

AN EXAMPLE OF MEDIEVAL LEAD-GLAZED CERAMIC ALTERATION

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ABSTRACT

A type of physico-chemical alteration of medieval lead glazes is explained by the presence of sulphate-reducing bacteria in the surrounding media. This alteration occurs in all anaerobic environments of organic decomposition such as rubbish dumps and latrines, as evidenced by many archaeological examples.

The hydrogen sulphide (H_2S) liberated during decomposition of organic matter results in precipitation of lead sulphide (PbS) and in a partial recrystallization of the glaze.

The chemical composition of the glaze, particularly its lead content, and the conditions during preparation and firing (developing, at different degrees, the cracked and bubbly aspect) are the parameters controlling the intensity of the degradation process and consequently the observed phenomenon.

Riassunto

Un tipo di alterazione chimico-fisica di vetrine piombifere medioevali viene spiegata con la presenza di batteri solfo-riducenti nell'ambiente circostante. Questa alterazione avviene in tutti gli ambienti anaerobici di decomposizione organica quali discariche e latrine come mostrato da molti esempi archeologici.

Il solfuro d'idrogeno (H_2S) liberato durante la decomposizione di materia organica provoca la precipitazione di solfuro di piombo (PbS) e una parziale ricristallizzazione della vetrina.

La composizione chimica della vetrina, in particolare il suo contenuto di piombo e le condizioni di preparazione e cottura (che sviluppano a differenti livelli l'aspetto fessurato e bolloso) sono i parametri che controllano l'intensità del processo di alterazione e conseguentemente il fenomeno osservato.

Introduction

This study deals with a physico-chemical alteration of a medieval lead glaze. The studied samples were uncovered during archaeological excavations at Cany-Barville (Seine-Maritime, France). Many of these glazed potteries presented a somewhat unfamiliar aspect: a deep blue-green to grey or black glaze but still brilliant. Other shards present a yellow to pale yellow glaze which characterizes a lead glaze applied on top of a light paste. Some shards of these two groups belong to the same vessel (Fig. 1, Tav. III). Red underglaze decorations are visible through the yellow glaze but indiscernible beneath the blue-green one. It is not in question as to which glaze is the abnormal one.

Our objectives are therefore to trace the origin of this blue-green or black colour and the mechanism of its formation.

Experimental techniques

Samples of the yellow and of the blue-green glazes were observed using optical and scanning electron microscopy (SEM) and analysed semi-quantitatively using an energy dispersive spectrometer. They were also studied by X-ray diffraction. Partial chemical analyses (for sulphur) were carried out. Some experiments were conducted to reproduce the assumed alteration phenomena.

Results

1. Preliminary observations

- Examination of an altered sample under binocular microscope showed some brilliant particles of a grey-black compound contained within most of the cracks and bubbles (Fig. 2, Tav. III). These particles are absent in the unaltered sample (Fig. 3, Tav. III).

- These particles disappear upon refiring ($< 600^{\circ}\text{C}$) or upon treatment with hydrogen peroxide (H_2O_2) or dilute acids and produces a yellow colour which is thought to be the original one (Fig. 4, Tav. III). These observations permit the rejection of some hypotheses on the presence of carbon or metallic lead and favour the hypothetical presence of lead sulphide (discoloration by H_2O_2 and especially the characteristic odour of H_2S usually produced when a metallic sulphide is treated with dilute acids).

- The inverse was then tried: an unaltered sample was placed in a reducing solution of sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) and in an aqueous solution of H_2S . In both cases the yellow glaze turned a blue-green colour comparable to that of the altered glaze under study.

2. Chemical analysis

A chemical analysis of altered and unaltered glazes confirmed the presence of sulphur in the former (1.6 wt.% S which corresponds approximately to 12 wt.% PbS), and its almost complete absence in the latter.

