LIME PLASTER, CEMENT AND THE FIRST PUZZOLANIC REACTION

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Abstract : *During the Pre-Pottery Neolithic, lime plaster was produced for architectural and artistic purposes all over the Middle East. The material is one of the earliest evidences of pyrotechnology. A sample of plastered floor from Aşıklı Höyük (Anatolia) was analysed for its chemical and mineralogical composition. It consists of lime mixed with ash-particles from (volcanic) tuffs. Puzzolanic reactions are shown between the two materials, which led to the formation of (hydrated) Ca-Si(-Al)-phases. The problem of the detection of cement phases in lime plaster is discussed. Hypotheses are presented that plant ashes could have acted as pozzolonas in lime too.*

Résumé : *Pendant la période Néolithique PPNB, dans tout le Proche-Orient le plâtre fut produit pour des besoins architecturaux ou pour des produits artistiques. Ce matériau est l'une des premières évidences de la pyrotechnologie. Un échantillon en provenance de Aşıklı Höyük (Anatolie) fut analysé en vue de voir quelle était sa composition chimique et minéralogique. Il est constitué par du calcaire mélangé avec des particules cendreuses d'origine de tuffs (volcanique). D'évidentes réactions pouzzolaniques entre les deux matériaux ont abouti à la formation de phases de Ca-Si(-Al) hydraté. Le problème de la détection de phases de ciment dans la chaux est discuté. Nous présentons l'hypothèse que des cendres résultant de la combustion de plantes ont pu agir aussi comme agent pouzzolanique.*

Key-Words : *Pre-Pottery Neolithic, Lime plaster, Volcanic tuffs, Pozzolanas, Cement phases, Aşıklı Höyük.*
Mots Clefs : *Néolithique précéramique, Plâtre, Tuffs volcaniques, Réactions pouzzolaniques, Ciment, Aşıklı Höyük.*

INTRODUCTION

Among a growing number of publications, which are dedicated to an exciting innovation of materials' processing and pyrotechnology during the Neolithic Revolution, three substantial contributions should be mentioned. It was Frierman who announced this innovation from the archaeological point of view, a few years later Kingery and his colleagues intensified the topic from the materials scientists viewpoint [1] : It concerns the production of plaster made of limestone or of gypsum which spread over the Middle East during the Pre-Pottery Neolithic, phase B (PPNB), *i.e.* between approximately 8 700 and 7 000 BC. In many dozens of settlements from the PPNB, lime plaster was utilized for floor construction inside the houses, for sculpturing faces of skulls and masks or for other artistic purposes such as making beads. Dishes and vessels published for a long time as "white ware" or "vaisselle blanche" were considered among these lime plaster finds. The authors mentioned above pointed out that plaster production, the first hard evidence for the controlled use of fire, the precursor of fired ceramic, had decisive impact on the development of pyrotechnology in pottery making and later in metallurgy. Recognizing the complicated and multistep manufacture necessary to obtain these materials, they adequately addressed plaster production as one of the earliest high-tech crafts, a hallmark of the PPNB in the Middle East. They concluded that the over-regional distribution of such a

1. FRIERMAN, 1971 ; GOURDIN and KINGERY, 1975 ; KINGERY *et al.*, 1988.

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complicated craftsmanship would have been only possible by a developed social and economic organisation and differentiation. For the most part, this would have been related to the processing of the material itself that was most probably based on an experience and a real know-how of burning limestone to quicklime, grinding and slaking the fired product, mixing with various additives, shaping and smoothing a paste in a skilled way, etc.

Lime plaster production was discovered at dozens of early Neolithic sites in the Middle East, and from the site of Aşıklı Höyük in Central Anatolia as well. According to Gourdin and Kingery [2], the plaster floors were made of recarbonated lime with additives of uncalcined limestone. No clay or gypsum constituents were present in the material. However, the authors observed inclusions of large mineral particles in the plaster but they did not give any comments concerning them.

In this contribution, mineralogical and chemical observations of a sample of plastered floor from Aşıklı Höyük, and two samples of volcanic rocks from the area around the site will be discussed to call attention to a chemical reaction that may be seen as a discovery or an invention of a new materials technology : the puzzolanic reaction [3].

