

Microstructural Evidence of Reconstituted Limestone Blocks in the Great Pyramids of Egypt

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How the Great Pyramids of Giza were built has remained an enduring mystery. In the mid-1980s, Davidovits proposed that the pyramids were cast *in situ* using granular limestone aggregate and an alkali alumino-silicate-based binder. Hard evidence for this idea, however, remained elusive. Using primarily scanning and transmission electron microscopy, we compared a number of pyramid limestone samples with six different limestone samples from their vicinity. The pyramid samples contained microconstituents (μc 's) with appreciable amounts of Si in combination with elements, such as Ca and Mg, in ratios that do not exist in any of the potential limestone sources. The intimate proximity of the μc 's suggests that at some time these elements had been together in a solution. Furthermore, between the natural limestone aggregates, the μc 's with chemistries reminiscent of calcite and dolomite—not known to hydrate in nature—were hydrated. The ubiquity of Si and the presence of submicron silica-based spheres in some of the micrographs strongly suggest that the solution was basic. Transmission electron microscope confirmed that some of these Si-containing μc 's were either amorphous or nanocrystalline, which is consistent with a relatively rapid precipitation reaction. The sophistication and endurance of this ancient concrete technology is simply astounding.

I. Introduction

How the Great Pyramids of Egypt were built has been, and remains, an enduring mystery. Attempts to fit the historical and physical evidence into a coherent whole have failed, leading to intemperate speculation. The prevailing model^{1–3} is one in which blocks of limestone were cut in local quarries, cut to shape using copper (Cu) tools (bronze came later), transported to the pyramid site, and then hauled up ramps and hoisted in place using wedges and levers. This “carve and hoist” hypothesis, based on accepted models of Egyptian life of the time, has a number of problems, some of which are:

(1) Khufu's pyramid contains some 2.3 million blocks, averaging 2.5 tons each, with average dimensions of $\approx 1.3 \text{ m} \times 1.3 \text{ m} \times 0.7 \text{ m}$. Some of these blocks are placed in tiers whose edges closely conform to the pyramidal envelope, although the tiers vary from 0.5 to 1.25 m in thickness with abrupt changes in the thickness of proximate tiers.¹ Precision surveying, masterful management, and expert craftsmanship in forming and placement of these massive blocks are implied.

And while at first blush the current paradigm appears plausible, on closer inspection the following problems are obvious: (i) quarrying limestone is wasteful, with substantial breakage; yet, waste piles of the expected magnitude are absent. (ii) Cu is soft, so chisels quickly blunt in carving limestone, requiring frequent sharpening, substantial supplies of Cu, slow work, and imperfect surfaces. As important, not a single Cu chisel was found on the Giza plateau. (iii) Ramps that can accommodate the range of blocks and hauling crews are projects comparable to the pyramids themselves; but no trace remains of the ramps. More important and despite several ingenious proposals, how the ramps could have extended to the top of the pyramids has remained a vexing problem in Egyptology.²

(2) Casing blocks, which at one time covered the pyramids, closely correspond with each other's shape on all contact surfaces. The currently remaining casing and backing blocks, which are just behind the former, of Khufu fit as close as 0.05 mm across their entire contiguous vertical faces in some areas and their flat outer surfaces' angle to produce the precise slope of the rising pyramid.³ Abd al-Latif reported that a hair would not fit between any two he was able to test.⁴ Arnold⁵ notes: “... the connection of the casing with the backing stones is very close and would have to be carefully prepared The backing stones were frequently dressed exactly to the shape of the rear face of the casing block.” Why such exactitude and toil would be expended on areas that were to be covered for eternity is never explained. This is particularly striking considering the speed at which the Great Pyramid was built. Morris,⁶ Davidovits, and Morris⁷, and Davidovits⁸ provide numerous other facts that the prevailing “carve and hoist” model completely fails to explain but, because of lack of space, cannot be discussed herein.

In the mid-1980s, Davidovits⁹ proposed an alternative theory that addressed most of the aforementioned facts. He proposed the idea that the pyramid blocks were cast *in situ*, with a wet mix of limestone particles and a binder, tamped into molds, which in time hardened into concrete, with the macroscopic appearance and properties of native limestone.^{7,8,9} According to Davidovits, the concrete is made by mixing kaolinitic limestone (like that found within the Giza plateau) with lime, plant and/or wood ash, and water. The water separates the clay from the limestone, and the basic solution, resulting from the lime/ash, dissolves the alumino-silicates. With time, the alumino-silicates react with the alkali hydroxide to form sodium and/or potassium poly-silico-oxo-aluminates, a glue he labeled a geopolymer.

Egyptologists agree that while the main bulk of pyramid core blocks were made from Giza limestone, the outer and inner casings were made from a much finer-grained limestone, presumed to be from the Tura formation found on the East side of the Nile.^{2,10} Davidovits,⁹ however, compared natural limestone samples taken from six different Tura sites with an inner casing stone from the Ascending Passageway of the Great Pyramid—the latter given to Davidovits by Egyptologist J. P. Lauer, and henceforth referred to as the Lauer sample—and showed that

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Table I. List of Samples Examined in this Work

Designation in text	Source area	Source	Type of sample	# of samples
Menk	Satellite of Menkaur Pyr.	Backing? Blocks	Small chunks	3
Flakes	Khufu	Outer casing	Chips	1
OC	Khufu	Outer casing	Small block	1
Lauer	Great Pyramid	Inner casing	Small slab	1
Gypsum	Maadi limestone formation (South of the pyramids)	Natural	Block	2
Quarry	Khufu's quarry	Natural	Block	1
Khafra's causeway	Khafra's causeway	Natural	Block	2
Tura	East of the Nile	Natural	Block	2
Maadi	West of the Nile	Natural	Block	2

With the exception of the outer casing samples, which were supplied by Demortier¹⁶ the rest were supplied to us by Davidovits. The latter has photographs of the exact locations from which all samples were taken; many of them can be found in Davidovits.⁸

the Tura samples were sufficiently different as to preclude them as the source of quarried casing.⁹

Among the now discredited objections to Davidovits's theory are the expectation that: (a) the pyramid blocks would resemble modern concrete, where the cement binder is clearly visible, (b) the cast mix would leak out of molds, (c) cast blocks would merge together, and (d) expectation that imprints of wood grain from molds would be seen in the concrete. With respect to (a), the silica in caustic solution chemically binds to the limestone, so that little is needed and is seen only, as this work shows, with specific analysis. All these objections have essentially been swept aside by the recent casting of massive "limestone" blocks in France.⁸

Despite the serious difficulties with the "carve and hoist" model,⁶⁻⁸ the idea of manufactured stone in ancient Egypt has not been accepted.^{2,11-15} The purpose of this paper is to present the results of a detailed microstructural examination of a number of samples taken from the pyramids and their vicinity, in an attempt to determine whether the pyramid materials are natural or synthetic. At the outset, it is important to appreciate that the samples examined were quite heterogeneous. Over 1000 individual micrographs, local chemical analyses, elemental maps, etc., were taken and analyzed over a 3-year period. A substantial fraction of our effort was spent carefully cataloguing the phases found in the natural rock. What we report here is what we believe to be representative of the microstructures observed, but not necessarily a complete catalogue of every phase, inclusion, or microconstituent (μc) present. In this work, we define a μc as a small, apparently homogeneous region, with a number of elements that are comprised of at least one phase.

