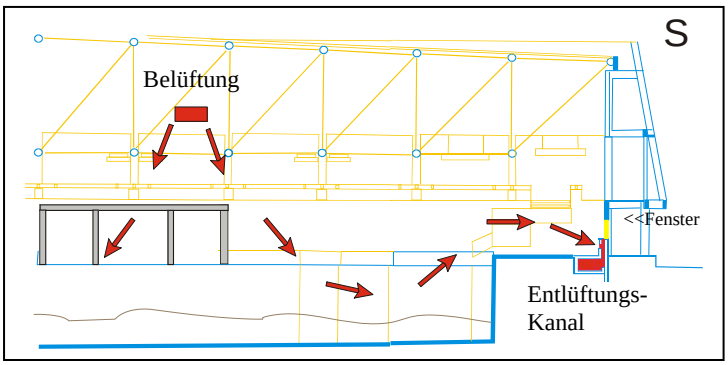



Abb.3: Lüftungsanlage in Grube II

werden und die Schleusentüren an den Besuchereingängen offen gehalten werden.

Die Öffnungszeiten für Besucher sind täglich von 9:00 bis 17:00. Normalerweise wird die Grube von drei- bis viertausend Menschen pro Tag besichtigt. An Spitzentagen werden bis über 10 000 Besucher gezählt.

Die Sorptionsfähigkeit der Hallenkonstruktion aus Stahl, Beton- und Ziegelwänden und einem Boden aus Granitpflaster ist im Vergleich zur der Lösserde der Grube vernachlässigbar klein.
Der Boden der Ausgrabung hat eine Grundfläche von ca. 6000m². Die tatsächliche Bodenoberfläche ist reliefbedingt derzeit 5%-10% höher. Nimmt man die Grubenwände mit ca. 450m Länge und durchschnittlich 4,5m Höhe hinzu, so ergibt sich für Grube II eine sorptionsfähige Lössoberfläche von mindestens 8300m². Die Sorptionsfähigkeit von Lehmerde liegt 10 –50 mal höher als bei gebrannten Ziegel und drei bis fünf mal höher als der Wert verschiedener Betone und Putze (W. Lemke, 1994). Die offene Ausgrabung ist demzufolge die wichtigste Sorptionsfläche für hygrische Feuchte in der Halle.

Ein wichtiger Faktor für die Beurteilung der Wertigkeiten genannter Parameter wie Luftströmung oder Wärmeleitung ist das Raumvolumen. Die Halle II verfügt bei einer Grundfläche von 11700m² +/-100m² über ein Raumvolumen von annähernd 200 000m³ (198800 +/- 500m³). Angesichts des großen Raumes ist die Belastung des Klimas durch die Besucher relativ gering. So rechnet man bei der Feuchtigkeitsabgabe einer Person drei bis fünf g/h (C. Arendt, 1993). Bei idealer Verteilung der Feuchtigkeitsabgabe von 4000 Personen, die sich je eine Stunde in der Halle aufhalten, ergibt sich eine Steigerung der absoluten Feuchte um 0,1g/m³. Bei der größten bisherigen Besucherzahl seit Bestehen des Museums mit 30 000 Besuchern (Museumstag 1999) errechnet sich somit eine maximale Feuchtigkeitszunahme von 0.75g/m³. Bei den bisherigen Testmessungen wurden Tagesschwankungen der Raumluftfeuchte mit bis zu 6g/m³ gemessen (vgl.: Messung 18.05.99). Die mittleren Tagesschwankungen lagen im Juni 1999 bei 1-3g/m³. Aus diesen Zahlen kann man bereits ablesen, dass der Einfluss der Besucherzahlen auf das Klima in Halle II gemessen an den vom Außenklima vorgegebenen Schwankungen vernachlässigbar klein ist. Bisherige Annahmen, dass sich das große Besucheraufkommen aufgrund seiner klimatischen Relevanz negative auf die ausgestellten Objekte auswirke, können im Fall der Grube II nicht bestätigt werden.

• Bisherige Entwicklung des Raumklimas in Grube II
Ausgrabungsgeschichte: Die Grube II wurde im Mai 1976 entdeckt. Im August 1977 waren bereits 17 Untersuchungsfelder (ca. 3m x 5m bis 25m x 15m) bis zum Boden (Brick level) ausgegraben. Sie wurden vor dem Bau der Halle wieder verfüllt. In den Jahren 1989 bis 1992 wurde die Halle über Grube II errichtet. Ab 1994 wurde die alten Probegrabungen wieder freigelegt und partiell erweitert. Auf der gesamten Fläche der Anlage wurde die Erde bis zum Niveau der Deckenbalken abgenommen (Abb.2). Seit Februar 1998 finden weiterführende Ausgrabungen in den östlichen Grabungssektoren statt.

• Messung des Mikroklimas in Grube II (“climate maping“).
Die Ausgrabungshallen I u. II in Lintong sind für eine detaillierte dreidimensionale Erfassung der Klimaentwicklung wie C. Arndt (Arendt, 1993) sie vorschlägt, zu groß und zu weit von München entfernt. Die Installation eines ausgeklügelten Meßsystems mit über 20 elektronischen Messfühlern für jede Grube wäre wünschenswert, ist demzufolge aber aus organisatorischen Gründen nicht möglich. Dennoch erschien es notwendig die Mechanismen der klimatischen Veränderungen in den Hallen zu verstehen. Es wurde der Versuch unternommen die Verteilung von Temperatur und relativer Feuchtigkeit in der Halle zu verschiedenen Tageszeiten möglichst genau zu erfassen (“climate mapping“). Die Ergebnisse der Messungen zeigen die möglichen Positionen der Extremwerte und die Beträge der Temperatur- und Feuchtigkeitsunterschiede innerhalb der Halle.
Die Positionierung der wenigen vorhandenen Datenlogger bei zukünftigen, langperiodischen Klimamessungen sollte mit den Daten des climate mappings optimiert werden.

