X-RAY ANALYSIS AND X-RAY DIFFRACTION OF CASING STONES FROM THE PYRAMIDS OF EGYPT, AND THE LIMESTONE OF THE ASSOCIATED QUARRIES.

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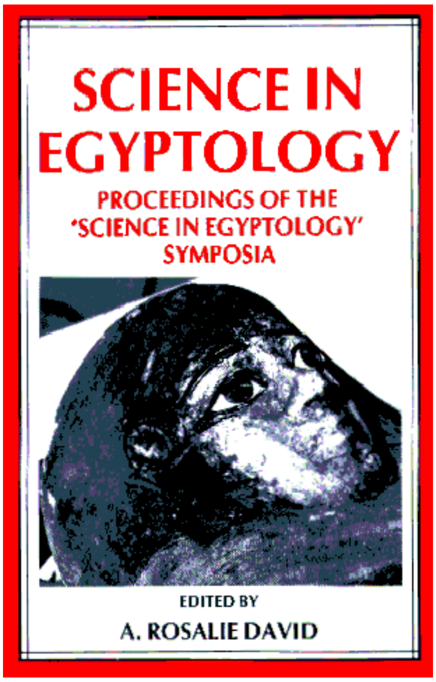

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X-Ray Analysis and X-Ray Diffraction of Casing Stones from the Pyramids of Egypt, and the Limestone of the Associated Quarries.

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SUMMARY

The hypothesis that the limestone that constitutes the major pyramids of the Old Kingdom of Egypt is man-made stone, is discussed. Samples from six different sites at the traditionally associated quarries of Turah and Mokattam have been studied using thin-section, chemical X-Ray analysis and X-Ray diffraction. The results were compared with pyramid casing stones of Cheops, Teti and Seneferu. The quarry samples are pure limestone consisting of 96-99% Calcite, 0.5-2.5% Quartz, and very small amount of dolomite, gypsum and iron-alumino-silicate. On the other hand the Cheops and Teti casing stones are limestone consisting of: calcite 85-90% and a high amount of special minerals such as Opal CT, hydroxy-apatite, a silico-aluminate, which are not found in the quarries. The pyramid casing stones are light in density and contain numerous trapped air bubbles, unlike the quarry samples which are uniformly dense. If the casing stones were natural limestone, quarries different from those traditionally associated with the pyramid sites must be found, but where? X-Ray diffraction of a red casing stone coating is the first proof to demonstrate the fact that a complicated man-made geopolymeric system was produced in Egypt 4,700 years ago.

INTRODUCTION

In 1982, during the Third International Congress of Egyptologists, held in Toronto, I presented a paper on pyramid construction, titled: «*No More than 1,400 Workers to Build the Pyramid of Cheops with Man-Made Stone*». I would now like to briefly present background information to illustrate why it was necessary to introduce such a controversial concept (Davidovits 1978b, 1979a, 1982a, 1982b, 1984).

As a scientist performing research in low temperature mineral synthesis, my specialization is to invent and improve certain industrial processes, which are generally based primarily upon inorganic chemical reactions (Davidovits 1978a, 1979b, 1981a, 1983). Since the 1960s, mineralogists and geochemists have been able to synthetically produce numerous rock forming minerals in the laboratory (Barrer 1957). The basis of this synthesis involves integrating silica and alumina materials to produce zeolites and feldspathoids, which are identical to those found in nature (Breck 1974). When the necessary elements are available, this process is easily accomplished without the use of heat, pressure, or other hard technology. Soluble silica is also easily produced beginning with different types of minerals or plant ashes or extracts, to which adding various elements can produce cement. After several years of research, I am able to propose numerous methods for producing cements which are different from modern Portland cement.

Calcinating calcium carbonate for the production of lime cement is a very ancient technique. Lime has been proven to have been first used as a cement in 10,000 BC. Perinet et al. (1980) have shown that white stone vessels (previously called lime vessels) from Tel-Ramad, in Syria, which date from 6,000 BC and excavated by Contenson (1963) (Contenson & Courtois 1979) contain up to 41% of a zeolite known as analcite. This is a mineral that is very easy to synthetically produce, and the high amount of analcite found in these stone vases show early proof of the production of a type of cement previously unknown in modern times (Davidovits & Courtois 1981, Boutterin & Davidovits 1982).