3. Semi-quantitative analysis using Energy Dispersive Spectrometry (EDS)

Semi-quantitative analyses were effected using EDS under high magnification (Fig. 5) on an altered glaze: in grey-black zones (cracks, bubbles, etc.) and light zones, and on an unaltered glaze.

In spite of the superposition of principal lines of lead and sulphur, it was noted that the lead proportion, compared to that of silicon and aluminum, is higher in the altered zones than in the unaltered zones. So, it is thought that there is some diffusion and concentration bias of lead towards cracks, bubbles and the surface of the glaze.

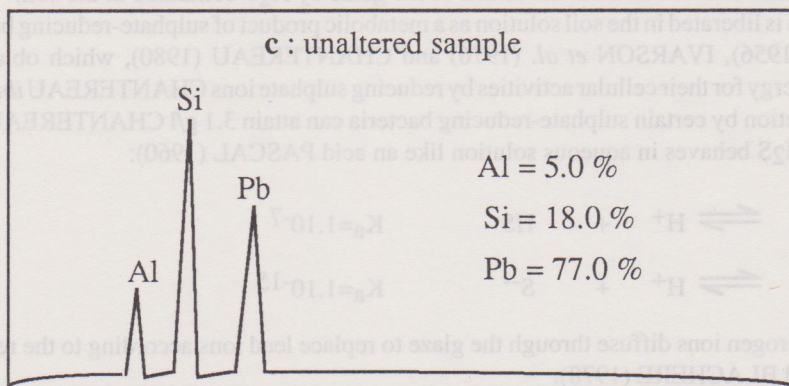
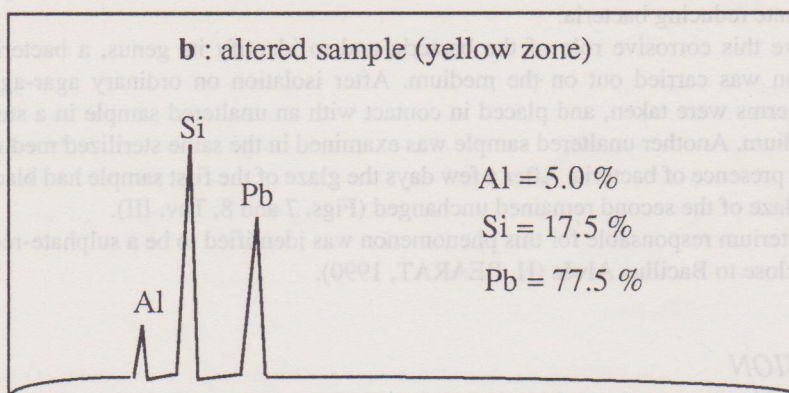
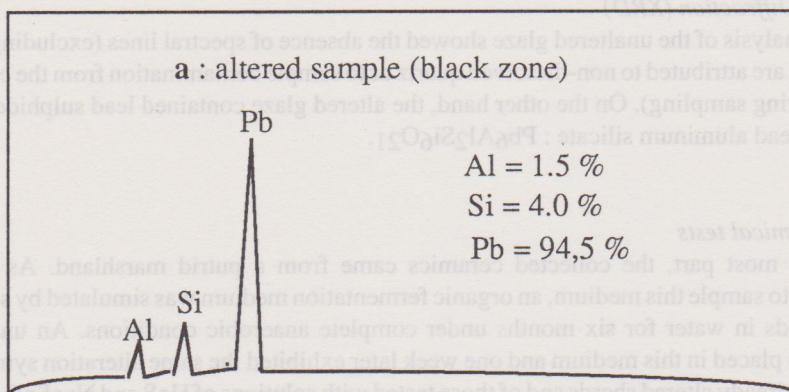


Fig. 5 a, b, c - Semi-quantitative analyses using Energy Dispersive Spectrometer (EDS)

4. X-Ray Diffraction (XRD)

XRD analysis of the unaltered glaze showed the absence of spectral lines (excluding some lines which are attributed to non-dissolved quartz or to sample contamination from the ceramic support during sampling). On the other hand, the altered glaze contained lead sulphide (PbS) as well as lead aluminum silicate : $\text{Pb}_6\text{Al}_2\text{Si}_6\text{O}_{21}$.