•Durchführung des climate mappings in Grube II
Die Daten für das climate mapping wurden von unserem chinesischen Kollegen Mr. Rong Bo mit einem tragbaren kombinierten Feuchte/Temperatur –Messgerät vom Typ: Testoterm Sekunden –

hygrometer 6010, aufgenommen. Als Sensor kam der Testotherm Standard Raumklimafühler,(Genauigkeit:+/- 2% rel.F., im Bereich 2-98%; +/- 0,4°C, im Bereich 0-50°C; t.90-Wert:<12 sec.) zum Einsatz. An 68 Messpunkten, die auf fünf verschiedenen Höhenniveaus liegen wurde jeweils gleichzeitig die Temperatur und die relative Feuchtigkeit der Raumluft gemessen (Abb.4 u. Abb.5). Die Daten wurden jeweils in einem Zeitraum von ca. 1.5 Stunden aufgenommen.

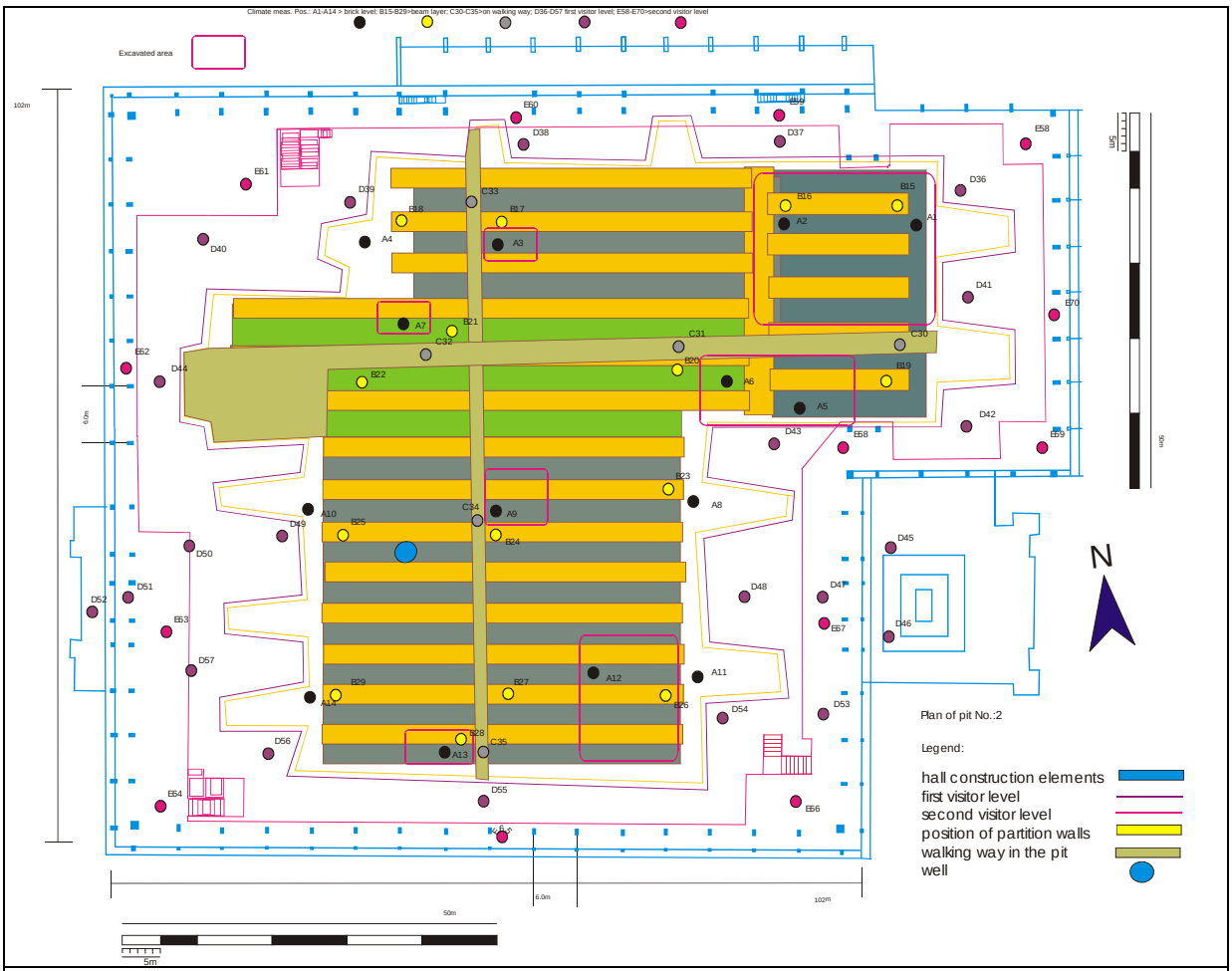



Abb. 4: Maßstabsgetreuer Aufsichtsplan der Grube II. Die Messpunkte des climate mapping sind entsprechend ihrer vertikalen Position mit verschiedenen Farben und Anfangsbuchstaben gekennzeichnet.

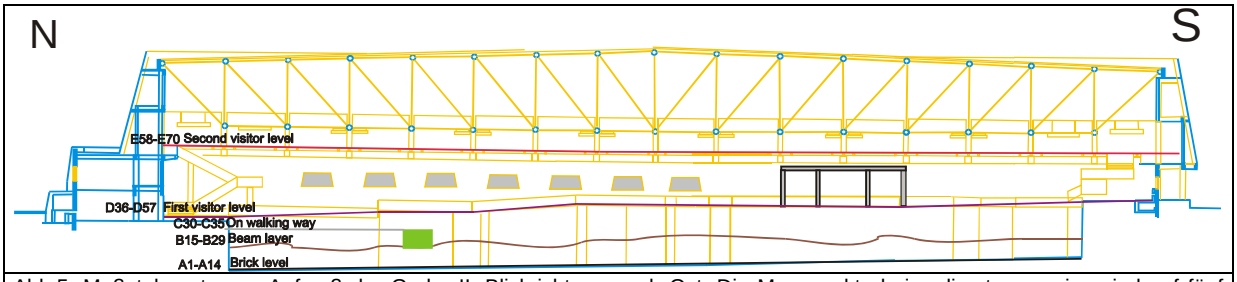



Abb.5: Maßstabsgetreues Aufmaß der Grube II. Blickrichtung nach Ost. Die Messpunkte beim climate mapping sind auf fünf Ebenen verteilt.