EVIDENCE FROM ANCIENT LITERATURE

Ancient literature offers an abundant amount of evidence to support my findings on the production of man-made stone, although the passages which describe this technique have not been understood until now. Pliny, the Elder, a well known Roman writer, was the author of an enormous encyclopedia, originally written in Latin, which describes the science of antiquity. Pliny described imported Egyptian stone vases called Murrhine vases. According to Pliny's descriptions, these vases possessed characteristic features of molded stone. In Book 37, Chapter 8, Pliny described the nature of the Murrhine vases:

"The Murrhine vases came from the Orient. They are found there in various little known places, especially in the Parthian. The finest come from Carmanie. They are said to be of a liquid to which heat, in conjunction with earth, gives consistency."

In 1830-1833, a general translation of Pliny's encyclopedia was made in France and annotated by members of the French Academy of Sciences (Ajasson de Crandsagne 1832). One of their many comments about Pliny's descriptions reads as follows:

A liquid which is hardened when it is heated: *It is difficult to understand that heat can cause solidification.*

The thermosetting of minerals, such as occurs in the geopolymeric chemistry that I have developed, was unknown. Geopolymers begin as a slurry which can harden at ambiant temperature, or in a few hours at 50 degrees centigrade. The Nineteenth Century scientists of the French Academy assumed that the Murrhine vases were made of natural stone because it was not known that a liquid could solidify under the action of heat. All such translations related to mineral materials should be reconsidered for updating. Another description by Pliny, from Book 31, Chapter 46, describes the production of stone with natron (sodium carbonate):

"In previous times, Egypt had no outcrops of natron, except those near Naucrates and Memphis. The products of Memphis being reputedly inferior. It is a fact that in accumulations of materials natron petrifies. In this way occurs a multitude of heaps of minerals which become transformed into real rocks. The Egyptians make vases in this way..."

Geopolymeric reactions require an alkaline ingredient. One of the first known reactions was based on lime and natron (sodium carbonate), which, when reacted together with water, yields caustic soda (Davidovits 1981b). Lime has been used since the Predynastic Period and natron is a natural salt available in Egypt in quantities of billions of tons. Their reaction is easily produced, enabling this basic technique to be used on a very large industrial scale.

EVIDENCE BASED ON THE EFFICIENCY OF THE STONEMAKING TECHNIQUE

Bronze tools were introduced into Egypt at about 1,900 BC and were used to carve soft sandstone. A comparison can be made between the efficiency of the carving VS the molding technique, based upon the hardness factor of the stone used and the time involved. For a given amount of labor, using the same bronze tools as were used to build and decorate the sandstone edifices of the New Kingdom, all that could be carved would be half of this amount for a medium-hardness limestone, such as that used in the Pyramid of Cheops (De Rozière, 1801). Only a quarter of this amount could have been carved of Carrare marble, and scarcely a twentieth of this amount from syenite (red granite). In other words, to cut, haul, polish, and hoist the 2,000,000 cubic meters of limestone for merely the Pyramid of Cheops during twenty years of work, the labor would correspond to the labor used to carve and erect the 4,000,000 cubic meters of sandstone of all the monuments built during the fifteen hundred years of the New Kingdom.

A period of twenty years is used for the construction of Cheops in this calculation for two reasons. First, each pyramid was built during the reign of the pharaoh for whom it was constructed. The official reign of Pharaoh Cheops was from 2704-2683 BC, a period of twenty-one years. Second, Herodotus, the Greek historian, cited twenty years in his account of the time spent for the construction of the Pyramid of Cheops. By using the agglomeration technique (the cast-in-place technique of map-made stone), Egyptians of the Old Kingdom without bronze tools, accomplished in 20 years, what it took Egyptians of the New Kingdom 1,500 years to accomplish, making it obvious that the workers could not have used the carving technique to build Cheops (Davidovits 1984).

QUARRY STUDIES

Perfectly fitted casing stone made of a very fine grained limestone once covered the Great Pyramid to form a smooth flat shell. The core blocks beneath the casing stone are made of very coarse nummulitic fossil shell limestone. Geological studies show that the stone constituting the core was quarried near the pyramid. The fine grained limestone casing stones date from the Middle Eocene geological epoch and are believed to come from the right side of the Nile River at the Turah and Mokattam quarries (Lucas and Harris 1962), as shown on the map of the region (Fig. 1 and 2).