5. Biochemical tests

For the most part, the collected ceramics came from a putrid marshland. As it was impossible to sample this medium, an organic fermentation medium was simulated by soaking vegetal seeds in water for six months under complete anaerobic conditions. An unaltered sample was placed in this medium and one week later exhibited the same alteration symptoms as those of already altered shards and of those tested with solutions of H_2S and $\text{Na}_2\text{S}_2\text{O}_4$. (Fig. 6, Tav. III).

The presence of H_2S in this medium can be attributed only to microorganisms, especially to the sulphate reducing bacteria.

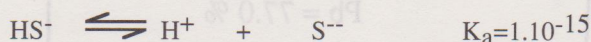
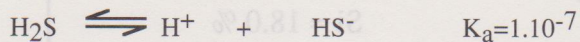
To prove this corrosive role of the bacteria and to identify its genus, a bacteriologic investigation was carried out on the medium. After isolation on ordinary agar-agar, the dominant germs were taken, and placed in contact with an unaltered sample in a sterilized culture medium. Another unaltered sample was examined in the same sterilized medium but without the presence of bacteria. After a few days the glaze of the first sample had blackened while the glaze of the second remained unchanged (Figs. 7 and 8, Tav. III).

The bacterium responsible for this phenomenon was identified to be a sulphate-reducing bacterium close to *Bacillus Alvéé* (H. BEARAT, 1990).

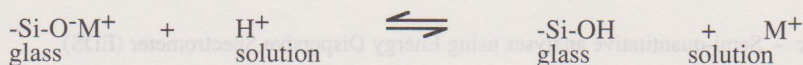
DISCUSSION

The deep blue-green colour of the altered glaze, in fact a mixture of yellow and grey-black, is due to the presence of PbS. It appears only in the cracks, the bubbles and some surface areas. This phenomenon resulted from the attack of the glaze by H_2S contained in the soil.

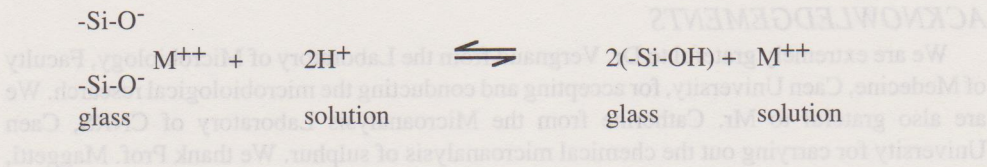
This gas is liberated in the soil solution as a metabolic product of sulphate-reducing bacteria MILLER (1956), IVARSON *et al.* (1976) and CHANTEREAU (1980), which obtain the required energy for their cellular activities by reducing sulphate ions CHANTEREAU *ibid.* The H_2S production by certain sulphate-reducing bacteria can attain 3.1 g/l CHANTEREAU *ibid.* Resultant H_2S behaves in aqueous solution like an acid PASCAL (1960):



The hydrogen ions diffuse through the glaze to replace lead ions according to the reaction WOOD and BLACHERÉ (1978):



or :



The cation "M" called a modifier, can be monovalent (like K^+ or Na^+) or bivalent (such as Pb^{++}). When liberated in solution, Pb cations combine with sulphide ions (S^{--}) to give PbS which precipitates.

The corrosion of glass by acid solution with the liberation of modifiers (K^+ , Na^+ , Pb^{++} , etc.) is a familiar phenomenon CLARK *et al.* (1976), WOOD and BLACHERE (1978 a, b) and KRAMER *et al.* (1980).