**•Ergebnisse des climate mappings in der Halle II.**
Die Klimaverteilung in der Halle in II wurden am Vormittag des 26.10.99 (9:30-11:00) und am Nachmittag des 28:10.99 (15:30-17:00) gemessen. Die Eckdaten der Messungen sind in Tab. 1 gegenübergestellt. Der 26. 10 war ein feuchter regnerischer Tag. Der 28.10 war ein sonniger, für die Jahreszeit sehr trockener Tag. Beide Tage sind im Vergleich mit den Klimamessungen von Oct. 1997 recht warm. Durchschnittsdaten des Außenklimas von Okt. 1997: Temp. (C°): min.:06; mittelw.:11; max.:24 // rel. F.(%): min.: 36; mittelw.:48; max.:72.

Tab.1: Eckwerte des climate mappings in Grube II

| Messungen in Halle II | 26.10.99 (9:30-11:00) | 28:10.99 (15:30-17:00) |
|---|---|---|
| Außenklima (°C / rel. F. %) | 18,1 / 69,6 | 19,8 / 35,2 |
| Temperaturbereich in der Halle (°C) | 17,1-19,3 δT: 2,2 | 19,1-22,2 δT: 3,1 |
| Rel. Luftfeuchtigkeit in der Halle (%) | 74,4 - 85.1 δφ: 10,7 | 46,2 – 83,6 δφ: 37,4 |
| Temperaturdifferenz δT in Ebene A: | 0,4 | 0,4 |

Die ermittelten Datenwerte sind in ihrer horizontalen räumlichen Verteilung auf den innerhalb der Grube liegenden Ebenen A, B, und C sehr ausgeglichen (Abb.6; Abb.7; Anhang Klimadaten). Auch auf der ersten Besucherebene (Ebene D) wurden lediglich in unmittelbarer Nähe der Eingänge Mischwerte mit der Außenluft gemessen (Position: D50, D51, D52, D57; D45, D46, D47, D48 vgl.Abb.:4 u. Anhang Klimadaten). Auf der zweiten Besucherebene (Ebene E) wurden am 28.10. sehr inhomogene Temperaturwerte gemessen (vgl. Abb.:7). Hier ist am 28.10 die Temperaturverteilung sehr uneinheitlich. Die ausgeprägte Diversifizierung auf dieser Ebene ist vermutlich auf das geringe Wärmedämmungsvermögen des Hallendaches und eine starke Wärmeentwicklung bei Sonneneinstrahlung zurückzuführen. Die aufsteigende Warmluft im Eingangsbereich und die positionsbedingte relative Abschottung der zweiten Besucherebene von der Luftkonvektion der Belüftungsanlage, spielen dabei sicher auch eine Rolle. Die klimatischen Ausnahmebedingungen auf der Ebene E scheinen damit auch hallentypisch zu sein.
Die insgesamt (E-Ausnahme) ausgeglichene horizontale Klimaverteilung scheint für die Grube II typisch zu sein. Lokale Wärme- oder Kältepools sind in den Ebenen A-D nicht erkennbar. Der Einfluss der Luftströmungen an den Eingängen ist sehr gering. Auf eine graphische Darstellung der horizontalen Temperaturverteilung wie sie für in Gr. I vorgenommen wurde, konnte demzufolge verzichtet werden.

Neben der horizontalen Gleichmäßigkeit ist aus den Messwerten auch eine deutliche vertikale Schichtung der Luft abzulesen.
Nachfolgend sind die Temperaturwerte und die relativen Feuchtigkeiten der Luft gegen die Hallenhöhe abgetragen (Abb. 7 u. Abb. 8). Aus den Punktwolken der Ebenen A – E und aus deren arithmetischen Mittelwerten ergeben sich Temperaturprofile (Abb.:7) und Luftfeuchtigkeitsprofile (Abb.:8). Die Verbindung der Mittelwerte zeigt die generelle Raumluftschichtung in der Halle II. Die tatsächlichen Temperaturprofile an ausgewählten Positionen stützen das Bild der Mittelwerte. Sie sind im Anhang beigefügt
Temperaturprofile (Abb.:7):
Am Vormittag des 26.10 liegen die Temperaturwerte der einzelnen Ebenen im Bereich von +/-0.2°C. Insgesamt ist ein Temperaturanstieg mit der Höhe feststellbar. Die Mittelwerte steigen von 18,2°C auf der Bodenebene A bis zur zweiten Besucherebene (Ebene E) um 0.4 Grad an. Der eigentliche Knick der Temperaturerhöhung befindet sich zwischen der Oberkante der Ebene C - also noch innerhalb der eigentlichen Grube- und der Besucherebene D. Das Luftklima innerhalb der Grube ist von der großen offenen Erdoberfläche bestimmt. Sie gleicht sich der mittleren Bodentemperatur der Grube II an, die im Sommer 1999 im Bereich zwischen 17,5 und 18,3°C lag (vgl. Testmessungen im Mai u. Juni Anhang).
Die mittlere Luftfeuchtigkeit in der Grube liegt bei 80%. In den Ebenen D u. E geht sie entsprechend höheren Temperatur leicht zurück ( Abb.:8).

Am Nachmittag des 28. 10 beginnt das mittlere Temperaturprofil bei 19.3°C auf der Ebene A und steigt bis zur Ebene E kontinuierlich auf den Mittelwert von 20.2°C an. Über die Lüftungsanlage wird trockene Warmluft in die Halle eingeblasen. Sie wirkt sich im gesamten Raum bis in die Ausgrabungsbereiche aus. So erwärmt sich die Luft in unmittelbarer Bodennähe trotz der starken Pufferwirkung der Erde um bis zu 1,5°C.
Die eingeblasene Außenluft ist an diesem Tag mit ca. 35% sehr trocken. Daher wird auch die Feuchtigkeit der Hallenluft stark reduziert und sinkt mit steigendem Abstand vom Boden auf Werte um

50%. Trotz erhöhter Lufttemperaturwerte bleibt die rel. Luftfeuchtigkeit auf der Ebene A bei Werten um 80%. Die Konstanz der Luftfeuchtigkeit am Boden der Ausgrabung lässt auf erhöhte Verdunstungsraten an der Erdoberfläche schließen (vgl.:Abschnitt Testmessung).