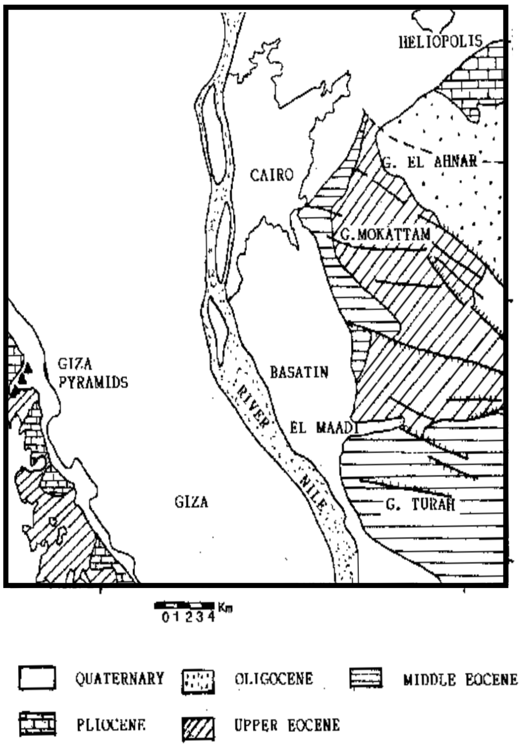

Figure 1: geological map of Giza

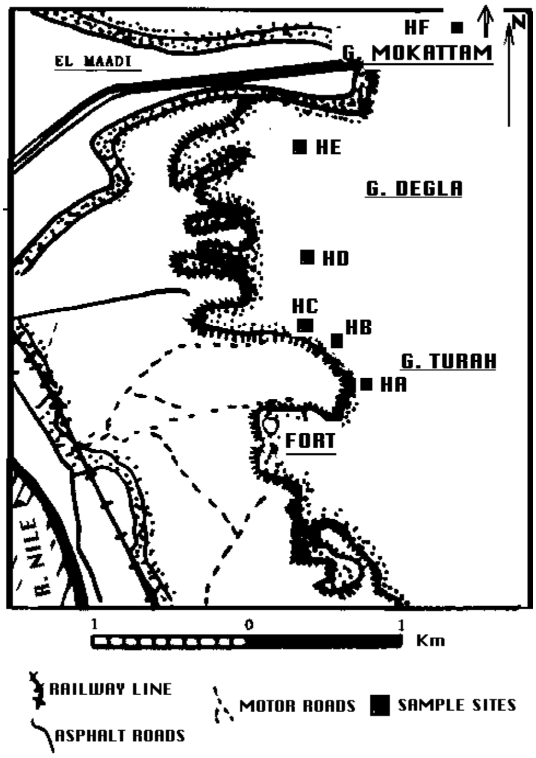

Figure 2: Gebel Turah

On samples of natural limestone from six different sites at Turah (sites HA, HB, HC, HD, HE) and Mokatatm (site HF), we performed thin-sections, X-ray analysis, and X-ray diffraction. We made the same types of tests on casing stone from the Pyramids of Teti and Cheops and compared them to the tests of the quarry samples.

CHEMICAL X-RAY ANALYSIS

Chemical X-ray analysis indicates that the casing stones tested are characterized by a high amount of silica (SiO_2) and strontium (SrO) (Fig.3). When comparing the amount of strontium (SrO) and sulphur (SO_3) in the casing stone to the amount of strontium (SrO) and sulphur (SO_3) in the quarry samples (Fig.4), it is apparent that the Cheops and Teti stones do not match the stones of Tura or Mokhatam. When comparing strontium (SrO) to calcium (CaO) -strontium is always associated with calcium-(Fig.5), there is a higher amount of strontium in the casing stone than in the quarry stone. $Si0_2$ content is higher in the casing stone than in the quarry samples. Iskander (1953) reported 9.54% SiO_2 in a casing stone sample from the Rhomboidal Pyramid of Seneferu at Dashur.