II. Experimental Procedure

In 1991, Davidovits collected samples from the pyramids and their vicinity. In toto, he supplied us with 11 samples. Six were natural limestone samples: one from the Tura, and two from the Maadi limestone formation (found on the west side of the Nile, a few kilometers to the south, and within clear view of the pyramids); one from a region of the Giza plateau believed to be Khufu's quarry; and two samples from Khafra's causeway leading to the Great Pyramid. He also supplied us with a gypsum sample from the Maadi formation. Davidovits also gave us the aforementioned Lauer sample and three samples taken from core blocks of the smallest satellite pyramid of Menkara,

henceforth referred to as the Menk samples. We independently obtained a small chunk from the outer casing of Khufu, henceforth referred to as the OC sample, and some flakes from another Khufu casing block.¹⁶ Table I summarizes the origin of the samples and their provenance.

Most samples were cut using Hyprez OS (Engis Corp., Wheeling, IL) or Puron DP (Struers, Westlake, OH) lubricating fluid and polished by a diamond suspension (3 μm and 1 μm) in glycol (Leco Corp., St. Joseph, MI). The use of water was avoided to prevent the solution and/or reprecipitation of water-soluble salts such as halite (NaCl) or gypsum. Most observations were of cut and polished or fractured internal surfaces, free of known external contamination.

Some micrographs were observed without a conductive coating; all micrographs shown in this paper had a thin C coating sputtered onto their surfaces to make them more conductive and prevent charging. Appendix A summarizes the details and limitations of the energy-dispersive spectroscopy (EDS) analyses carried out in the scanning electron microscope (SEM). For the sake of brevity and clarity, most of the EDS results are represented in the form of a chemical formula. The procedure for converting the EDS results to a chemical formula is outlined in Appendix A.

To exclude totally the possibility of contamination from the polishing media, we also examined the fractured surfaces of a number of samples. Select OC flakes were also examined in a TEM equipped with an electron energy loss spectrometer, (EELS).

III. Results

(1) Microstructural Evaluation

(A) *Natural Stone:* In all natural samples (see Table I), microstructural analysis in the SEM indicated that the predominant phase was a porous calcite (CaCO_3) that contained halite (NaCl) in the form of small crystals and sometimes thin whiskers. All samples contained silica, viz., a phase wherein the O/Si ratio was 2:1, in which the concentration of every other element was $<0.05\%$. All samples also contained an organic substance, rich in C and O, found in a myriad of shapes including fibers, whiskers, and thin membranes, mostly at grain boundaries. The ubiquity of this substance was only appreciated when fractured surfaces were examined, indicating that it existed mostly at grain junctions (not shown). This substance was also found in the

Table II. Summary of Elemental Analyses of a Number of OC Flakes Determined by EELS in the TEM

	Ca	Mg	Si	Al	O	C
1	5	8	36	2	25	25
2	8	20	28	2	41	1
3	2	11	18	0.0	54	15
4	<1.0	27	61	2	8.5	2

Why the oxygen content in some of the EELS results is depressed is not clear at this time but could reflect the instability of the water of hydration under the electron beam. OC, outer casing; TEM, transmission electron microscopy; EELS, electron energy loss spectroscopy.

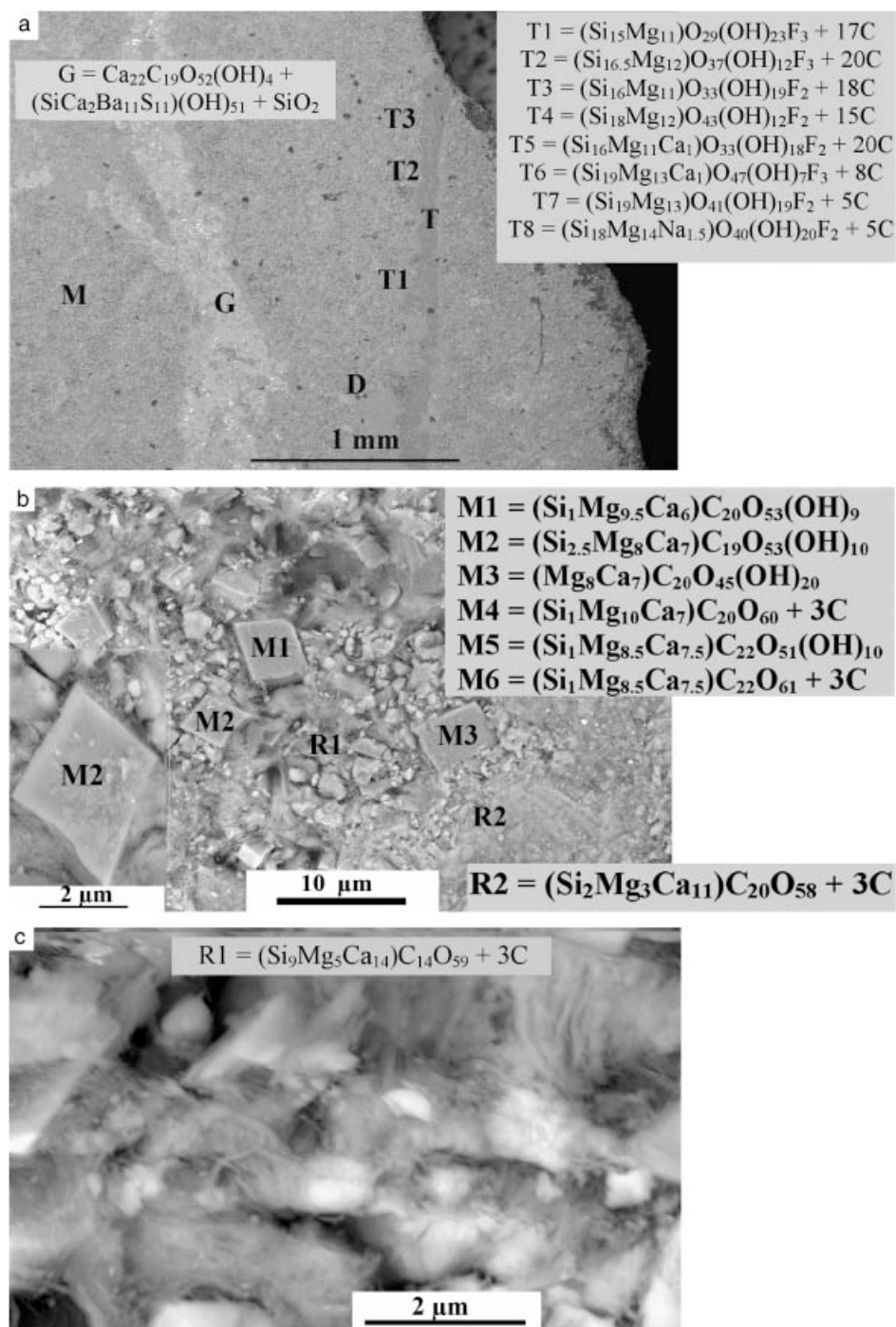


Fig. 1. Backscattered, scanning electron microscopy micrographs of outer casing sample (a) at low magnification showing a striated microstructure. Framed compositions reflect the chemistry as determined from electron dispersive X-ray spectroscopy point analysis of the various areas (see Appendix A). (b). Higher magnification of region M showing small cuboid particles. The inset shows a much higher magnification of the latter. (c) Higher magnification of region R1 in b. Most energy dispersive X-ray spectroscopy measurements were made at magnifications of $\times 10\,000$ or higher. Note in (a) and (b), compositions T1–T3 and M1–M3 were determined from the locations shown; T4–T7 and M4–M6 are from other areas not shown.

form of a thin coating that covered many of the phases identified in the natural limestone, such as calcite, halite, and possibly CaCl_2 . This C-rich substance sometimes also contained multiple ions in appreciable concentrations.