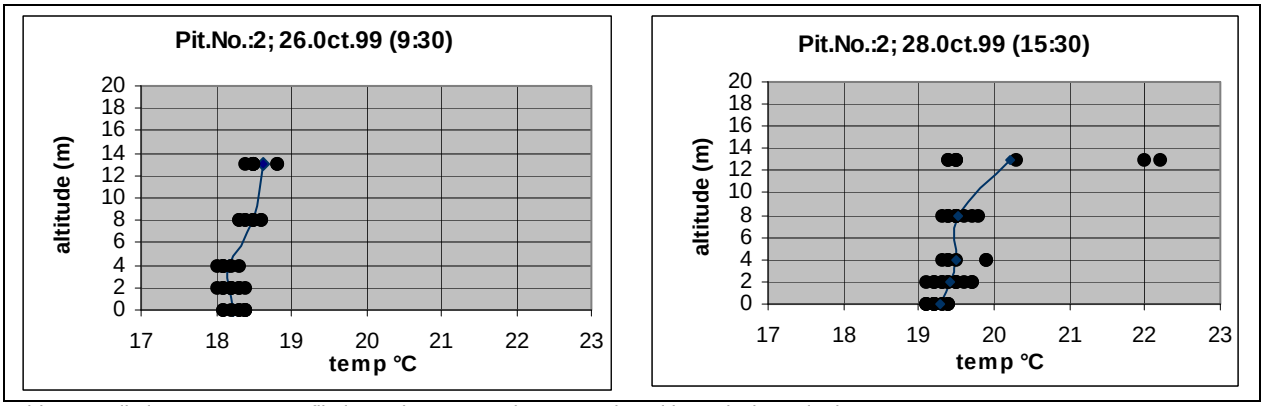



Abb.7: Vertikale Temperaturprofile in Grube II; Messdaten und arithmetrischer Mittelwert

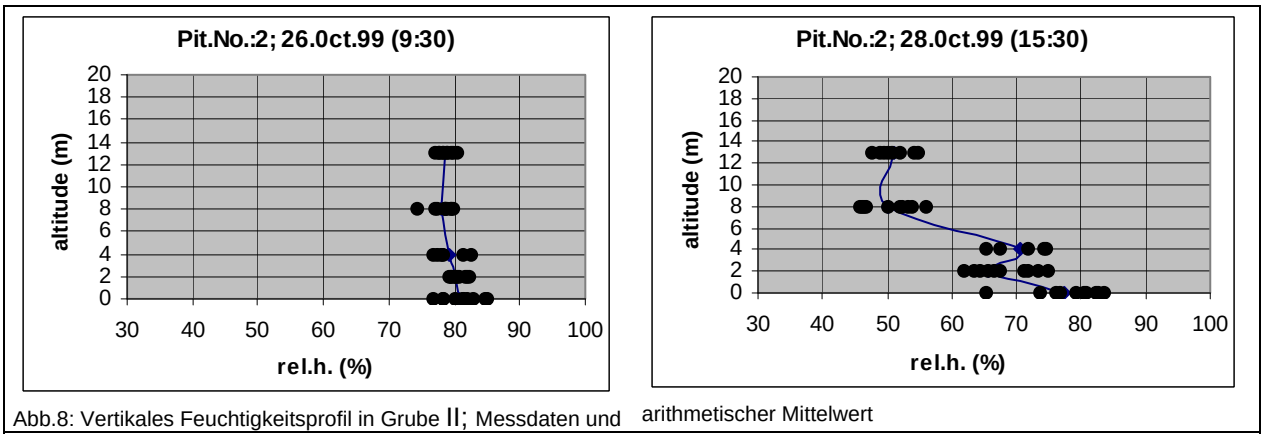



Abb.8: Vertikales Feuchtigkeitsprofil in Grube II; Messdaten und arithmetischer Mittelwert

Das vertikale Hallenklima der Grube II wird sehr deutlich vom Ausgrabungskörper bestimmt. Über der Erde stellt sich derzeit während des Sommers eine mittlere Temperatur von ca. 18°C und eine rel. Luftfeuchtigkeit von 80% ein. Dieses Klima breitet sich in der Nacht über die gesamte Halle aus. Das normale Temperaturprofil und das Feuchtigkeitsprofil in der Halle II ist steil und gleichmäßig. Am 26.10. weichen die Werte der zugeführten Außenluft nur geringfügig vom Hallenklima ab. Die Auswirkung der Luftzufuhr auf den Profilverlauf ist somit klein. Am 28.10 wird das Innenklima von der trockenen Luftzufuhr deutlich gestört. Die Profile gabeln sich mit der Höhe auf. Je höher die Divergenz von Außenklima und dem Klima über der Erde ist, umso stärker werden sich beim Belüften die Profile aufgabeln.

In beiden Fällen ist davon auszugehen, daß die eingeschaltete Belüftungsanlage das Hauptvolumen der Raumluft an die Bedingungen der Außenluft angleicht. Am Vormittag des 26. 10. ist offensichtlich nur eine geringe Veränderung der grundsätzlich feuchten Hallenluft durch das Außenklima zu beobachten. Temperatur und rel. Feuchtigkeit in der Halle sind sehr ausgeglichen. Die trockene Außenluft am Nachmittag des 28.10 wirkt sich entsprechend stärker auf das Hallenklima aus. Die gemessenen Temperaturen steigen mit der Höhe, die Relativen Feuchten nehmen entsprechend ab.

Fazit:

Insgesamt kann das Hallenklima in der Grube II als sehr ausgewogen beurteilt werden. Die Luftfeuchtigkeit und die Lufttemperaturen sind horizontal ausgeglichen und vertikal geschichtet. Das Innenklima wird von der Erdoberfläche der Ausgrabung, die als kontinuierliche Wärme- und Feuchtespender dient, und von der über die Lüftungsanlage zugeführte Außenluft gesteuert. Zusätzliche Luftströmungen an den Eingangsbereichen, und lokale Schwankungen der Lufttemperatur im Dachbereich (Erwärmung an Sonnentagen) sind vergleichsweise gering und haben keinen Einfluss auf das Klima in der Grube selbst. Fenster und Besucher haben ebenfalls keine nachweisliche Wirkung auf das Hallenklima. Insgesamt gleicht sich die Hallenluft den feuchtkühlen Verhältnissen der Bodennahen Luft an. Tagsüber wirkt sich die Belüftung deutlich aber gleichmäßig auf das Hallenklima

aus. Entsprechend dem Differenzbetrag zwischen Außenluft und bodennaher Luft neigt sich das Klimaprofil mit der Höhe hin zu höheren Temperaturen und geringeren Luftfeuchtigkeiten. Auch der umgekehrte Fall mit niedrigeren Temperaturen ist denkbar. Der Einfluss der Luftzufuhr nimmt mit der Bodennähe ab. Die Luft im direkten Grubenbereich verändert sich nur bei hohen Differenzbeträgen. Zusätzlich werden Klimaschwankungen in Bodennähe vom Erdkörper mit Veränderungen in der Verdunstungsrate abgepuffert.