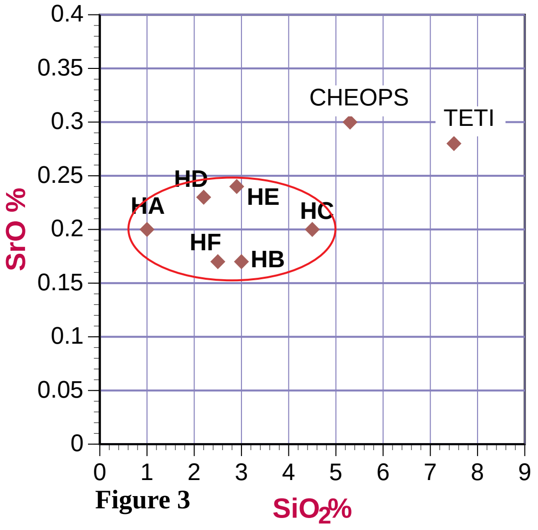

Figure 3

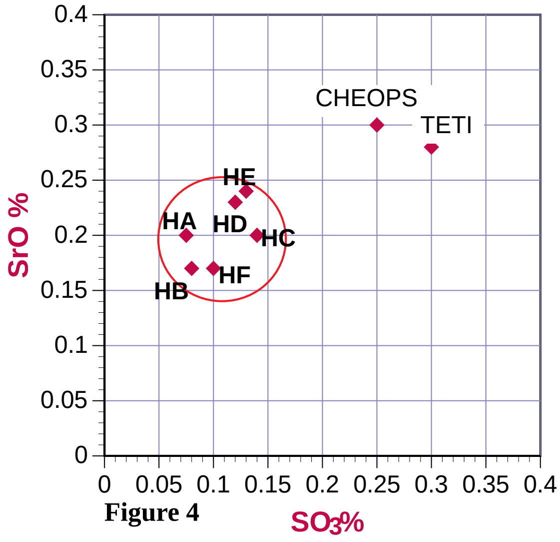

Figure 4

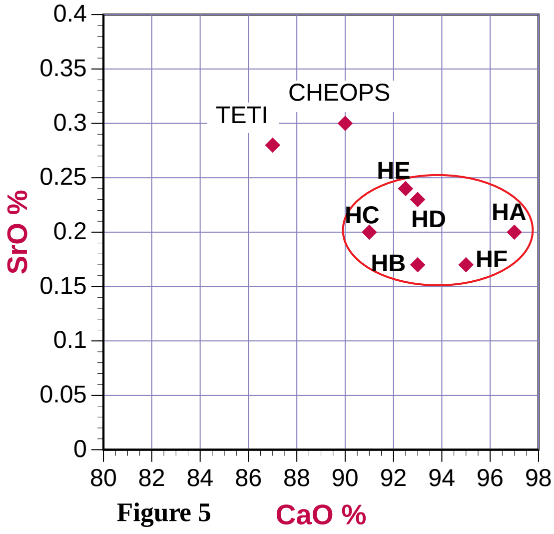

Figure 5

Figutres 3-5: Chemical analysis SrO/SiO_2/SO_3/CaO for quarry samples HA, HB, HC, HD, HE, HF and pyramid samples Cheops, Teti.

X-RAY DIFFRACTION

The chemical X-ray analysis of the casing stone of Cheops shows a high amount of silica, so we looked at the intensity of the quartz peak in the X-ray diffraction at 3.35A. We were surprised to find that practically no quartz was evident on the X-ray diffraction diagrams of Cheops casing stone (Fig.6). Instead, we detected hydroxy apatite, a calcium phosphate (lines at 2.81, 2.78, 2.72). We then compared

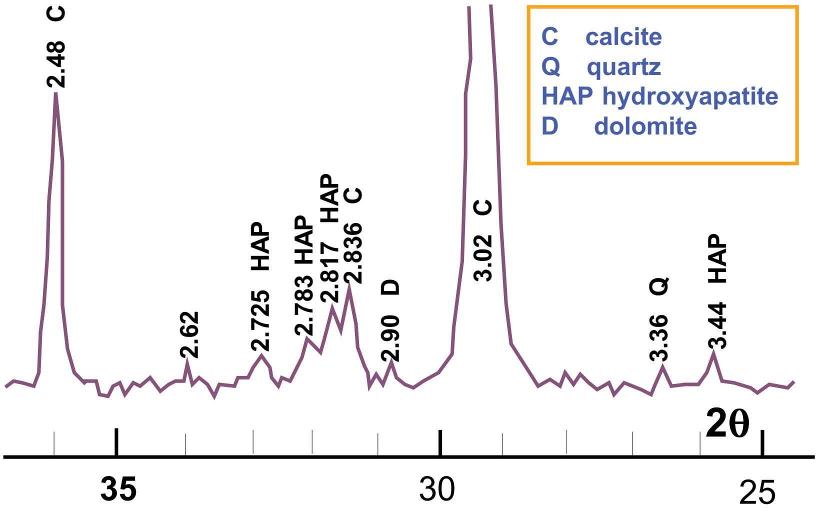

Figure 6: X-Ray diffaction, Cheops casing stone.

the amount of quartz and calcium phosphate in the casing stone of Cheops with the amount of quartz and calcium phosphate in the quarry samples. Each quarry sample contains quartz which corresponds in intensity to the silica content, and no hydroxy apatite, while hydroxy apatite is consistently associated with a calcite peak in the casing stone (Fig.7). Most quarry samples are pure calcite containing 0.5% to 2.5% of quartz.