THE LOCATION OF AŞIKLI HÖYÜK

Aşıklı Höyük is located 25 km south-east of Aksaray, near the village of Kızılkaya, which gave its name to a widespread formation of volcanic rocks in this region. The settlement was built on an alluvial flood plain of the Melendiz river. It is surrounded by tuff cones and other volcanic-sedimentary (pyroclastic) rocks which are due to Miocene and Pliocene volcanic activities and are a characteristic feature of the geomorphology of wide areas in Cappadocia [4]. The Kızılkaya Ignimbrite formation covers an area of some 5 000 km^2. These volcanic rocks are of dacitic composition (*i.e.* high in silica) and originated from a fallout of hot, tiny particles of rock fragments, minerals such as quartz, feldspar, mica, pyroxene, hornblende etc., ashes, pumices, with a high content of glass mixed with hot gases. They were welded together after deposition.

The main cultural layer of the site of Aşıklı, level II, is dated approximately to the middle of the 8th millennium BC, *i.e.* the Pre-Pottery Neolithic. The houses in the village were built of mudbricks. Limestone was also used for wall construction in the settlement, the oldest known in Anatolia. The so-called T-building had most probably a ritual function. This building has a 6-8 cm thick red-colored floor, which was suggested to be made either of gypsum or of a cement-type mortar made of grounded (volcanic) tuff mixed with clay [5]. White lime plaster covered the walls. Next to plastered floors objects made of baked clay and hot-worked copper beads made of native metal have been found which also prove high-temperature craftsmanship [6].

THE MAKING OF LIME PLASTER AND RELATED PRODUCTS : BASICS

Plaster chemistry with special attention to ancient technologies has already been published in detail elsewhere [7]. Basic equations are :

I $CaSO_4\ 2H_2O \rightarrow CaSO_4 \cdot 1/2\ H_2O + 3/2\ H_2O$ (plaster of Paris)

II $CaCO_3 \rightarrow CaO + CO_2$ (quicklime)

The production of plaster of Paris is the easiest. Gypsum is burned at temperatures between 150 and 400 °C. The calcination of limestone to quicklime (CaO) is more complicated and needs higher temperatures. The reaction starts slowly at 533 °C, and proceeds in a charcoal bed, under slightly reducing conditions, at 780 °C. A fast reaction takes place at approximately 900 °C, in bright heat under moderate reducing conditions.

When water is added, plaster of Paris reverts to its original chemical composition; it is soft and not much water resistant. Quicklime forms portlandite according to

III $CaO + H_2O\ (\rho)\ \ Ca(OH)_2$

Portlandite is a white powder, which, with additional water, gets a pasty consistence. It can be shaped, and by evaporation of water, it recarbonizes to $CaCO_3$, reaches a higher hardness, and is more or less water resistant.

From the pyrotechnological viewpoint, lime plaster production is a rather simple process; in its primitive version, it

2. GOURDIN and KINGERY, 1975.
3. This paper is a slightly modified version of a lecture presented by the first author as part of his habilitation at the Ruhr-University Bochum in June 1998. Detailed investigations in preparation by Yalçin.
4. ESIN, 1999; ESIN and HERMANKAYA, 1999.
5. ESIN, 1993, 1998; Investigations of Prof. Geckinli, cited in ESIN and HERMANKAYA, 1999.
6. YALCIN and PERNICKA, 1999.
7. GOURDIN and KINGERY, 1975; REHDER, 2000.

does not require sophisticated kilns or furnaces such as the ones developed in the early stages of pottery production. It does not need the strong reducing conditions that are necessary in extractive metallurgy. Temperatures needed can be reached in a windblown camp fire, certainly in a pile of wood [8] or in simple stone settings as the ones observed in the cave of Hayonim [9]. In addition, it does not require special treatment of biomass to prepare densely packed fuel with high heating values such as charcoal. However, a long-lasting firing process is necessary to produce quicklime. As known from traditional craftsmanship, it takes hours and days until heat penetrates and decomposes lumps of limestone to quicklime [10].