**Exemplarische Wochenkurve des Hallenklimas in Grube II**

Im Juni 1999 wurden in der Grube II mehrere exemplarische Testmessungen zum zeitlichen Verlauf des Hallenklimas durchgeführt. Die Temperatur und -Feuchtigkeitskurven für die Woche vom 18.-24.05.99 sind in den Abbildungen 8-10 dargestellt. Daneben sind die jeweiligen Mittel und –Extremwerte der Meßpositionen gegenübergestellt. Die Daten wurden von vier Testostor-171-4 Datenloggern der Firma Testo aufgezeichnet. Das Meßintervall war 15 Minuten. Die genaue Positionierung der Geräte ist in den Abbildungen 4 u. 5 abzulesen.

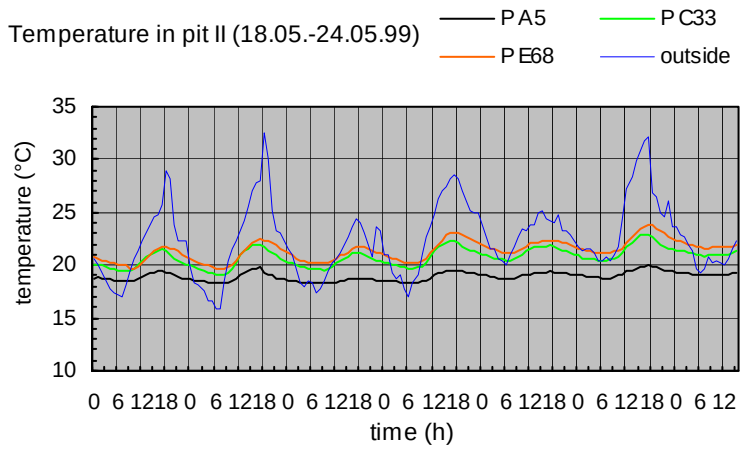
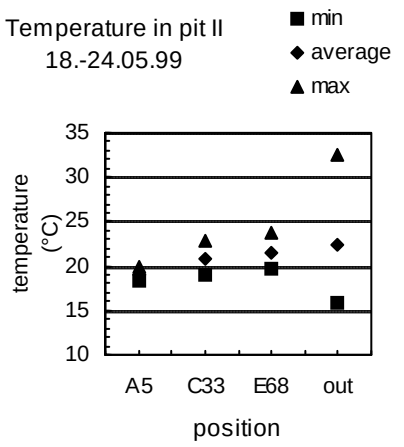



Abb. 8: Zeitliche Entwicklung der Lufttemperaturen in Grube II




Gegenüberstellung der Temperatur-bereiche

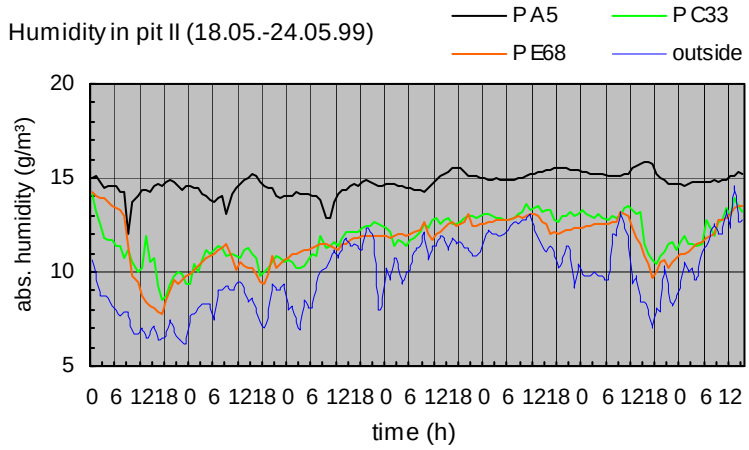
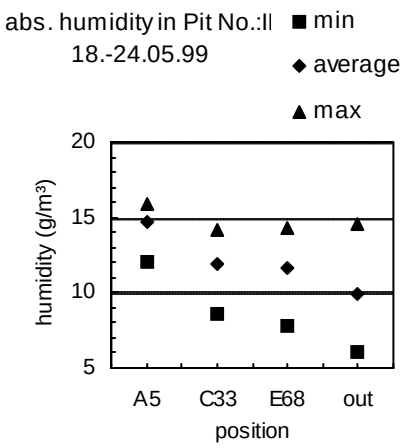



Abb. 9: Zeitliche Entwicklung der absoluten Luftfeuchtigkeit in Grube II




Gegenüberstellung der Feuchtigkeitsbereiche

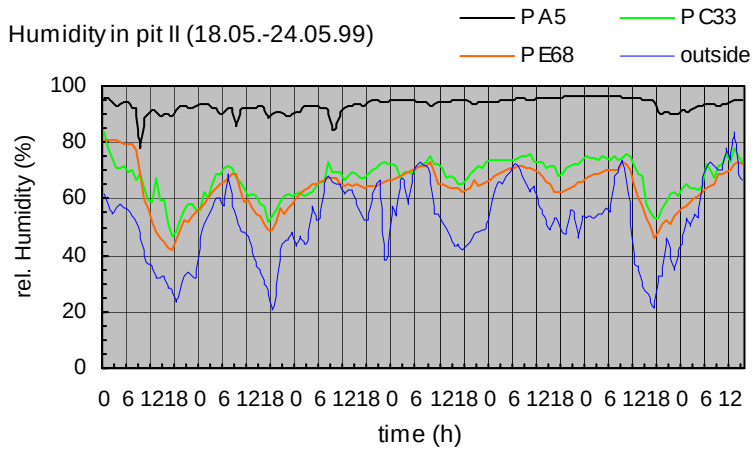
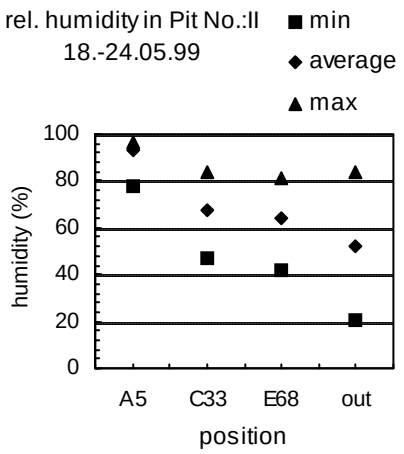