KRAMER *et al.* (1980) showed that liberation of the cations depends on the number of neighbouring "non-bridging" oxygen atoms (Sphere of Influence Theory). This number can be calculated for each cation from its concentration in the glass and the radius of its sphere of influence. WOOD and BLACHERE (1978) observed that the liberation of Pb^{++} , K^+ and Na^+ varies linearly with " \sqrt{t} " (t =time) and that corrosion is proportionally related to the concentration of the cation and that it is inversely proportional to the concentration of silica and alumina.

The presence of lead aluminum silicate ($\text{Pb}_6\text{Al}_2\text{Si}_6\text{O}_{21}$) in the altered glaze and its absence in the unaltered glaze shows that the alteration process due to H_2S (liberation and migration of Pb^{++} followed by precipitation of PbS) is accompanied by the modification of the glass (glaze) structure leading to its recrystallization and partial destruction.

This phenomenon is visible particularly in cracks and bubbles because it is at these sites where the glaze could have come into contact with the surrounding medium. It does not appear all across the glaze surface as the samples have been cleaned before study. However we observe that some zones, which are more altered than others, have a grey-black metallic aspect and leave some black traces on the hand if touched (Fig. 9, Tav. III). These zones appear to be thicker and certainly richer in lead. In fact, we can detect an enrichment in silica and alumina contents of the glaze towards the ceramic body. The enrichment of the glaze in lead towards the outer surface lowers its resistance to acid attack from surrounding medium and therefore increases the degradation of these zones with respect to those zones containing lower lead contents.

CONCLUSION

This type of alteration concerning lead glazes, is not exceptional. It results in all anaerobic media of organic decomposition, especially in latrines and rubbish dumps as evidenced by many archaeological cases.

It is understood, however, that the chemical composition of the glaze, especially its lead content and its preparation and firing conditions (which develop the physical aspect: cracks, bubbles, thickness, etc.) are the parameters which control the intensity of this degradation process and consequently the observed phenomenon.