With the exception of the Maadi and Tura samples—which are from geologic formations different from the limestone of the Giza plateau—most other natural samples contained small amounts of a tubular kaolinitic mineral, halloysite, characterized by a 1:1 ratio of Si to Al. The halloysite fibers were visible in some of the pores; and some were free standing, some were collapsed. If halloysites were present in the Tura and Maadi samples, we did not observe them.

One Al_2O_3 and a few dolomite $\text{CaMg}(\text{CO}_3)_2$ grains were also found in one of the Tura samples. One sample contained a particle of K-aluminosilicate with a K:Al:Si ratio of 7:9:25 at.%, respectively, which was most probably a feldspar-like phase with an approximate chemistry of $(\text{K},\text{Na})\text{AlSi}_3\text{O}_8$. To sum up, for the most part, all samples contained calcite, dolomite, silica, halite, an organic substance, plus smaller amounts of a number of aluminosilicates and chlorides. Some contained halloysites.

(B) Outer Casing: In the OC microstructure, at least six μc 's and/or phases—four of which are labeled, M, G, D, and T in Fig. 1(a)—were identified. Region Q, not shown, with a com-

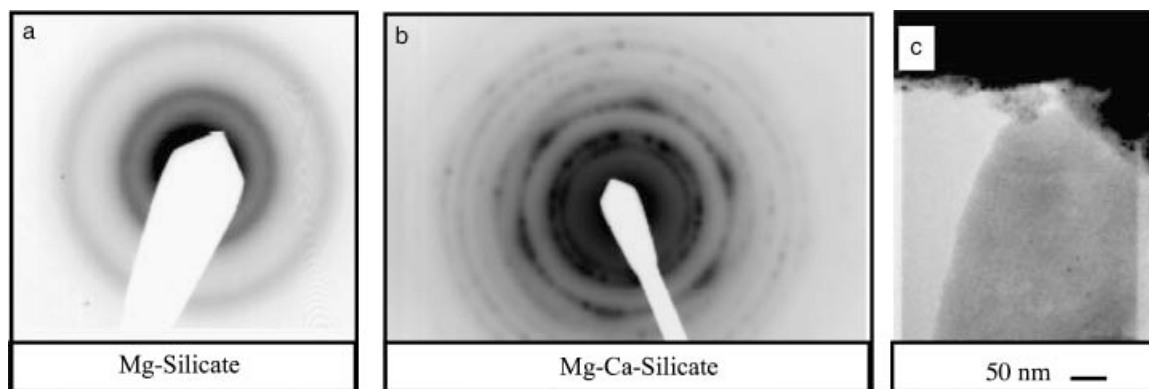


Fig. 2. Selected area diffraction of select outer casing flakes confirming that they were either (a) amorphous and/or (b) nanocrystalline, (c) shows a transmission electron microscopy (TEM) micrograph of a typical region examined. Making electron transparent foils was difficult because most of the samples were easily friable. Instead, TEM samples were produced by grinding parts of the samples in an agate mortar and pestle and transferred onto holley carbon films. Although this provided a rapid way to produce TEM samples, its drawback was that the microstructure was lost. To insure that only the samples contributed to the observed signals, only grains that bridged holes of the carbon film were analyzed. The primary energy of the incident electrons was 400 keV, which allowed us to observe relatively thick samples.

position, $\text{Ca}_{19}\text{C}_{19}\text{O}_{61}$, is most likely calcite; region O (not shown) was comprised of 58 at.% C, 29 at.% O, ≈ 1.5 at.% each of Na, Mg, Si, and S, 5.5 at.% Ca and ≈ 1 at.% Cl. This region was reminiscent of the organic phases observed in the natural limestone. Based on its chemistry, viz. $(\text{Mg}_{10}\text{Ca}_{12})\text{C}_{18}\text{O}_{58}$, region D is most probably dolomite.

Higher magnification SEM micrographs of region M (Figs. 1(b) and (c)) indicate that its microstructure is quite complex. In many locations, small equant euhedral crystals resembling cubes or rhombohedra (labeled M1–M3) roughly 2 μm in diameter (inset in Fig. 2(b)) are clearly visible. Based on their morphology, it is reasonable to assume the cubes are single crystals. The chemistry of these particles is quite intriguing and one of the key results of this work because they contain Si, apparently in solid solution in dolomite; note that the Mg:Ca atomic ratio is $\approx 1:1$. The importance of this observation is that Si is not known to dissolve in dolomite.¹⁷ The chemistry of region R1 in Fig. 2(b), shown at higher magnification in Fig. 2(c), was not too different from that of the cuboids, except that at 9 at.%, its Si concentration was significantly higher. Furthermore, at this magnification, the fine scale of the microstructure and the fact that this region contains significant amounts of Si, together with Ca and Mg, is clear.

The rationale for assuming that some of the phases and/or constituents (μc 's) are partially hydrated is discussed in Appendix A and stems from the fact that in some cases (e.g., M1–M5 in Fig. 1(b)) the sum of the negative charges significantly exceeds that of the positive charges. Some may argue that such an approach is unorthodox, but is bolstered by the very important observation that when a phase was clearly identifiable as calcite (which after all comprised more than 80% of all samples), the Ca:C:O elemental ratio was $\approx 0.2:0.2:0.6$, with an error margin of ± 0.02 . In a number of cases (e.g., M4, M6 in Fig. 1(a)), the as-measured charges actually balance. There was no correlation between the C concentration and the imbalance in charge. It is also important to appreciate that the margin of error in the amount of hydration—which we estimate to be $\approx \pm 6$ at.%—is significantly higher than the margin of error for the cation compositions. As important, such hydration was not found in the natural samples.

Region G (Fig. 1(a)) is also quite complex. Most conspicuous were bright areas with a chemistry corresponding to $(\text{SiCa}_2\text{Ba}_{12}\text{S}_{11})\text{O}_{50}$ embedded in a matrix that in some regions was calcite based [$\approx \text{Ca}_{22}\text{C}_{19}\text{O}_{58}$]. The Ba–S-rich areas are most probably barite, with the Si and Ca signals probably coming from adjacent phases. There are also some areas with a Si:O ratio of 1:2 that are presumably silica. In another area, a C-rich region was found with a plethora of cations, most notably Si, Mg, and Ca.

The most intriguing μc in the OC sample, however, has to be region T (Fig. 1(a)). This thin strip, conspicuous by its dark gray color, contains very little Ca. Based on its chemistry, viz., a Si:Mg:O atomic ratio of $\approx 1:1:3$, it is reasonable to conclude that it is a MgSiO_3 -type structure that is, in some cases, considerably hydrated (e.g., T1–T5, and T7). This μc additionally contains 2–3 at.% F, and in many cases, but not all, roughly 15–20 at.% C; the lowest C content was 5 at.% (e.g., T7 and T8). In some locations, this μc contained up to 1.5 at.% Na. As far as we are aware this phase does not hydrate in nature and, as important if it did, does not exist in calcite.¹⁷

TEM of some OC sample flakes revealed that, in addition to well-crystallized calcite and dolomite regions, amorphous regions containing Mg, Si, and O and sometimes Ca were also found (Table II). These regions were either fully amorphous (Fig. 2(a)) or consisted of nanosized crystals that exhibited broad Bragg peaks (Fig. 2(b)). EELS confirmed that these regions did not have a fixed, known chemistry but one that varied from particle to particle (Table II). It is not clear why the O content was depressed for some of these samples, but a likely explanation is that the water of hydration was lost under the electron beam. It is well established that some minerals, like biotite, for example, can degrade quite rapidly (≈ 30 s) under an electron beam in a TEM (see for e.g., Bell and Wilson¹⁸).