Abb. 10: Zeitliche Entwicklung der relativen Luftfeuchtigkeit in Grube II




Gegenüberstellung der Feuchtigkeitsbereiche

**Ergebnisse der Wochenmessung in Grube II**

Die Lufttemperaturkurven zeigen deutlich, daß sich die Tagesschwankungen der Außenlufttemperatur mit bis zu 17°C Temperaturunterschied (19.05.99) in der Halle stark abgedämpft wiederfinden (Abb.: 8). Die Lufttemperatur am Ziegelboden (p A5) steigt an diesem Tag nur um zwei Grad, die Temperaturen auf den Ebenen C und E jeweils um vier Grad.
Unabhängig von der Tageskurve der Außenluft beginnt der Temperaturanstieg in der Halle immer um 9:00 Uhr mit dem Einschalten der Belüftung. Der Anstieg ist auf allen Ebenen zu beobachten. An der Überlagerung der Anstiegskurven in Ebene C und E ist die belüftungsbedingte Vermischung (Umwälzung) im Zentralbereich der Halle abzulesen. Die bodennahe Luft der kleinräumigen Ausgrabungsbereiche sind von diesen Luftumwälzungen nur wenig betroffen. Nach der Belüftungsphase (16:00-17:00) sinken die Raumlufttemperaturen sofort wieder ab obwohl die Außentemperatur bis mindestens 24:00 über der Innentemperatur liegt. Das beweist die gute Wärmedämmung durch die Hallenkonstruktion und die Wärmepufferwirkung der Erde und Hallenwände, die eingeströmte Warmluft wieder abkühlen. In den absteigenden Temperaturkurven der Nachtstunden entwickelt sich auch zwischen den ebenen C und E ein deutlicher Temperaturgradient. Auch die Gegenüberstellung der Mittel- und Extremwerte (Abb.:8) zeigt, daß die starken Tagesschwankungen der Außentemperatur in der Hallenluft stark abgedämpft werden. Die Mitteltemperatur der Hallenluft liegt zwischen der Mitteltemperatur der Außenluft und der Mitteltemperatur der bodennahen Luft, die von der Bodenwärme dominiert wird.

Auch die Luftfeuchtigkeiten in der Halle sind deutlich von der Klimaanlage abhängig. Die absolute- und die relative Luftfeuchtigkeit (Abb. 9 u. 10) in Ebene C u. E sinken bei laufender Klimaanlage von neun Uhr bis 18:00. Sie gleichen sich der Außenluft an. Nach dem Ausschalten der Belüftung steigen die Luftfeuchtigkeiten wieder an. Die jeweiligen Steigungen der Klimakurven sind dabei proportional zur Differenz zwischen Außenluftfeuchtigkeit und der Luftfeuchtigkeit der in Position A gemessenen Bodennahen Luft. Demgegenüber steht die geringe Beeinflussung der in A gemessenen bodennahen Luftfeuchtigkeit.
Im Mittel bleibt die relative Luftfeuchtigkeit der Bodennahen Luft im Bereich zwischen 90% und 95% konstant. Dieser Wert entspricht vermutlich dem gegenwärtigen Dampfdruck der Erde. Die hohe relative Feuchtigkeit wird in der Regel eingehalten (vgl.:21-24-05.99). Bei Erwärmung steigt die Absolute Feuchtigkeit (>Verdunstung aus dem Erdkörper). Bei Abkühlung geht sie wieder zurück (Feuchtigkeitsaufnahme durch die Erde?).

Nur wenn die Außenluft bei laufender Belüftung kälter als die bodennahe Luft ist, kann sie problemlos in diese Bereiche absinken. Am 18.- 19.- und 20. Mai 99 ist daher ein steiler Abfall in der bodennahen Luftfeuchtigkeit zu beobachten. Der schnelle Wiederanstieg der Kurve ist nur mit der guten Pufferwirkung der Erde zu erklären, die sehr schnell Feuchtigkeit und Wärme an die neu eingeströmte Luft abgibt. Man kann sich gut vorstellen, daß dieser Effekt für die Situation in den Wintermonaten mit trockener und kalter Außenluft eine erhebliche Austrocknung der Erde und der neuen polychrom-konservierten Figuren zur Folge haben wird.
Die Gegenüberstellung der Mittel- und Extremwerte verdeutlicht auch bei der Luftfeuchtigkeit, daß die Hallenluft im Schwankungsbetrag und im Mittelwert zwischen der Außenluft und der Bodennahen Luft liegt. Auch die grundsätzliche vertikale Schichtung der Hallenluft ist an den Mittelwerten abzulesen.

Fazit: Die Ergebnisse der Wochenmessungen bestätigen die Beobachtungen des climate mappings. Das Hallenklima der Grube II ist vertikal ausgeglichen. Ohne Klimaanlage stellt sich in der Halle ein feuchtkaltes, vertikal geschichtetes Klima ein, das eindeutig von der Wärme- und Feuchtigkeitsabgabe der Erde gesteuert ist. Die Belüftungsanlage mischt das Innenklima mit dem momentanen äußeren Klima. Die Wirkung der Klimaanlage ist horizontal gleichmäßig. Die Luftschichten über der Grube werden stärker gestört als die bodennahe Luft in der Grube. Beim Einbringen trockener, kalter Luft ist die Wirkung auf die bodennahe Luft besonders stark. Durch erhöhte Verdunstung wird jedoch ein schneller Ausgleich in der bodennahen Luftschicht geschaffen. Die Austrocknung des Erdkörpers mit den bekannten Folgeschäden wird mit dieser unkontrollierten Belüftung sehr gefördert. Der Einfluß der Besucher und der Eingangsbereiche ist demgegenüber gering.
Andererseits bietet die Belüftungsanlage in der Halle der Grube bei vernünftigem Einsatz eine gute Möglichkeit das Hallenklima zu steuern. Die Austrocknungsgeschwindigkeit und damit die Schadensentwicklung am Erdkörper kann bei einer klimatisch abgestimmten Belüftung reduziert werden. Bei Schimmelbildung ist eine gezielte, lokal begrenzte Belüftung anzuraten.