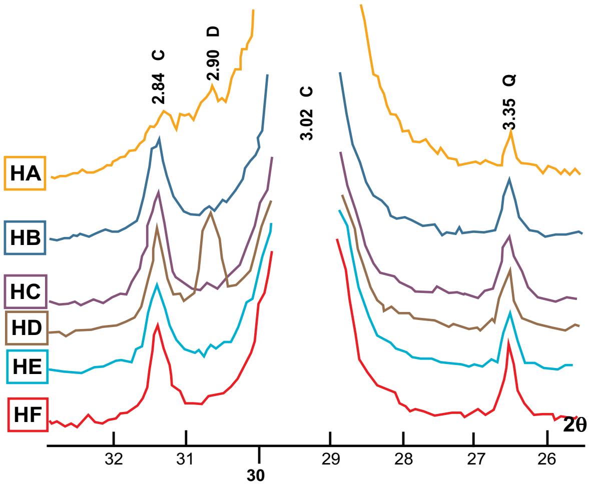

Figure 7: X-Ray diffraction: quarry samples

Quarry sample HD contains a small amount of dolomite and quartz. There is always a relationship between the heights of the two main quartz peaks (3.35 and 4.26). In all quarry samples the intensity of the 4.26 peak is aprox. 10% the intensity of the 3.35 peak. Comparing the Cheops and Teti samples with the silica peaks, we find that at 4.26 there is an exceptional high intensity (Fig.8). The additional 4.07 peak yielded to the assumption that the silica in the casing stone might have been cristobalite-low and volcanic quartz, a completely different silica system than found in the quarries. To make a determination, we destroyed the calcites and the phosphates of Cheops limestone with hydrochloric acid 2N, and were able to differentiate in the insoluble parts between the siliceous materials: silico-aluminate at 13.38A, cristobalite-low at 4.07A, and volcanic quartz at 4.26A (Fig.9)

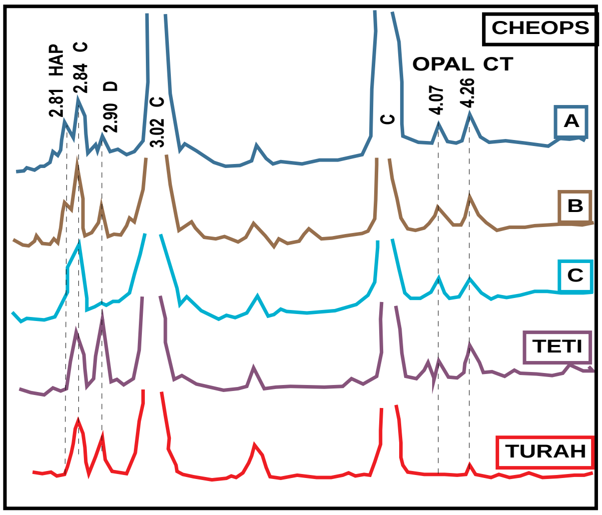

Figure 8: X-Ray: high intensity lines at 4.26/4.07 A, Cheops samples A,B,C, Teti, compared with quarry Turah

I presented these results in May of 1984, at the Archaeometry 1984 Symposium, in Washington, D.C., at the Smithsonian Institution (Davidovits et al 1984). An analysis of one fragment of casing stone with no comparative quarry studies was presented during the discussion by M.S. Tite, of the British Museum, in London. Members of his research laboratory found that the insoluble part of their casing stone sample is what is geologically known as Opal CT (opal cristobalite-tridymite) (Calvert 1977), instead of cristobalite low or volcanic quartz. The amount of Opal CT identified by Tite corresponded to the X-ray diffraction lines at 4.07 and 4.26, as identified in our samples. However, Tite interpreted the presence of Opal CT as being natural in origin, and stated, «*There is no need to introduce the hypothesis of reconstituted stone.* «(Tite 1984).