(C) *Lauer Sample:* The microstructure of the bulk of the Lauer sample was characterized by a matrix phase and two μc 's (Fig. 3). The large matrix phase is comprised of exceptionally pure CaCO_3 (Columns 9 and 10 in Table III); other areas contained up to 1 at.% Mg and Na. Note that in this phase the charges balance. The darkest μc in Fig. 4(b) was Si and O rich, with ≈ 1 at.% S (Table III). Almost invariably these Si- and O-rich-based islands were ringed by a bright μc comprised of roughly equal (≈ 10 – 15 at.%) amounts of S and Ca, 3–5 at.% Si, and 1–1.5 at.% Na, and a relatively weak C signal (Table III). Note that the Na is present without Cl.

On freshly prepared polished bulk Lauer samples, this S-containing μc is absent; it only becomes prevalent after exposure to air for a few weeks. Its chemistry suggests it is fully hydrated. Its morphology (Fig. 3(a)) suggests that it oozes out from around the Si- and O-rich islands and the grain boundaries. The micrographs shown in Fig. 3, more than any other, show the distribution of the Si-O-rich cementing phase relative to the calcite aggregates. It is worth noting here that any μc 's or phases found in the pyramid stones for which the chemistry was within 1–2 at.% of a well-known mineral and was also found in the natural stones (calcite, dolomite, silica, etc.) were presumed to be the aggregates. The chemistry of these regions corresponded to well-known minerals, and no water of hydration was needed to balance the cationic and anionic charges.

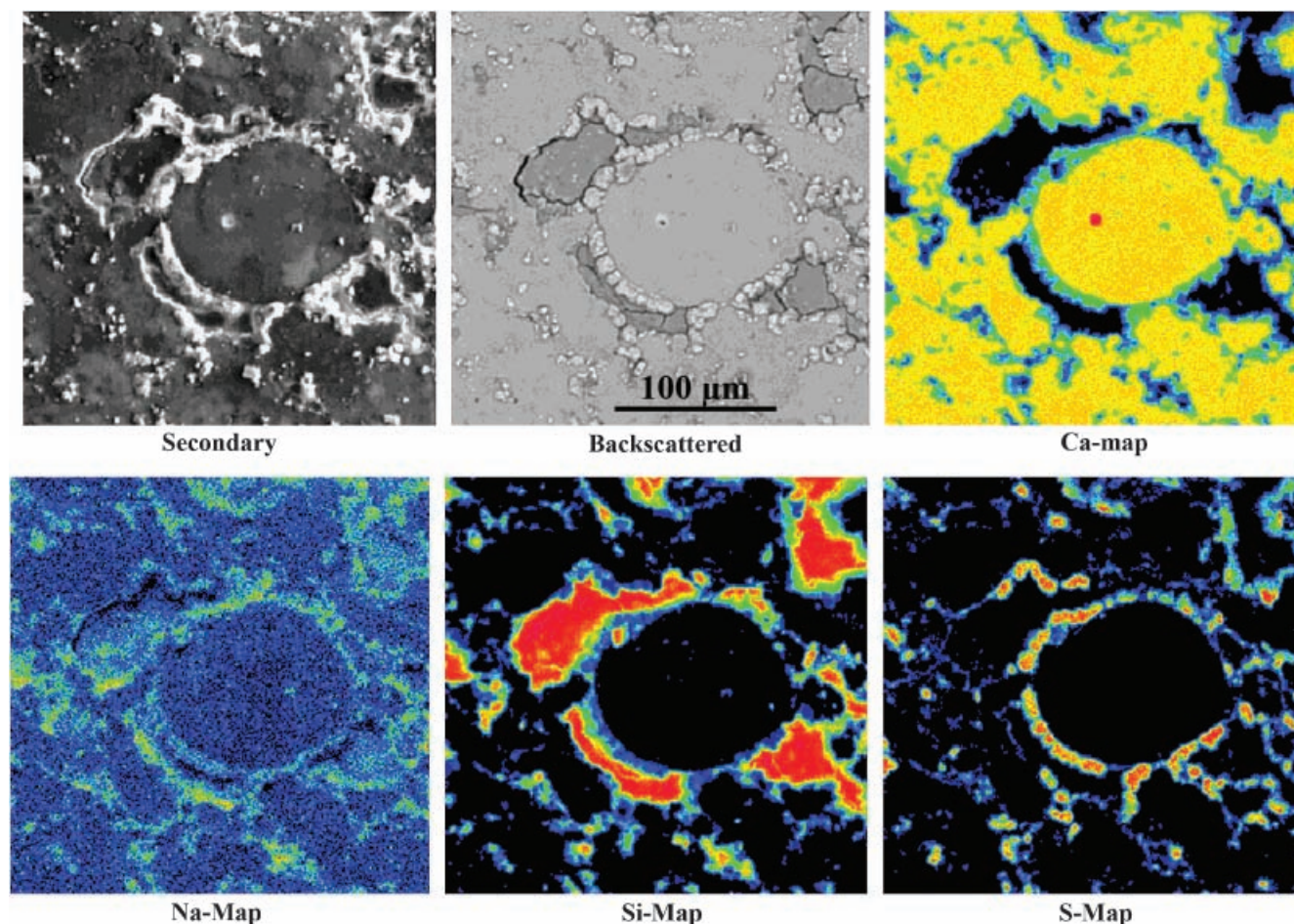


Fig. 3. Scanning electron microscopy micrographs and elemental maps of bulk of Lauer sample showing (a) secondary and (b) backscattered images; the rest of the images represent elemental maps of Ca, Na, Si, and S. Note that the size of the calcite aggregates is 50–500 μm .

The microstructure of the near surface of the Lauer sample—which is white and visible to the naked eye—is even more interesting (Fig. 4). It is a μc with roughly equal atomic fractions of Ca and P, and a relatively high concentration of C. Within this phase, darker gray Si-rich islands (Fig. 4(a)), similar to those shown in Fig. 3(b), were observed. Some of these islands were not monolithic, but comprised of silica-rich submicron spheres (Fig. 4(b)), together with P, Ca, and significant amounts of C. When the electron beam was focused on one of the spheres, the C, Ca, and P concentrations were significantly reduced, suggesting that the spheres were silica based, with the other elements mostly found in the areas in between.

In another area near the surface, the microstructure was even more heterogeneous, where some of the μc 's contained various concentrations of Ca, P, S, Si, and C in addition to O. Based on their chemistries, it is fair to conclude that some of these areas contained hydroxyapatite, in agreement with previous work on the same sample.⁹ Other areas were composed of CaSO_4 , in

addition to appreciable concentrations of Si. A titania inclusion (not shown) was also found.

(D) Menk Samples: In contrast to the OC and Lauer samples that are clearly synthetic, the three Menk samples appeared to be predominantly comprised of grains of natural calcite. However, in between grains of what EDS showed to be calcite were other areas that contained a plethora of μc 's (Fig. 5(a)). One “grain boundary” region contained a small cube-like structure, with a chemistry reminiscent of feldspar (Fig. 5(b)). The two regions to either side of the cube were chemically similar to regions R1 and R2 in the OC samples (Fig. 1) and were basically Si-containing calcite. Interestingly, the area to the left of the cube-like feature contained Mg, and even Al in addition to Si. In another area of one of the Menk samples (not shown), hydrated calcium sulphate grains [$\text{Ca}_{10}\text{S}_{11}\text{O}_{22}(\text{OH})_{36} \approx \text{Ca}_{10}\text{S}_{10}\text{O}_{40}\text{H}_{40}\text{O}_{20} \approx \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] with ≈ 19 at.% C were found.