## Abbauversuche an Festigungsmitteln, biologische Untersuchungen 1999

Thomas Warscheid (MPA Bremen), mit Anmerkungen von Ingo Rogner

1. Ausgehärtete Festigungsmittel in dunklen Rollrandgläsern (10 Stück)
2. Flüssiges Konservierungsmittel PEG 200
3. Flexible Kunststoffstückchen PU und HEMA
4. Lackschicht auf Terrakotta
5. ATP Messungen / Xenotest Versuch

**zu 1** ausgehärtete Verfestigungsmittel in Rollrandgläsern (Plex 6803-1)

In den Gläsern befand sich durch Elektronenstrahlen unter verschiedenen Bedingungen gehärtetes Festigungsmittel Plex 6803-1. Die Polymerfilme hatten eine Schichtdicke von ≥ 1 mm. Von 10 Pilz-Isolaten, die aus der chinesischen Erde isoliert wurden, wurde eine Sporen- Suspension ($10^6$ Zellen/ml) hergestellt und jedes, in den Rollrandgläsern befindlichen, Verfestigungsmittel mit 500 µl angeimpft. Hiernach wurden diese in der Feuchtekammer inkubiert. Nach vierwöchiger Inkubation sahen die vorher klaren und durchsichtigen Verfestigungsmittel aufgrund von aufgenommenen Wasser milchig und trübe aus. Makroskopisch konnte kein Pilzwachstum ausgemacht werden, mikroskopisch waren einige wenige Pilzhyphen zu sehen, höchstwahrscheinlich aufgrund der Animpfung. Ein aktives Wachstum war nicht nachzuweisen. Nach einjähriger Inkubation keine Veränderung.

**zu 2** flüssiges Verfestigungsmittel PEG 200

Zur Durchführung des Agar-Diffusions-Test wurden ML- und CzD-Medium angewandt und diese mit 1 ml Sporensuspension angeimpft und mit dem Drigalsky-Spatel ausplattiert. In jedes der vier ausgestanzten Löcher wurden je 500 µl Verfestigungsmittel PEG 200 pipettiert. Nach vierwöchiger Inkubation konnte keine fungizide Wirkung und kein bevorzugtes Wachstum im Bereich der ausgestanzten Bereiche festgestellt werden. Nach einjähriger Inkubation keine Veränderung.

**zu 3** „flexible Kunststoffstückchen“ PU, HEMA

CzD- (Czapek-DOX, Medium als reine Kohlenstoffquelle) und ML-Medium (Mineral Medium, Mischung verschiedener Mineralsalze, keine Kohlenstoffquelle) werden mit je 1 ml Sporensuspension angeimpft und mit dem Drigalsky-Spatel ausplattiert. Jede Petrischale wird mit 2 Probenstückchen belegt und für vier Wochen inkubiert. Nach vierwöchiger Inkubation sind die Randbereiche von PU und HEMA auf CzD- und ML-Medium überwachsen. Die Pilzhyphen überwuchern vom Nährmedium aus die Probenstückchen, ein Bewuchs der Probestückchen findet nicht statt. Auf ML-Medium ist kein bevorzugtes Wachstum im Bereich der Proben zu erkennen. Nach einjähriger Inkubation keine Veränderung.

**zu 4** Lackschicht auf Terrakotta

Mit 1 ml Sporensuspension angeimpftes CzD- und ML-Medium wurde mit Terrakotta- Lackschicht-Proben belegt. Nach 14-tägiger Inkubation ist der CzD-Agar und auch die Probe stark überwachsen, auf dem ML-Medium ist der Bewuchs deutlich geringer auch hier ist die Probe bewachsen, aber nur gleichschwach wie das Medium.

**Zu 5** Ermittlung der ATP-Gehalte, März 2000, Beprobung durch Catharina Blänsdorf

| Probenbeschreibung | ATP (RLU = relative light units)<br>Je höher der Wert, desto größer ist die Aktivität der Mikro-Organismen. |
|---|---|
| empty 1 | 73.478 |
| empty 1 | 90.260 |
| empty 2 | 75.914 |
| 005/00 | 37 |
| 005/00 | 94.226 |
| 005/00 | 47.037 |
| 006/00 | 35.892 |
| 006/00 | 38.214 |
| 006/00 | 63.976 |
| 003/00 | 48.994 |
| 003/00 | 43.948 |
| 003/00 | 50.411 |
| 002/00 | 44.534 |
| 002/00 | 51.726 |
| 002/00 | 47.857 |
| 004/00 | 106.140 |
| 004/00 | 24.472 |
| 004/00 | 104.524 |
| 001/00 | 36.955 |
| 001/00 | 55.463 |

**zu 5** Xenotest Untersuchung der elektronenstrahlgehärteten Plex Proben

Diese Untersuchungen wurden nicht durchgeführt, da die Untersuchung einen großen finanziellen wie personellen Aufwand bedeutet. Die Zusage dafür erfolgte unter der Prämisse, daß gleichzeitig eine Probe aus einem anderen Projekt der MPA Bremen untersucht wird. Dies ist allerdings im Berichtszeitraum nicht geschehen. Die Xenotest Apparatur entspricht nicht mehr der gültigen DIN Norm, da die Proben nicht auf einer rotierenden Halterung aufgebracht sind, und Flüssigkeiten von Hand auf die Proben aufgesprüht werden müssen. An der MPA Bremen ist Herr Lange für das Gerät zuständig.

# Preliminary summary on the actual results of the microbiological investigations on object and soil samples from the excavation of the Terracotta Army

Date of report: Nov. 1st, 2000

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*Introduction*

Microbial contamination can be observed on nearly all materials inside the excavation sites in Lintong (painted layers, terracotta, wood, soil). Following, it was necessary to analyse the microbial contamination of the terracotta fragments and the excavation sites and to determine its taxonomical composition, distribution and metabolic activity (e.g. impression plates, quantification of air-borne micro-organisms, ATP-analysis), to evaluate the supporting growth conditions (e.g. monitoring of climate data) and to develop effective countermeasures via climate controls and subsequent biocidal treatments (e.g. arrangement of test-fields).