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a

b



Fig. 1 a, b - a: fraction of altered sample; b: fraction of unaltered sample

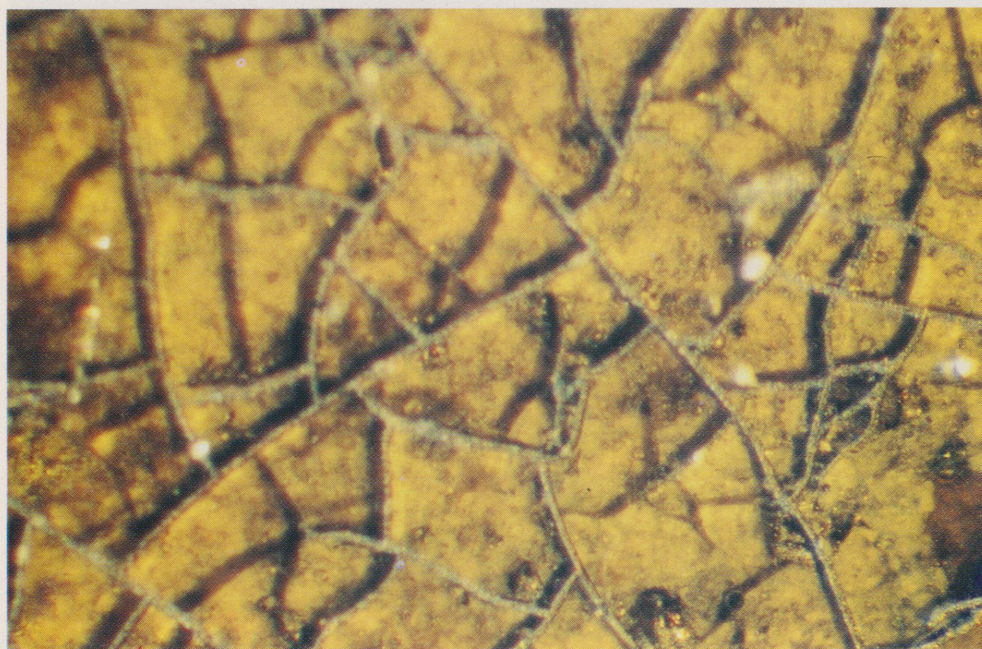


Fig. 2 - Altered sample

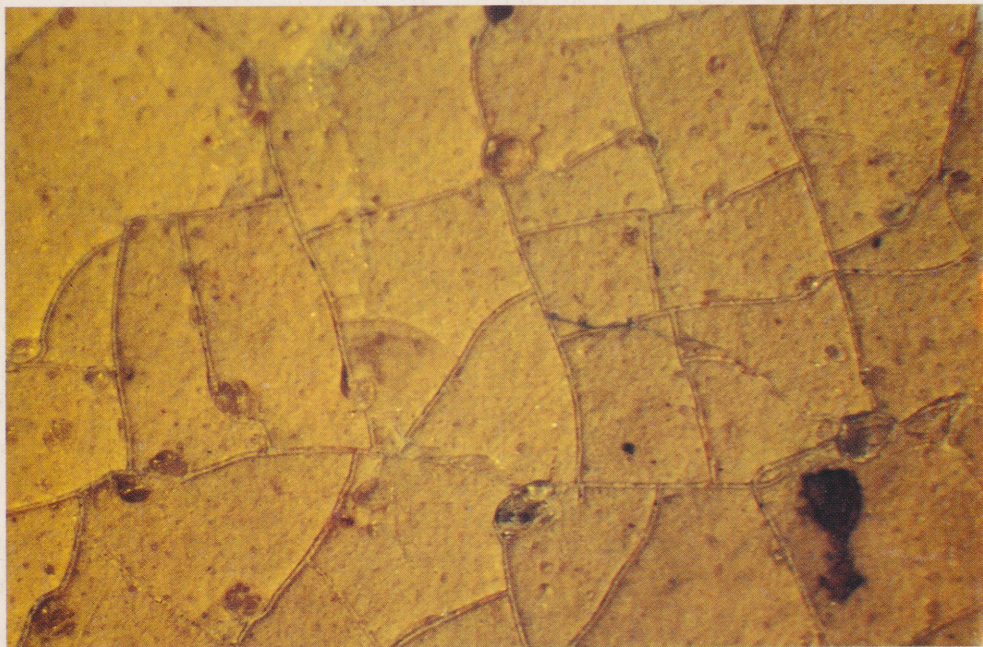


Fig. 3 - Unaltered sample

0 1 mm



Fig. 4 - a: fraction of altered sample; b: fraction of the same sample after refiring at 900°C