In another “grain boundary” area (Fig. 5(c)), a region was identified with the chemistry shown in the figure, which

Table III. Typical EDS Results Obtained from Micrographs Similar to those Shown in Fig. 3

	S-rich μc				Ca-rich				Si-rich areas		
C	2.5	6.3	2.5	2.3	4.2	4.2	2.9	19.4	20.6	3.7	3.6
O	65.8	65.3	64.8	62.8	69.8	61.4	65.4	60.5	58.7	63.6	64.5
Na	1.4	0.7	1.4	1.0	0.8	1.1	1.4	0.3	0.6	0.9	0.9
Si	2.4	2.9	2.4	7.9	8.1	3.4	6.3	0.5	0.2	31.0	29.3
P	0.9	0.6	0.9	0.8	0.7	1.1	0.9	0.4	0.4	0.3	0.6
S	14.2	13.0	14.2	12.5	8.6	14.7	12.0	0.3	0.3	0.3	0.5
Ca	13.9	11.2	13.9	12.7	7.7	14.0	11.1	18.9	19.0	0.1	0.2

The elemental maps indicate the presence of at least 3 μc 's: S, Ca, and Si rich. EDS, energy dispersive X-ray spectroscopy.

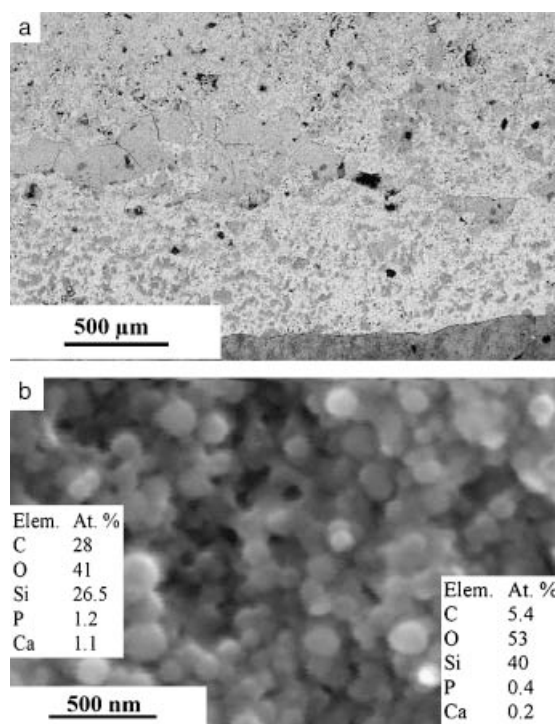


Fig. 4. Backscattered scanning electron microscopy micrographs of the white edge of a Lauer sample showing (a) a Ca-phosphate-based outermost layer (bottom bright area) and bulk (top) and (b) higher magnification of the SiO_2 -rich area shown in (a). Energy dispersive X-ray spectroscopy (EDS) on LHS is that of the entire area shown. The EDS that resulted when the electron beam was focused on one of the spheres is shown on the RHS. Note the ubiquity of Si.

translates to the following formula: $(\text{NaSi}_6\text{Al}_4\text{MgCa}_7)\text{C}_{11}\text{O}_{32}\text{Cl}(\text{OH})_{32}$, or, $\text{NaCl}, (\text{Si}_6\text{Al}_4\text{MgCa}_7)\text{O}_{32}(\text{OH})_{32}$, and 11 C. Note here that the spectra shown in Fig. 5(c) were collected at $\times 50\,000$; the micrograph shown was taken at $\times 20\,000$ in order to minimize contamination from adjacent phases. In yet another area, an Fe-rich region was found that curiously contained ≈ 11 at.% F (Fig. 5(d)).

IV. Discussion

(1) Ubiquity of Si Between Calcite Particles

According to Davidovits, the pyramid blocks are made of calcite aggregates held together with a silica-based binding phase. It follows that if his theory is correct, Si should be ubiquitous in the “grain boundary” areas, i.e., the areas between the calcite or other aggregates. Based on our results, the ubiquity of Si is clear; it was found bound with Mg alone (T in Fig. 1(a)) and together with Mg and Ca (regions M and R in Figs. 1(b) and (c)) in the OC samples. It was found together with S and Ca, or P (Table III and Figs. 3 and 4) in the Lauer sample. In the Menk samples, it combined with Ca alone, Ca, Al, and Mg (Figs. 5(b) and (c)). Most of these regions also appear to be hydrated to some extent, which we interpret to reflect additional hydrated, metal-bearing phases that are not indigenous to the natural limestone aggregate.

Some may argue that as Si is a common geologic element, it is not surprising that it is found everywhere. It is thus crucial to note that it is not the presence of Si *per se* that is surprising, but its presence in combination with elements and structures that, as far as we are aware, if they existed at all in nature in general, and in calcite in particular, have not been reported on to date.¹⁷ This is especially true considering that most of our EDS analyses were carried at magnifications of $\times 10\,000$ or higher (many were at taken at $\times 25\,000$, and some at $\times 50\,000$) in order to try and

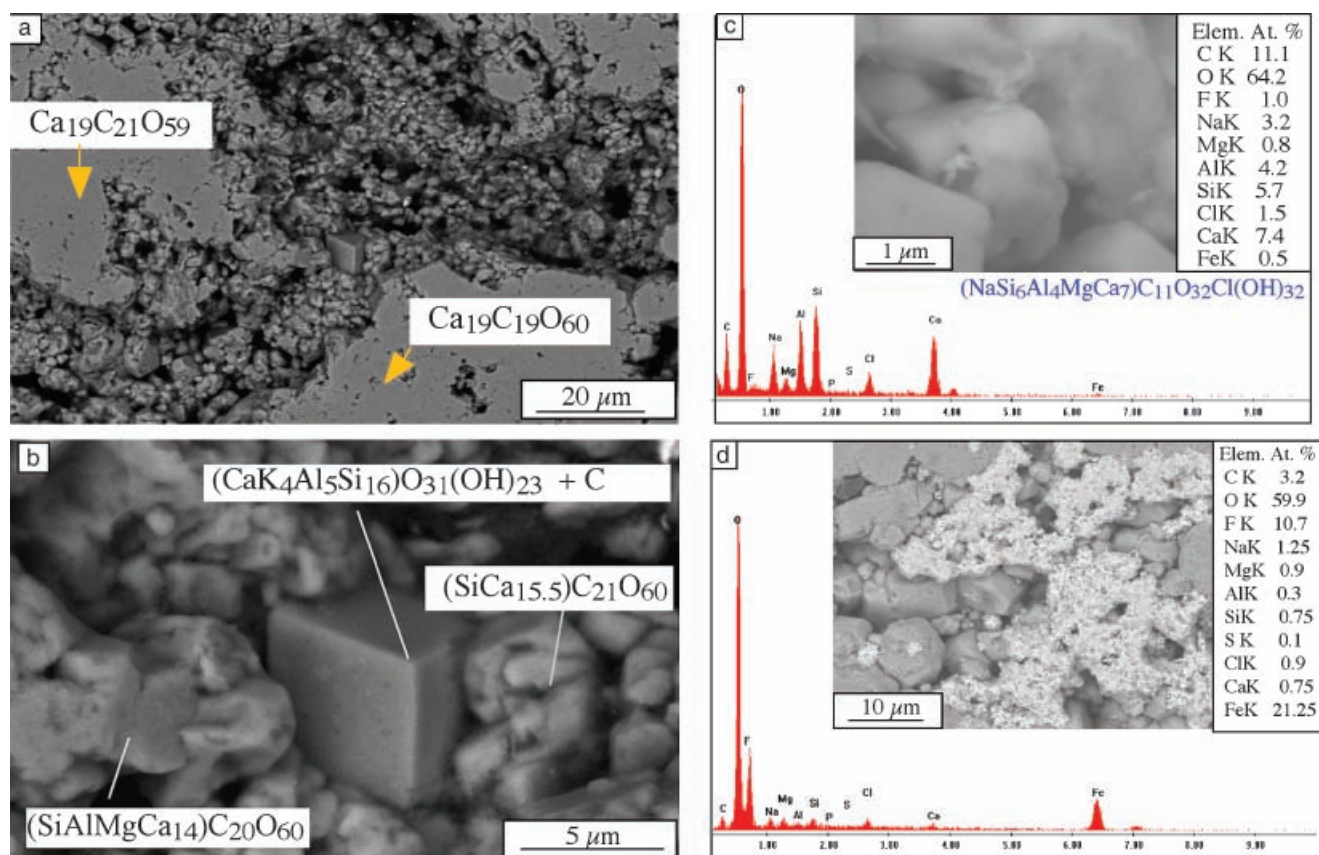


Fig. 5. Backscattered scanning electron microscopy micrographs of a Menk sample (a) at low magnification showing matrix grains and “grain boundary” area; (b) higher magnification of latter showing cuboid feature and vicinity; (c) showing another “grain boundary” area. Note the multiple elements and ubiquity of Si. (d) Fe-rich area that also contains F.