Within the conservation treatments of the polychromy the terracotta figures the deformation (by dehydration) of the organic lacquer layer plays an important role. The conservation treatments have to be carried out at high humidity levels. During the treatment the microbial contamination has to be controlled at humidity levels of 90-95 % RH necessary for the preservation of the non-fixed lacquer layers. It was also necessary to test the consequences of the proposed conservation treatments on the microbial contamination in order to minimise the microbial endangerment of the fragments by an adequate selection of protectives.

The results of the investigations in pit no. 2 revealed that fungi are the most important contamination on the analysed fragments and in the excavation site itself. Especially in the soil samples the presence of actinomycetes could be proved. From the terracotta *in situ* various cyanobacteria could be isolated. The isolated microflora possesses a strong biocorrosive activity, including acid production and manganese-oxidation properties. The microbial contamination was also supposed to cause hygienic problems within the excavation areas.
The regular application of organic biocides has to be evaluated critically. The clayish, loamy soil absorbs and neutralises the active substances of the biocides very rapidly in its clay structure. In the long-term this situation also leads to the microbial mineralisation of the organic biocides and provides an important nutritive source for the reoccurring microflora.

While the function of the lacquer layer as potential nutrient source could not be proven so far, the underlying microflora can infiltrate and detach the paint layer from the fragments. This hidden contamination represents an important problem especially for the preservation of the lacquer layer on the terracotta figures.

Provisional recommendations to control the biodeterioration problems in the excavation sites scheduled regular climate control and ventilation. However a controlled drying, the disinfecting and subsequent biocidal treatment of the loamy soil of the bulwark by medical alcohol and inorganic biocidal solution (e.g. 5-10 % borax in tap water) have to be considered. Further biocidal additives are still going to be tested. The cleaning, impregnation and consolidation of the terracotta fragments showed a considerable relieve from microbial contamination and biodeterioration processes. If necessary at all the application of medical alcohol is sufficient to control the infecting microflora during the conservation treatment.

*Recent and actual investigations*

Recent microbiological studies have revealed that the consolidation polymers (i.e. PU (in PEG-200) or HEMA), proposed for the conservation treatment of the terracotta fragments, are not or only scarcely subject to microbial attack. Some slight contamination problems on HEMA (under extreme favourable moist growth conditions) have to be studied more intensively during the remaining time of the research project.

During the biocide testing in the laboratory of the IWT the best results were obtained by the application of **Mergal S 88** (Allied Signal, Seelze, Germany; active ingredients: zinc-dimethyldithiocarbamat and methylbenzimidazol-2-yl-carbamat) and **CMK** (Bayer, Leverkusen; active ingredient: p-chloro-m-cresol). The inhibitory effect on fungi was more or less sufficient when **PHB-esters**, **Thymol** or **Borax** were applied.
The biocide treatment with **Mergal S 90** (Allied Signal, Seelze; active ingredients: 2-Methylthio-4-cyclopropylamino-6-tert-butylamino-s-triazin, methylbenzimidazol-2-yl-carbamat and n-octylisothiazolin-3-on) and **Sanosil TRdes** (active ingredient: hydrogenperoxide and silver-ions) showed only poor inhibiting effect on the microbial contamination.
It is important to stress the fact that a pre-treatment of the contaminated soil with medical alcohol before the biocide application will increase the effectiveness of the treatment and of the biocide fungal control.

During the recent visit of Dr. Th. Warscheid from November 1$^{st}$ to 5$^{th}$ 2000, it was the objective

(i) to discuss with Zhou Tie and Yan Sumei (Museum of the Terracotta Warriors and Horses) the results of the laboratory investigations on the effectiveness of the tested biocide treatments on the fungi. The biodegradability of consolidating polymers due to fungal attack was also explained.

(ii) to get an overview of the actual development of the fungal contamination in pit No. 1, 2 and 3 and in the new pits around the mausoleum. It was also necessary to evaluate the biocide test-fields created in May 1998 in pit no. 2 (excavation quadrant 8) and the application of Borax (T20 outer wall) created in June 1999 by Dr. Juling (MPA Bremen). In order to continue the laboratory evaluation on the biocide effectiveness Dr. Th. Warscheid took some more contact samples from the soil of contaminated areas in pit No. 2.

(iii) to prepare the set-up of a new biocide test-field in pit no. 006 (planned for Nov. 6$^{th}$ -11$^{th}$ 2000) comprising the most satisfying biocides so far (**Meidi**, **TBZ/BCM**, **Mergal S 88**), an inorganic biocide (**Borax** 5 %) and a new biocides **Parmetol DF 12** (Schülke und Mayr, Norderstedt Germany; active ingredients: Isothiazolinone: 2-octyl-2H-isothiazole-3-on; 5-chlor-2-methyl-2H-isothiazole-3-on, 2-methyl-2H-isothiazole-3-on, [2-(2-butoxyethoxy) ethoxy]-methanol, ethylendioxy-dimethanol). During the arrangement of the test-field the effect of a pre-treatment of the soil surfaces by medical alcohol will be studied as well.

(iv) to talk about recommendations which could be gained from the results of our investigations concerning the fungal treatment which are proposed in the following statements:

The mould growth in pit no. 2 is obviously in retreat, due to the drying of the surrounding soil. Freshly exposed excavation sites show again fungal contamination (i.e. Pit No. 006); here the new biocide test-field will be established to find a suitable treatment to control the fungal contamination. A biocidal treatment of terracotta fragments during and after the conservation treatments seems to be scarcely needed.

Thus, biocidal treatments should be restricted to areas and terracotta fragments on which mould growth cannot be controlled by improvement of the exposure and climatic situation.

Based on our actual knowledge, the biocidal treatment of the soil samples could be performed by the application of a combination of **TBZ** and **BCM** (3000 ppm in ethanol) or by similar commercial products like **Mergal S 88** (2,5 % in water) or **Parmetol DF 12** (3-4 % for the control of active contamination and 1-2 % as protective, diluted in tap water). Considering the possible nutritive effect of synthetic organic biocides to the loamy soil in the long term, the application of inorganic **Borax** (5 % in tap water) to control the mould growth more constantly (and with less toxic effect) has to be advised as an important alternative.

If necessary the biocidal treatment of contaminated terracotta fragments could be performed by the application of **CMK** (0,5 % in *iso*-propanol), **Thymol** (1 % in *iso*-propanol) or **Solbrol M+P** (1,5 % in *iso*-propanol); its application should be restricted to severe contamination problems and the possible interference with the polychromy should be considered.