This process needs sufficient amounts of biomass, in form either of dung, peat, straw, or of wood from shrubs and trees. Considering the extent of lime plaster production postulated for numerous sites in the Near East, the discussion of fuel problems quickly found a literary forum : the use of tons of burned lime and gypsum during the PPN for architectural purposes was believed to have caused vast deforestations and hence the first human environmental damages. Considering settlements such as 'Ain Ghazal (Jordan) or Yiftahel (Israel), where more than hundred square meters, or, alternatively, tons of plastered floor have been used in a number of houses, it was suggested that the use of plaster had extraordinary impacts on the surrounding landscape [11]. Calculations suggest the ratio biomass : quicklime being between (2-5) : 1 ; this means that 3.5-8 tons of wood would have been necessary to produce quicklime for one single house [12]. The question whether or not these amounts of fuel had serious impacts on the climate and vegetation in the Middle East at this period remains open. If we consider that plastered floors found in the Middle East were made only for a certain percentage of quicklime itself [13] and were mixed to large extents with various additives, the edges of the problem are taken off. It was argued, that settlements, food, and fibre were probably much more important factors in land clearance considering the needs of arable land, pasture and places for housing. Grazing of free-ranging goats might have been one of the factors that inhibited considerably the vegetation to regrow [14].

8. AFFONSO, 1997, in a firing experiment, produced quicklime from limestone in a pile of wood measuring 1.2 × 1.3 × 0.7 m.
9. BAR-YOSEF, 1983.
10. GOURDIN and KINGERY, 1975.
11. ROLLEFSON and KÖHLER-ROLLEFSON, 1992 ; REDMAN, 1999.
12. RONEN *et al.*, 1991 ; KINGERY *et al.*, 1992.
13. AFFONSO, 1997.
14. REHDER, 2000.

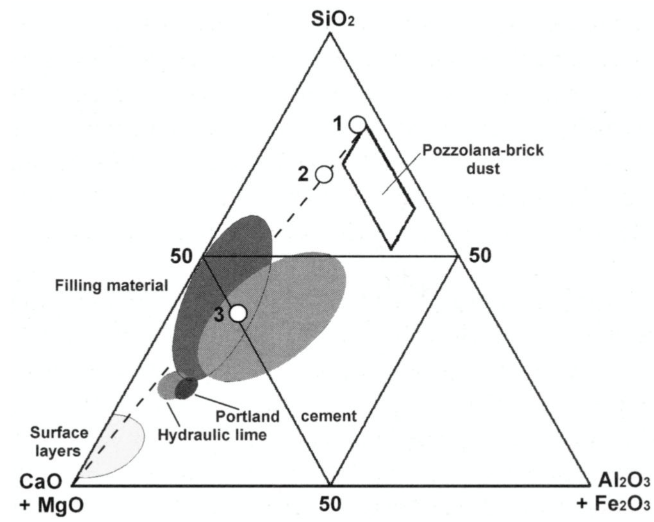

Fig. 3 : *Composition of the Kızılkaya-Ignimbrite (1), of a (volcanic) tuff from Güvercin Kayasi at Aksaray, some 3 km southeast of Aşıklı (2), and of plastered floor from Aşıklı (3) in the C-A-S-system (SiO_2 – CaO+MgO – Al2O3+Fe2O3). The analyses indicate a mixing between limestone (or lime) and the volcanic rocks, which, in turn, are almost identical with modern pozzolanic materials. For comparison, the limited range of (modern) hydraulic lime and portland cement are shown. The grey ellipsis provides compositions of (PPN-) plastered floors from Nevalı Çori (after data from AFFONSO, 1997) and the dark grey one of modeled skulls from Jericho (after data from GOREN and SEGAL, 1995).*

The equations mentioned above are based upon pure raw materials. In nature, limestone may contain varying concentrations of magnesium, aluminum, and silica. These "clay-components" lead to mixtures roughly classified as calcareous marl, marl, and argillaceous marl [15], the last being the raw material for portland cement (fig. 3). This hydraulic binder is characterized by compounds of CaO with silica, alumina, and possibly iron oxide (clinker phases), which, *in modern times*, have been produced by sintering or melting at temperatures that are much higher – approximately 1 400 °C – than those required for burning lime. These extremely high temperatures, however, are not indispensably necessary : as shown by a series of experimental laboratory work [16], clinker phases are formed already at temperatures of ca. 750 °C. When mixed with water, these compounds are hydrated and form a variety

15. After LUFTSCHITZ, cited in CORRENS, 1968.
16. KLENK, 1987.
17. In materials science and process mineralogy, the following abbrevations are in use, among others : C for CaO, S for SiO_2, A for Al_2O_3, f for FeO, H for H_2O.