0 5cm

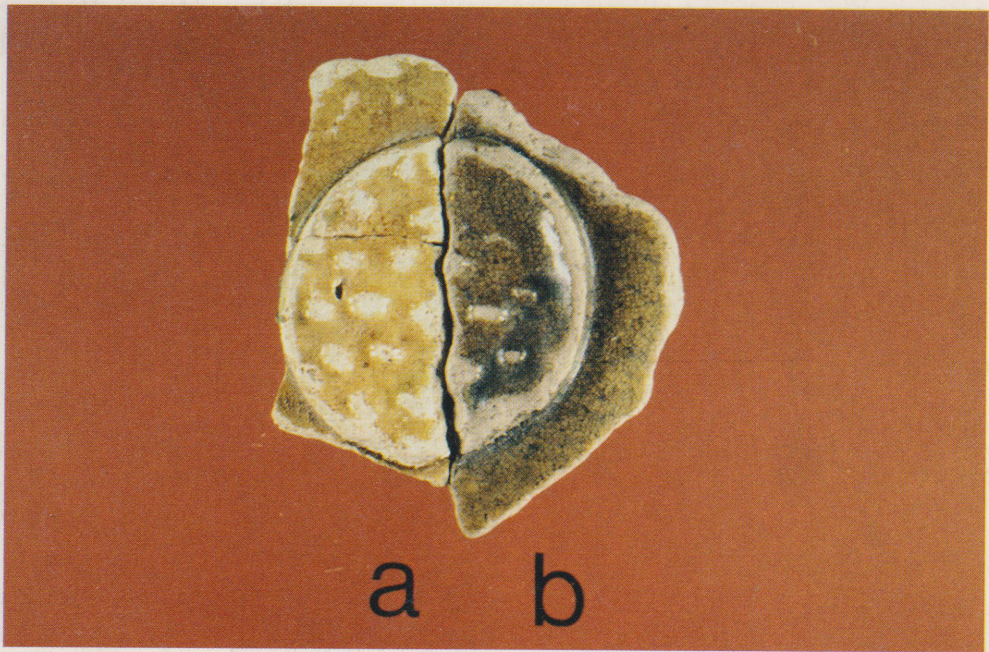


Fig. 6 a, b - a: fraction of unaltered sample; b: fraction of the same sample after one month in a putrid organic medium

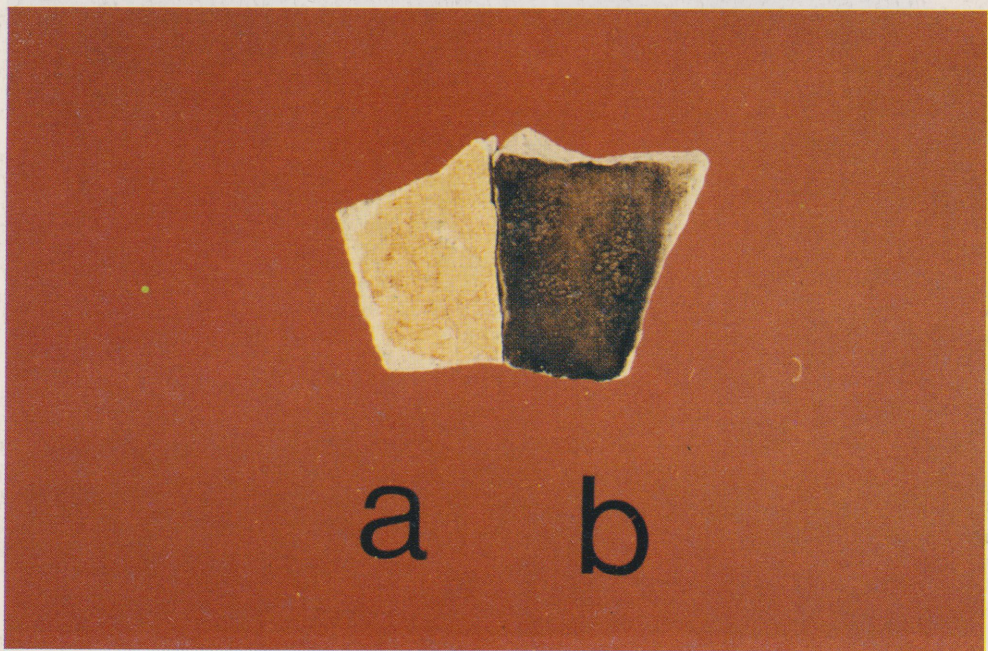


Fig. 7 a, b - a: fraction of a glazed sample after a month in a sterilized culture medium; b: another fraction of the same sample after a month in the same medium but with sulphate reducing bacteria