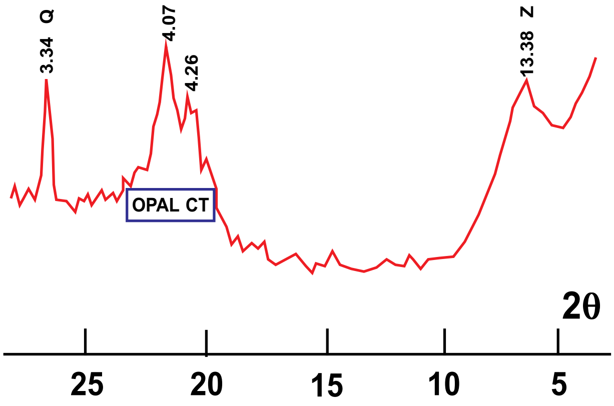

Figure 9: X-Ray: insoluble with HCl, 2N, Cheops casing stone.

DISCUSSION

Nature is able to produce an infinite variety of geological combinations. Opal CT is the metastable intermediary stage in the conversion of amorphous silica to quartz. What occurs is a low temperature conversion into an undimensionally disordered cristobalite and tridymite. There are therefore two possible interpretations of Opal CT's presence in the pyramid casing stone: man-made stone, since it would be the fingerprint of amorphous silica and silicates, a necessary ingredient, or a rare occurrence in natural stone. Which is correct? Traditionally, silica is found as quartz in limestone and not as Opal CT, although, geologists have recently found Opal CT in chalk sediments in the Atlantic Ocean, indicating that there are rare cases in nature where Opal CT is found in calcium carbonate sediments (Wise and Weaver 1974), when the «in situ» temperature of the site is lower than 15˚C (Neath & Moberly, 1971).

Continental limestone from the Middle Eocene Epoch in Egypt has a higher «in situ» temperature and should show the presence of quartz. Hypothetical calcareous Opal CT would have undergone a transformation into quartz. High amount of Silica exists in the casing stone of Cheops and Teti, yet, in the associated quarries there is only quartz and no presence of Opal CT. The presence of Opal CT in the casing stone of Cheops does not indicate that it is naturally occurring, since Opal CT is not found in the quarries.

Klemm et al (1979) analyzed trace elements from twenty stones of the core of the Cheops Pyramid. He came to the conclusion that each stone analyzed corresponded to a different quarry, suggesting that if the stones were natural, that the Egyptians quarried stones from all over Egypt: an incredible feat. However, trace elements for the production of a binder to agglomerate stone aggregates would come from all regions of Egypt. The solution to Klemm's dilemma, and to the presence of Opal CT in the stone, is to understand exactly how the pyramid stone was made, and to find numerous types of tests to show that the stone is not natural.

To further demonstrate that the casing stone is not natural stone, we made a reproduction with crushed limestone and a mineral binder composed of a synthetic zeolite that was obtained by mixing soluble silica, alumina, and caustic soda (Davidovits 1979c). We submitted the reproduction to X-ray diffraction analysis and obtained intense calcite peaks and very low intensity peaks for the mineral ingredients added (Fig.10). The X-ray diagrams exactly matched that of the Cheops casing stone, although for anyone who does not understand the chemical make-up of geopolymeric setting, our reproduction, like the pyramid casing stone, appears to be almost pure calcite.

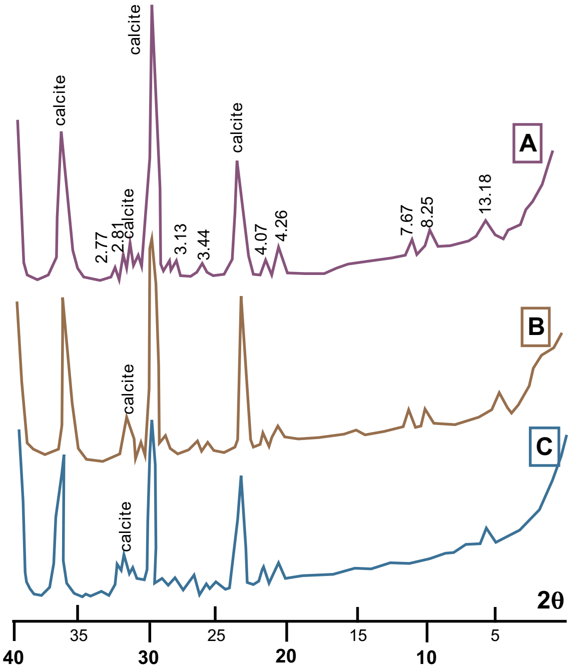

Figure 10a: X-Ray diffraction, Cheops samples A,B,C.