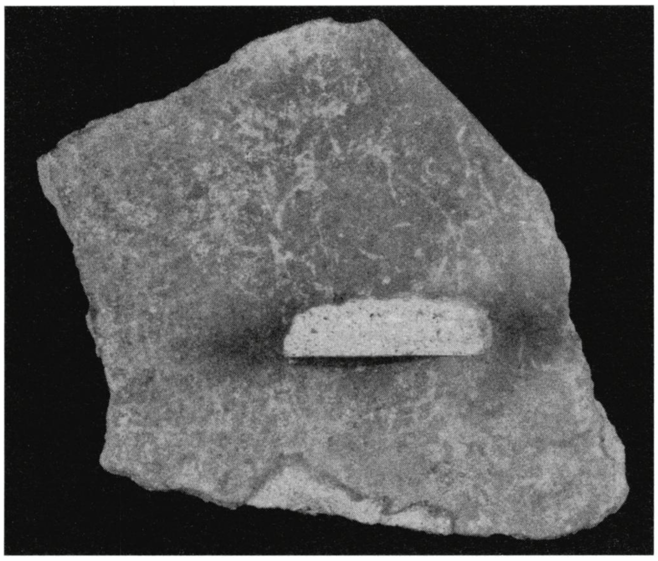

Fig. 1 : *Aşıklı Höyük, level II, T-building (Pre-Pottery Neolithic B, ca. 7 500 BC). Sample from an architectural lime plaster floor. Red surface colored by hematite. The sample consists of burned lime mixed with volcanic ashes and is considerably hardened by pozzolanic reaction. Width of the sample : 8 cm.*

of (water-insoluble) cement phases. These are Ca-silicate-(alumina-)hydrates (CS(A)H– or Taylor-phases) [17].

The utilization of different marls instead of pure limestone was previously observed in PPN context [18], and it was actually proposed by engineers working in the cement industry that early lime plaster production could be seen as a precursor of cement production [19]. Hence, there was considerable effort by many scholars to determine cement phases in ancient objects by analytical methods to prove this hypothesis [20]. This undertaking was hardly successful for two reasons. First, in many cases lime plaster analysed contained remains of fossils and minerals which indicated a rather low firing – not sufficient for the reaction described above. Second, it is extremely difficult to detect cement phases in the small amounts in lime plaster that we have in prehistoric times. They are not stable in the course of weathering, and when built by low temperatured pozzolanic reactions, they form badly crystallized hydrates and geles of non-defined and variable composition [21].

The formation of cement phases by pozzolanic reactions is the "cold way". If siliceous materials such as volcanic ashes, flye ashes, or sediments such as kieselgur (diatomaceous earth), high in silica (glass), in a state of high reactivity [22] are mixed with with portlandite in the presence of water, they develop also hydraulic properties by formation of CS(A)H-phases. They are called puzzolanas after the locality of Pozzuoli near Naples, where volcanic tuffs were utilized in Roman antiquity to produce *opus caementitium* [23]. The puzzolanic reaction is closely connected with the architectural craftsmanship of this period; it is generally accepted that this technology arose during the late first millennium BC. Comparable to the materials mentioned are the tuffs of the island of Santorin which were extensively used during the last century at the channel of Suez for the construction, and volcanic pyroclastic rocks (ignimbrites) widely distributed in Cappadocia as well. Artificial puzzolanas are pulverized, fired bricks.