a

b

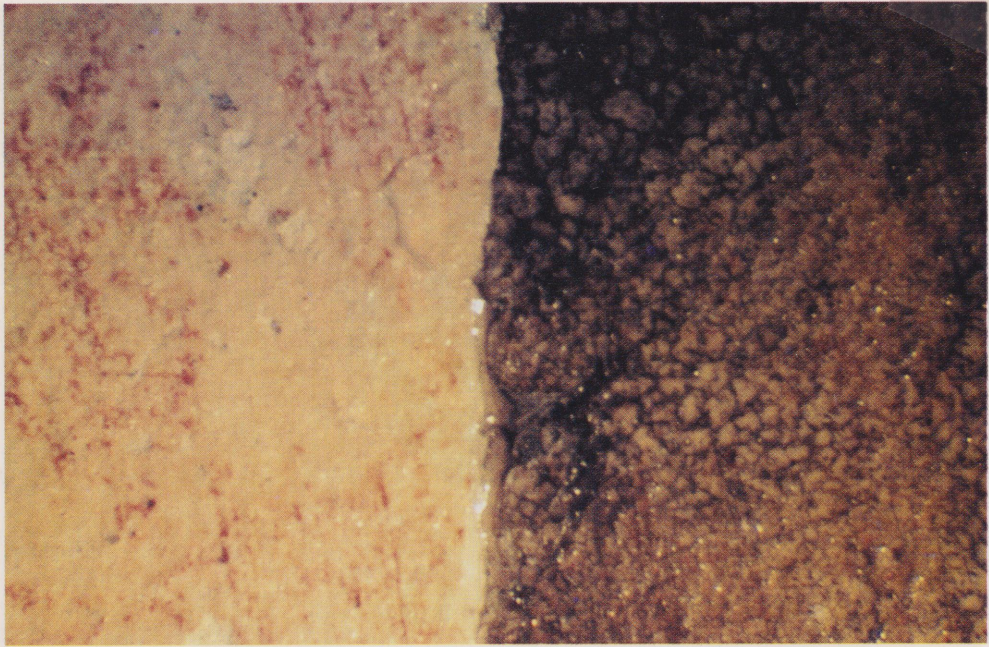
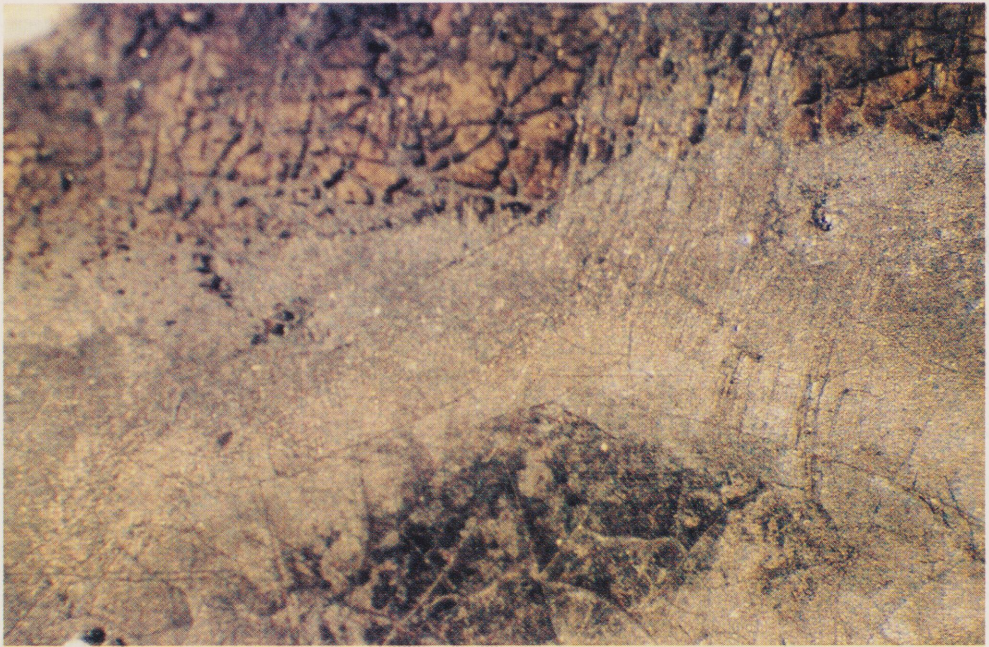


Fig. 8 a, b - The same samples as on figure 7 a, b

0

2 cm



0

2 mm

Fig. 9 - Altered sample: metallic grey-black phase in cracks and on surface of thicker zones of the glaze