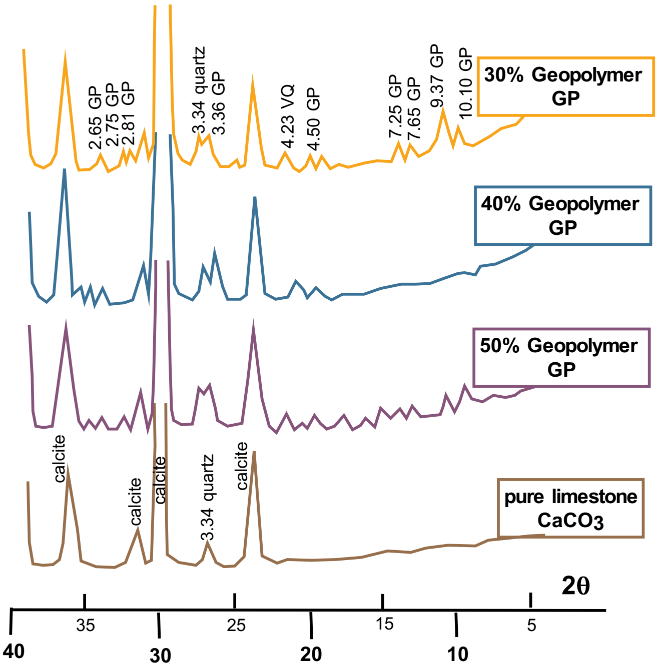

Figure 10b: X-Ray diffraction, limestone agglomerated with 30%, 40%, 50% by weight Geopolymer GP

Thin sections and optical investigations also show differences between artificial and natural stone. The core of the casing stone contains air bubbles which are not round, but oval, like stressed bubbles trapped in during the manipulation of clay. At high magnification bundles of organic fibers, which appear to be hair, can be seen, and clusters of air bubbles are associated with the fiber bundles (Fig.11). A thin section from Teti (Fig.12) shows microcrystals of calcite, a natural nummulite is imbedded in calcite surrounded with gaps and gaps appear in a very loose matrix, which is less dense than the matrix of stone from the quarries (Fig.13). A problem of analysis, assuming that this stone is made by agglomerating crushed limestone using lime as a binder, is that lime hardens over a period of time and becomes recarbonated into calcium carbonate. It is impossible to distinguish a natural calcite microcrystal and a microcrystal of calcite which is the result of the recarbonation of lime. This is an obstacle involved in the detection of geopolymeric setting and new techniques must be developed to resolve it.