minimize contamination from adjacent phases (see Appendix A). Probably the most compelling evidence that Si is in solid solution in calcite or dolomite are the small cuboid precipitates shown in Fig. 1(b). From their size and morphology, it is quite reasonable to assume they are single phase, with the chemistries shown, i.e., with Si in solid solution.

It is hereby acknowledged that the Si in some of those μc 's may not be in solid solution—which is why we label them μc 's in the first place—but is present as a distinct minor phase, with say a 1:2 Si:O ratio. Even if that were the case, our conclusion remains valid because the results still imply that Si was precipitating out of solution roughly at the same time as the other cations.

Nature is quite resourceful. And yet, we are unaware of any literature report¹⁷ in which a natural limestone has been shown to have as many phases or μc 's—with the plethora of compositions—that are less than 50 μm apart as shown in Figs. 1–5. Certainly, they are not typical of the natural limestones we examined. The presence of S in most of the pyramid samples, and its absence in the natural stone (with the exception of trace amounts in the Maadi limestone, known to have a gypsum layer) is consistent with the synthetic nature of the pyramid blocks.

Similarly, it is equally difficult to explain the presence of barite; F is found in only two samples, the OC (Fig. 1(a)) and a Menk sample (Fig. 5(d)). Its signature in the EDS spectra is unambiguous (Fig. 5(d)). At this time, it is not clear whether its presence is intentional or accidental.

Other less compelling evidence, but one compatible with our hypothesis, includes the results of Iskander, who reported the presence of 9.5 at.% SiO_2 in a casing stone from the Pyramid of Seneferu at Dahshur.¹⁹

(2) Presence of Moisture

Most of the regions that we explored appear to be hydrated to some extent. It is crucial to note that only the “calcite” in the “grain boundary” areas is hydrated. This is a significant result because neither calcite nor dolomite is known to form hydrates.¹⁷ The latter was confirmed in our work; neither the aggregates in the pyramid samples, nor the natural limestones we examined, contained any water of hydration.

At the time of the opening of the Great Pyramid by Caliph Al Mamun in AD 820, after it had been sealed for many centuries, the interior chambers were found to be “mysteriously encrusted with salt as much as one-half inch thick,” consistent with rock that is by nature damp and porous.²⁰ Even today, the pyramids are not dry. More recently, the relative humidity inside the pyramids was measured to be $\approx 80\%$, even in pyramids not frequented by tourists.²¹ It is this high moisture content of the pyramid stone that doomed the 1974 electromagnetic sounder experiments, whose primary objective was to locate archeologically significant chambers in the Giza area.²¹ This independent evidence for the presence of considerable amounts of moisture—estimated to be 100 million gallons in Khufu—in essentially a desert environment, should not be easily dismissed.

The simplest explanation—Occam's razor—is that the various ions found in those μc 's were at some time present in solution and co-precipitated or reacted together to form the geopolymeric glue necessary to fabricate the synthetic stone. Note that in such a scheme, some of the added water would end up bound in the “stone” as observed. Based on our results, it is reasonable to assume that in the OC sample the ions in solution were Mg^{2+} , Ca^{2+} , $(\text{CO}_3)^{2-}$ and complex Si-containing anions.²² In the Lauer sample, the ions would have been complex Si anions, SO_4^{2-} , and Ca^{2+} . Interestingly, the Lauer sample had very little Mg and Al. The presence and size of the Si-rich spheres, shown in Fig. 4(b), is also consistent with our conjecture.

As important, under the circumstances described above, the resulting μc 's would tend to be amorphous and/or nanocrystalline, in agreement with our TEM observations (Fig. 2). The TEM results are crucial and cannot be overemphasized.

(3) Feasibility

The main purpose of this paper was to present evidence that at least some of the pyramid blocks were fabricated with reconstituted “stone,” a goal we believe we accomplished. In the remainder of this paper, we speculate on the chemistry of the mixes, and the availability of raw materials needed, subject to the following caveat: because our sample size was tiny, what we see is most probably skewed. Other circumstantial evidence is shown below in the form of photographs of various pyramids (Fig. 6) that is consistent with our conjectures.

Clearly, much more work is needed before full understanding is achieved. What renders the task more complicated is the fact, obvious from this work, that the ancient Egyptians utilized a sophisticated knowledge of Ca-based cements. We explored three different pyramid stones (Lauer, OC, and Menk) and, if the surface of the Lauer sample is included, essentially found four different chemistries. It is hereby acknowledged that some of what follows is by its very nature more speculative than the first part. We also make some excursions in defense of some unstated criticisms that have dogged the limestone concrete theory since its inception. It is important to note, however, that nothing in this section should detract from the evidence presented above or the major conclusion of this work.

(4) Availability of Raw Materials

Lime-based cements existed in antiquity centuries before the Great Pyramids were built,^{23,24} and their presence here is thus not too surprising. Critics of Davidovits's theory, however, have claimed that the amount of fuel needed to calcine the tons of lime needed, for a project of the scale of the pyramids, would have been very difficult to procure and/or afford, as the making of lime from limestone requires temperatures in the vicinity of 900°C.²⁵ This is a very legitimate criticism that is dealt with below. In the meantime, we note that the high Mg content of the OC sample suggests that it was added to the mix. The source of this Mg is most probably dolomite and/or magnesite (MgCO_3) known to exist in Egypt.²⁶ The major attraction of the latter over limestone is its lower calcination temperatures; thermodynamically, magnesite decomposes at 303°C, and dolomite at 414°C (into MgO and CaCO_3).²⁵ The slaking of dolomitic lime, however, may have presented a problem, which may be why it was confined to the outer casing blocks.

Another key to the entire operation is the availability of a source of silica that is readily soluble in basic solutions. Possible sources, in addition to the indigenous clay and halloysite found in the Giza limestone, are diatoms found in the Holocene lacustrine diatomaceous earth of Fayum, south west of Cairo. This is the region where the Maidum and other pyramids were built. Note that the absence of Na and Al excludes all minerals but diatomaceous earth.

All pyramid samples contained S, while the natural stones did not. It thus follows that S must have been added to the mix, most probably in the form of gypsum. As noted above, the Maadi limestone formation—with its readily identifiable gypsum layer and near proximity of the Giza plateau—is its most likely source. The presence of S is also not too surprising as it is established that the Egyptians were using gypsum,^{13–15} as well as lime-based mortars in the fourth dynasty.¹⁵ Gypsum mortars were much more common, however, because as Lucas²⁷ pointed out, they served all the purposes of lime mortars, were plentiful, and could be activated at a much lower temperature. The binders identified in this work are clearly not gypsum based, however. What is also obvious is the builders' local use of a phosphate-based mortar or plaster as well (Fig. 4(a)). It is conceivable that they used the latter to seal the surfaces to prevent the development of effluorescences.