PLASTERED FLOOR FROM AŞIKLI HÖYÜK

With special focus to detect CS(A)H-phases, a sample of extraordinary hard plastered floor (lime plaster) from Aşıklı Höyük, level II, (fig. 1) was analysed for its chemical and mineralogical composition. The surface of the cm-thick sample was red colored by a thin layer of powdered hematite. A fragment was cut to provide sufficient material for chemical analyses and X-ray diffraction, and to prepare a surface-polished thin section.

The chemical composition of the floor (table 1) was analysed by ICP-OES (Type TJA IRIS/AP); it is characterised by high concentrations of CaO (38 wt. %) and of SiO_2 (31 wt. %). In addition, major amounts of Al_2O_3 (7.2 wt. %) were measured. The loss of ignition is 16.5 wt. %, it includes CO_2 and H_2O. This indicates that most of the CaO is due to high contents of $CaCO_3$ or limestone, respectively, in the floor, but it also indicates that it partly formed compounds with silica and possibly alumina. Microscopic examination under polarised light showed that plenty of inclusions such as feldspar (albite, microcline), partly Y-shaped glass particles, and quartz (fig. 2) were distributed in the sample. As previously

18. TUBB and GRISSOM, 1995; GRIFFIN *et al.*, 1998.
19. MALINOWSKI, 1991.
20. The analytical determination of CS(A)H-phases in prehistoric materials is difficult and doubtful due to the decomposition of these phases. GOURDIN and KINGERY, 1975, suggested CSH-phases for Tell Ramad; AFFONSO, 1997, GRIFFIN *et al.*, 1998, suggested them for 'Ain Ghazal.
21. PETZOLD and HINZ, 1979.
22. *I.e.* before SiO_4 units polymerize and progressively increase in size and complexity to $(SiO_2)_x$-compounds.
23. LAMPRECHT, 1996.