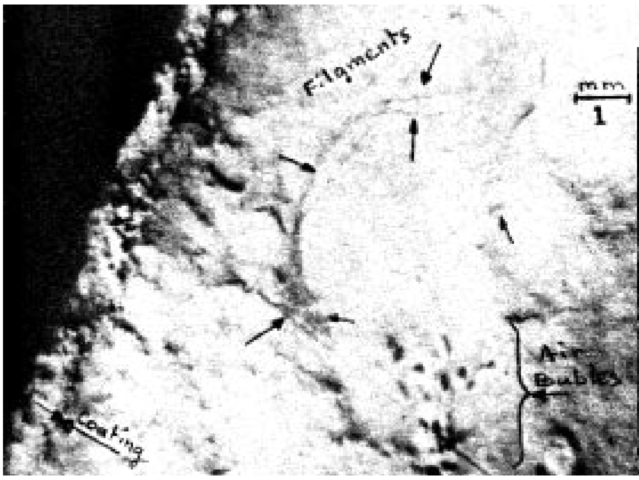

Figure 11: cross section, Cheops casing stone with coating of Fig. 14

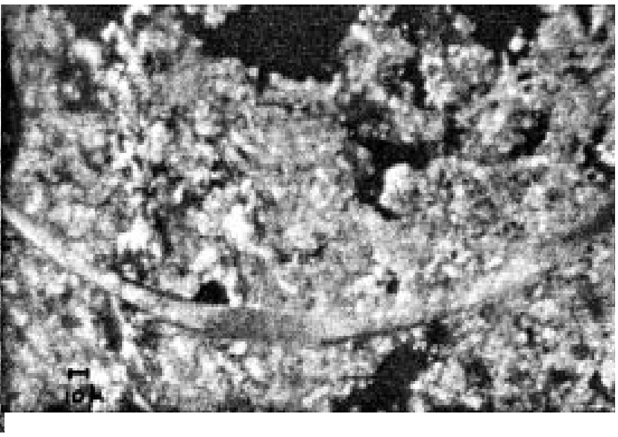

Figure 12: thin section, Teti casing stone, calcite microcrystal, 2-5 μ

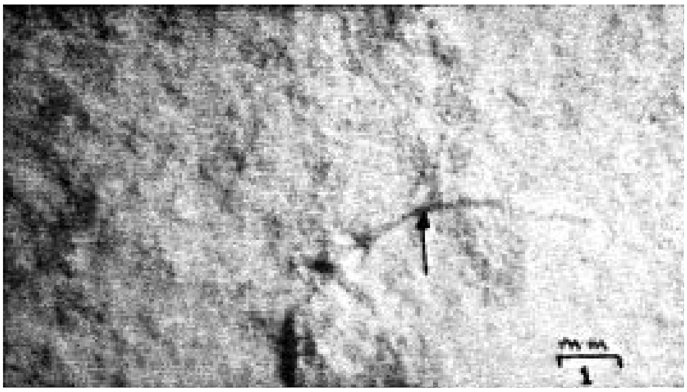

Figure 13: cross section, quarry sample HC with quartz inclusion (arrow)

One casing stone sample from Cheops was tested, which has a red coating on it. This sample is completely unweathered and should represent the prototype of the missing casing stones (Lauer, 1982). Usually, like the Teti casing stone, rain and sand would have eroded the shiny colored surface (Lauer 1953). We analyzed the red coating and were amazed to distinguish a tremendously complicated geopolymeric system made of crystalline hydroxy apatite and brushite (Davidovits, 1982b) (Fig.14). This red coating constitutes the key to the geopolymeric system used. The X-ray pat-

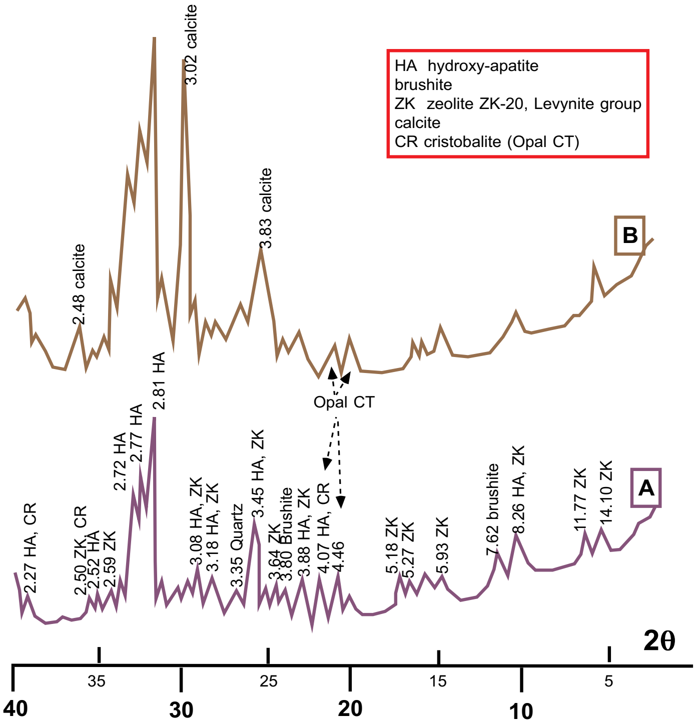

Figure 14: X-Ray diffraction, coating of Cheops casing stone, sample A. Sample B is polluted with calcite from the core

tern of the coating indicates a zeolite and opal CT, as found in the other casing stone samples. The coating is undoubtedly made from a pure man-made geopolymeric binder.

CONCLUSION

The hydroxy-apatite (a calcium phosphate) in the red coating is a mineral found in bone, and the brushite (an other calcium phosphate) is only associated with organic material. Tite (1984) did not find hydroxy-apatite in his casing stone sample, as we did. A.Pochan (1934,1953) who claimed that the casing stones were painted, reported the presence of Ca-phosphate in the limestone of three different casing stone samples of the Pyramid of Cheops. The synthetic zeolite, which we now call ZK 20, and the other ingredients found in the red coating are the first proof to demonstrate the fact that such a binder was produced in Egypt 4,700 years ago. This level of technology is far in advance of the traditional plaster and simple lime cement production which is always associated with the technology of ancient Egypt (Lauer 1953).

We hope to gather numerous samples from the core and casing stones of Cheops and other pyramids. We feel that with additional samples, and other means of testing, we will be able to demonstrate that the Egyptian pyramids were made entirely of man-made stone. A lot of work is involved, with the help of both Egyptologists and the Egyptian authorities.

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