The most compelling evidence, albeit indirect, that at some time during the fabrication process the solution was highly basic—which is central to Davidovits's conjecture—is the sub-micron silicon-rich spheres found in the Lauer sample (Fig. 4(b)). It is well established that silica will readily dissolve

in basic solutions and reprecipitate as submicron spheres when the water evaporates.²⁸ Interestingly, a recent paper described how diatoms from hot spring waters with a pH of 8–9 were abiotically converted to submicron spheres reminiscent of the ones shown in Fig. 4(b).²⁹ The Si-rich spheres shown in Fig. 4(b) cannot be due to the breakdown of a thermodynamically unstable cement phase, viz., $2\text{CaO} \cdot \text{SiO}_2$, as postulated by Klemm and Klemm,¹⁵ because there is very little Ca in their vicinity (Fig. 4(b)). Weathering could also not have been a factor here as the Lauer sample was from the interior of the pyramid.

In general, our results are in agreement with Davidovits' proposal, as in both, the key is the presence of complex Si anions in solution. In contradistinction, however, the samples we examined were held together by a Ca–Mg silicate (OC), or amorphous silica (Lauer), rather than a Na–Al silicate, binder. Based on our admittedly tiny sample, it is unlikely that Al played a major role, as there is no evidence for its presence in the “binding” phases or for it being added. The role of Na is also unclear at this time and does not appear central in the samples we examined.

(5) Other Evidence

A careful examination of the visible pyramid blocks on the Giza plateau suggests that most—especially in the core—appear to have been carved (Fig. 6(a)); some—near the surface, including the outer casing—appear to be cast (Fig. 6(b)). Figure 6a shows a photograph of the gash made by Vyse in the south face of Khufu during his 1836–1838 explorations. Here, the blocks do not appear to have been cast. Just below the gash, however, the

blocks appear to be cast (Fig. 6(b)). The same is true of some of the blocks in the bottom left of Fig. 6(a).

This observation begs the question: why were the pyramids not made wholly of these cast stones? After all it is easier to cast a stone than to cut and hoist it into place. The answer, embedded in our finding, is simple: making geopolymeric stone was an expensive proposition. For a primitive society, the fabrication of lime is non-trivial, especially the millions of tons that would have been required. Along the same lines, crushing tons of limestone is non-trivial either. Under these constraints, the ancient builders apparently compromised and apparently built an outside constraining ring of cast blocks surrounding a core that was carved and hauled into place. It is important to note that the same is true of the interior chambers and passageway of the pyramids: most were probably cast, either for esthetic or, much more likely, for structural reasons.

The question of how the builders were able to level the roughly $230\text{ m} \times 230\text{ m}$ of the base to within 2.1 cm becomes almost a non-issue, as Davidovits and Morris have pointed out. The other difficult question of how the builders were able to maintain precisely the angle of the pyramids such that the four planes met at a point² also becomes easier to answer: the angle was probably built into the molds of the casing blocks.

Another ramification of our conclusions is that the ramps would not have had to extend to the top of the pyramids, and the serious problem of how the ramps would extend to the very top² is no longer an issue. It is thus tempting to speculate that near the top of the pyramids, the stone was cast. This is especially true as Lehner² notes that in Khufu's pyramid, “... towards the top higher quality limestone was used ...” Later, he remarks, “... the quality of the core stone becomes gradually finer in the last several courses that are preserved before the top, until it almost matches that of the Turah limestone casing.”

As importantly, the top of Khafre's pyramid is described as follows by Lehner² “Just beneath the lowest surviving course of casing stones, a band of regular stepped core stones is visible. The rest of the surface down to the base—the greater part of the pyramid—consists of very rough, irregular loose stone.” Could it be that the regular stepped stones—visible to the naked eye—are cast?

Hard evidence—in the form of chemical analysis such as carried out herein—is clearly needed to confirm some of those hypothesis. And while we believe this paper furthers our understanding of how these magnificent and enduring monuments were built, it does in no way dispel or answer some of the more important questions, the most impressive and mysterious of which is how the massive granite beams—estimated to weigh 70 tons each—spanning the width of the King's Chamber, $\approx 70\text{ m}$ up the Great Pyramid, were cut and hauled in place.

V. Summary and Conclusions

In summary, the simplest explanation for the presence of the plethora of μc 's, some of which appear to possess chemistries and morphologies not found in the natural stone, is that the various ions were in solution and precipitated or geopolymerized relatively rapidly. This comment notwithstanding, we hereby acknowledge that nature is quite resourceful and could have—however unlikely—produced all the microstructures examined herein. We believe, however, that our work presents enough evidence to entertain the possibility that crucial parts of the Great Pyramids are indeed made of reconstituted limestone; only more research will tell.

The conclusions reached herein, if confirmed by others on larger samples clearly show that the Ancient Egyptians were not only exceptional civil and architectural engineers but also superb chemists and material scientists. They would also have to be credited with the invention of concrete, thousands of years before the Romans. That a lime-based cement cast and cured at room temperature would survive for 5000 years—while the best our civilization has to offer, Portland cement, which under the best of circumstances lasts 150 years or less—is both awe inspiring and humbling. Lastly, we note that the full implications



Fig. 6. Photographs of (a) Vyse's gash in Khufu's south face. It is clear that these blocks were most probably not cast, (b) blocks just below the gash; these appear to have been cast.

of our conclusions to history, in general, and Egyptology, in particular, have not escaped us.

Appendix A

The conclusions of this work depend critically, but not solely, on the accuracy of the EDS analyses carried out at 12 kV. It is thus important to estimate its accuracy. Ideally, EDS spectra should be collected from polished and smooth surfaces. When spectra are collected from pores and/or fractured surfaces, i.e., rough surfaces, they are less accurate. It is also non-trivial to quantify C accurately because it is a common contaminant and its signal is weak. With these caveats in mind, it is useful to review our results. Whenever the morphology of the matrix visually appeared to be calcite (e.g., Ca-rich phase or matrix phase in Fig. 3(a), columns 9 and 10 in Table III, or phase Q in the OC sample), the composition, as determined by EDS, fell in a narrow range of $\text{Ca}_{19\pm1}\text{C}_{20\pm2}\text{O}_{59\pm2}$, viz. acceptably close to the 1:1:3 ratio of Ca:C:O of calcite. This result is important because it allowed us to use such areas as internal calibration standards in most of our analyses. In another area, the chemistry was $\text{Ca}_{10}\text{Si}_{11}\text{O}_{22}(\text{OH})_{36}\approx\text{Ca}_{10}\text{Si}_{10}\text{O}_{40}\text{H}_{40}\text{O}_{20}\approx\text{CaSO}_4\cdot 2\text{H}_2\text{O}$. In other words, our chemistry matches that of fully hydrated calcium sulfate with an accuracy of ± 2 at.%. In an OC sample, we found regions with the following chemistries: $(\text{Ca}_{12}\text{Mg}_{11})\text{C}_{20}\text{O}_{58}$ and $(\text{Mg}_{10}\text{Ca}_{12})\text{C}_{18}\text{O}_{58}$. Both are clearly natural dolomite, which we believe was part of the aggregate used.

In the cases where the EDS information was taken from porous regions, the accuracy per force was less good. In these situations, we tried to find areas that were as flat and horizontal as possible (e.g., inset in Fig. 1(b)). It is crucial to note that the Si signal in most areas was strong and unambiguous and > 1 at.% (e.g., Figs. 1(c) and 5(c)). However, as it is the presence of Si in these μc 's, rather than its absolute value that is most telling, any loss in accuracy does not in any way alter our conclusions.