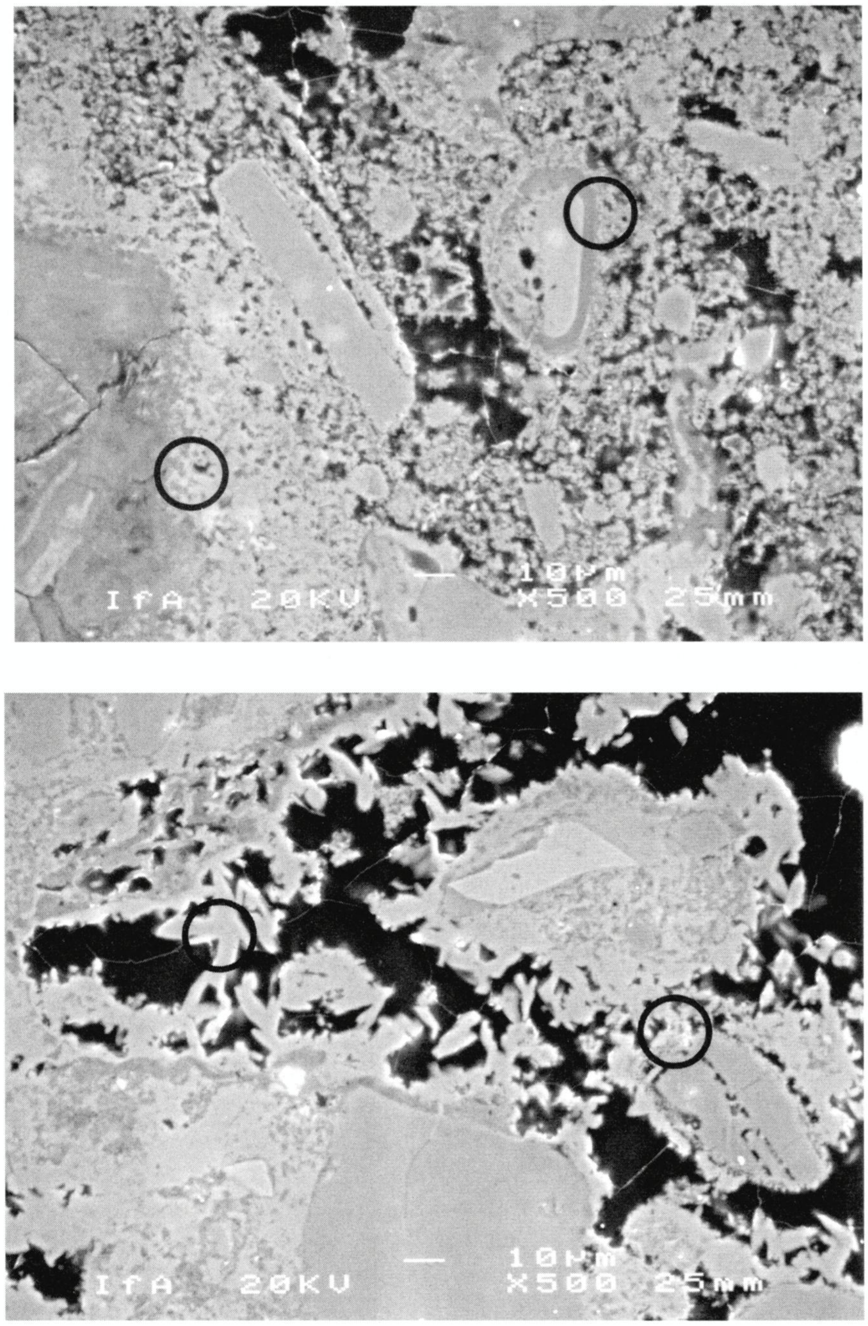

Fig. 2a, b : *Aşıklı Höyük, level II, T-building (Pre-Pottery Neolithic B, ca. 7 500 BC). Microtexture of the sample in figure 1 showing inclusions of volcanic ashes such as glass, feldspar and quartz. At the transition to the fine grained matrix of lime formation of Ca-Si-Al-(H?)-phases (○) such as gehlenitehydrate by pozzolanic reactions. Surface-polished thin section, scanning electron micrograph, back-scattered mode.*

Table 1 : *Chemical composition of volcanic rocks and of lime plaster from Aşıklı Höyük. Note the high concentrations of silica, CaO and of the high loss of ignition (LOI) which is mainly due to CO_2 from lime. 1. Kızılkaya Ignimbrite, 30 km east of Aşıklı Höyük (BATUM 1975). 2. (Volcanic) tuff, excavation Güvercin Kayasi, Aksaray, 3 km southeast of Aşıklı Höyük. 3. plaster floor, Aşıklı Höyük.*

	1	2		3	
SiO_2	71,90	53,0		31	●
TiO_2	0,24	0,25		0,4	
Al_2O_3	13,0	5,66		7,2	
Fe_2O_3	1,65	2,03	+ Lime	2,3	
MgO	0,20	3,14	(CaO) ⇒	2,0	
CaO	3,34	13,6		38	●
Na_2O	3,06	2,22		1,4	
K_2O	3 89	4,38		1,3	
LOI	2,0	11,5		16,5	●

suggested they could be identified as components from volcanic rocks or ignimbrites. These inclusions were consistently surrounded by coronas of tiny, often sub-microscopic fibrous or long-prismatic crystals or amorphous particles formed at the contact of the lime matrix, and, herewith, were a component of the material which was obviously formed after the volcanic material was mixed with lime. The coronas are comparable to those caused in nature by a hydration (palagonitization) of (volcanic) tuffs. The coronas were further investigated for their qualitative composition by an energy-dispersive spectrometer (TRACOR/NORAN) attached to a scanning electron microscope (JEOL 6400), and by X-ray diffraction (SIEMENS D-500). They were found to consist of Ca-Si and of Ca-Si-Al, occasionally with some potassium. No detailed mineralogical composition could be analysed due to the size of the phases, but the X-ray diffraction showed among a variety of 9-10 different phases [24] the existence of gehlenite ($Ca_2Al_2SiO_7$), and possibly also of Taylor-phases with compositions near Ca_3SiO_5. While this group is well known in modern cement materials, gehlenite and related phases are not. However, they do occur as typical phases at pozzolanic reactions, *i.e.* they are formed at rather low temperatures [25], and are hydrated from the glassy or crystalline state to gehlenitehydrate (and a number of other phases which are difficult to determine with mineralogical methods [26]) which may also contain some iron and alkalis.