Most EDS measurements were made at magnifications of $\times 10,000$ or higher. This was done to ensure that the spectra were collected from a well-defined homogeneous location. A typical protocol as follows was: First, find a calcite area and confirm its chemistry, second, identify the area for which the spectra were to be collected in the backscattered mode, third, increase the magnification up to a point where the area to be analyzed took up the entire screen, and fourth, the spectra were collected only if the microstructure at the highest magnification appeared homogeneous. In some cases, the microstructure even at high magnifications did not appear homogeneous. In that case, the microstructure is shown (e.g., Fig. 1(c) and inset in Fig. 5(c)).

The procedure to convert the EDS results to chemical formulae was as follows: the sum of the positive charges and negative charges was added and compared. If the negative charges were higher than the positive, protons, i.e., water of hydration, were added to balance the charges. When the opposite was found, we assumed any excess C was present, not as a $+4$ cation, but as an organic phase. This amount of extra C is included in all the formulae for the sake of completion. In many cases, the charges did balance as measured. This was especially true of the calcite and dolomite grains making up the bulk of the samples, viz., the aggregate. Note that in some cases, the charges may not exactly balance due to rounding errors.

Lastly, in order to estimate the EDS excitation volume in calcite, we carried out a Monte Carlo simulation of 100 trajectories. For electron energies of 14 kV, the volume probed was found to be $\approx 1\ \mu\text{m}^3$. (The details of the simulation can be found in Joy.³⁰) As noted above, by taking our EDS spectra at $\times 20,000$ or $\times 50,000$, the chemical information was obtained from a lateral area that was roughly the size of the area seen on the screen. Needless to say, if the thickness of the areas examined was thinner than $1\ \mu\text{m}$, the EDS would necessarily contain information from adjacent phases. We do not believe this to have been a major problem here because: (a) many of the features were clearly thicker than $1\ \mu\text{m}$ (e.g., Figs. 1(a), (b), 3, 5(b) and (d)). (b) Given the brittle nature of the stone, it is unlikely

that too many areas were covered by $\approx 1\ \mu\text{m}$ thick slivers. If anything, the polishing appears to remove material more easily from the "grain boundary areas" than from the limestone aggregates (e.g., Figs. 1(b) and 5(a)).

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References

- Goyon, "Les Rangs d'assises de la Grande Pyramide," *Bulletin de l'Institut Français d'Archeologie Orientale*, Cairo, **78**, 405–13 (1978).
- M. Lehner, *The Complete Pyramids*. The American University in Cairo Press, Cairo, Egypt, 2004.
- W. M. F. Petrie, *Pyramids and Temple of Gizeh, Field*, London. Histories and Mysteries of Man, Ltd., London, 1883, reprint 1990.
- Abd al-Latif, *The Eastern Key: Kitab al-iftadah wa'l-i'tibar of 'Abd al-Latif al-Baghdadi*. Translated by K. H. Zand, p. 117. Allen and Unwin, London, 1965.
- D. Arnold, *Building in Egypt: Pharaonic Stone Masonry*, pp. 168–9. Oxford University Press, New York, 1991.
- M. Morris, *The Egyptian Pyramid Mystery Is Solved!*, Vols. 1 and 2, pp. 20, 154, 157. Scribal Arts, Detroit, 2004.
- J. Davidovits and M. Morris, *The Pyramids: An Enigma Solved*. Hippocrene, New York, 1988.
- J. Davidovits, Ils ont bâti les pyramides, Jean-Cyrille Godefroy, Paris, 2002; see also <http://www.geopolymers.org/archaeol.html>
- J. Davidovits, "X-Rays Analysis and X-Rays Diffraction of Casing Stones from the Pyramids of Egypt, and the Limestone of the Associated Quarries"; pp. 511–20 in *Science in Egyptology Symposia*, Edited by R. A. David. Manchester University Press, Manchester, U.K., 1986.
- J. A. Harrell, "An Inventory of Ancient Egyptian Quarries," *Newslett. Am. Res. Center Egypt*, **146**, 1–7 (1989).
- K. D. Ingram, K. E. Daugherty, and J. L. Marshall, "The Pyramids—Cement or Stone," *J. Archaeol. Science*, **20**, 681–7 (1993).
- D. H. Campbell and R. L. Folk, "Are the Pyramids of Egypt Built of Poured Concrete Blocks?," *J. Geol. Educ.*, **40**, 25–34 (1992).
- D. D. Klemm and R. Klemm, "The Munich Pyramid Project: Origin of the Stone Material of the Royal Monuments of the Old Kingdom Between Abn Roash and Meidum. Abstract papers," *V. Intern. Congr. Egyptol.*, 158–9 (1988).
- M. Regourd, J. Kerisel, P. Deletie, and B. Hagenauer, "Microstructure of Mortars from Three Egyptian Pyramids," *Cement Concrete Res.*, **18**, 81–90 (1988).
- D. D. Klemm and R. Klemm, *Mortar Evolution in the Old Kingdom of Egypt*, *Archaeometry '90*. Birkhäuser Verlag, Basel, 1990.
- G. Demortier, Professor Emeritus, Facul. Universitaires de Namur, F.U.N.D.P. Namur, Belgium.
- H. A. Ireland, "Terminology for Insoluble Residues," *Am. Assoc. Petrol. Geol. Bull.*, **31**, 1479–90 (1947).
- A. Bell and C. J. Wilson, "Deformation of Biotite and Muscovite—TEM microstructure and Deformation Model," *Tectophysics*, **78**, 201–28 (1981).
- Z. Iskander, "Desert Varnish and Mortar in Rhombohedral Pyramid at Dahs-hour," *Ann. Serv. Antiq. Egypte*, **LII**, 271–4 (1952).
- P. Tompkins, *Secrets of the Great Pyramid*. Harper & Row, San Francisco, 1971.
- L. T. Dolphin and N. Barakat, et al., "Electromagnetic Sounder Experiments at the Pyramids of Giza"; Stanford Research International, Menlo Park, CA, 1975, <http://www.ldolphin.org/egypt/egypt1/>.
- D. A. Sverjensky, E. L. Shock, and H. C. Helgeson, "Prediction of the Thermodynamic Properties of Aqueous Metal Complexes to 1000°C and 5 kb," *Geochim. Cosmochim. Acta*, **61**, 1359–412 (1997).
- H. Gourdin and W. D. Kingery, "The Beginnings of Pyrotechnology. Neolithic and Egyptian Lime Plaster," *J. Field Archaeol.*, **15**, 219–44 (1988).
- W. D. Kingery, P. B. Vandiver, and M. Prickett, "The Beginnings of Pyrotechnology, Part II: Production and Use of Lime and Gypsum Plaster in the Pre-pottery Neolithic Near East," *J. Field Archaeol.*, **15**, 219–44 (1988).
- W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics*, 2d edition, Wiley, New York, 1976.
- R. Said, *The Geology of Egypt*. Balkema Publishers, Rotterdam, 1990.
- A. Lucas, "Mistakes in Chemical Matters Frequently Made in Archaeology," *J. Egypt. Archaeol.*, 128–32 (1924).
- R. K. Iler, *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry*. John Wiley Inc, New York, 1979.
- A. Channing, D. Edwards, and S. Sturtevant, "A Geothermally Influenced Wetland Containing Unconsolidated Geochemical Sediments," *Can. J. Earth Sciences*, **41**, 809–27 (2004).
- D. C. Joy, *Monte Carlo Modeling for Electron Microscopy and Microanalysis*. Oxford University Press, Oxford, 1995.