Two samples of ignimbritic rocks were compared with the plaster floor from Aşıklı Höyük, the one being a typical ignimbrite from the Kızılkaya formation [27], the second a (volcanic) tuff in direct contact with calcareous sediments from the excavation of Güvercin Kayasi at Aksaray, some 3 km southeast of Aşıklı. The chemical compositions (table 1) were plotted along with the plastered floor from Aşıklı in the compositional system C-A-S (fig. 3). Here, a mixing line becomes obvious which superbly underlines the mixing of the different materials : as expected, the plastered floor is roughly halfway between pure limestone (or lime plaster), calculated as CaO+MgO, and the two volcanic rocks. As stated above, these have pozzolanic properties and are close to the field defined for modern pozzolanic materials (including brick dust). The figure also shows that the Aşıklı floor is far from modern materials such as hydraulic lime and portland cement. It falls into the field of marl-binders as analysed from PPN plastered floors and skulls from Nevalı Çori [28] and Jericho [29].

CONCLUSIONS

The plastered floor from Aşıklı Höyük is a result of a pozzolanic reaction between Ca-rich material and grounded, weathered or loosely welded volcanic rocks (ignimbrites). As the pozzolanic reaction is based upon the existence of portlandite ($Ca(OH)_2$) and silica (SiO_2) in its reactive state, we conclude two possibilities of production. The first is that limestone was burned at Aşıklı to quicklime. Water was added to produce a paste which was mixed with ignimbrite available in large quantities around the village. The second started from a calcium-rich clay high in volcanic ashes (pozzolanas *per se* !), which, again, was burned as the limestone was. In both cases, cement phases were formed by reaction between the two materials, building coronas around the volcanic particles. This caused a hardening of the material, supported decisively by recarbonation of portlandite.

24. We determined by X-ray diffraction calcite to be the predominant component, followed by quartz, albite and microcline (= feldspar), montmorillonite (= clay mineral), pyroxene, cristobalite, analcime.
25. PETZOLD and HINZ, 1979.
26. *Ibid.*
27. The analyses of this sample was taken from BATUM, 1975.
28. AFFONSO, 1997.
29. GOREN and SEGAL, 1995.

It was possible to detect analytically clinker phases, and with a high degree of probability by means of (scanning electron) microscopy cement phases, their hydrated products. Due to reasons outlined above, we postulate a much higher amount of these phases at the time when the Aşıklı plaster was produced.

As yet, the existence of plaster hardened by pozzolanic reactions seems to be unique and the earliest evidence that man benefit from this physico-chemical property. It provides new insights into early pyrotechnology : Lime plaster production should be separated from pottery technology, which, in contrast, does not start with fired material, but starts with the shaping of a pasty clay, followed by a subsequent hardening by fire. Hence, we do not agree with the hypothesis that lime plaster production would be the precursor of fired ceramics. The results obtained rather support the model proposed by Malinowski [30] who suggested here the roots of cement technology.

As previously suggested by other authors [31], we are convinced too, that, by chance, pozzolanic reactions affected the quality of PPN lime plaster at numerous other sites, even if cement phases are hardly detectable. This hypothesis is based upon the lack of evidence that burning of lime plaster in the Neolithic was performed in kilns where fuel and charge was separated like it was the case with pottery [32]. Quicklime, in a simple constructed kiln, inevitably was mixed with varying amounts of plant ash. The ash, in turn, contains among carbonates and phosphates also "siliceous aggregates" [33] in a state of high reactivity. These are pozzolanas too, like volcanic ashes. Plant ash, hence, is *a priori* a hydraulic material. Remains of plant ashes were found indeed in PPN lime plaster. The detection of minor amounts of CS(A)H-phases, however, was and is a hard nut to crack !

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30. MALINOWSKI, 1991.
31. GOURDIN and KINGERY, 1975 ; HERSHKOVITZ *et al.*, 1995.
32. See HANSEN STREILY, this volume : 69.
33. SCHIEGL *et al.*, 1994. She analyzed opal-CT + quartz + Si-Al-K-Ca-Fe-glass and minerals such as bütschliite, fairchildite and dahllite.

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