# THE GREAT PYRAMID DEBATE

## Evidence from Detailed Petrographic Examinations of Casing Stones from the Great Pyramid of Khufu, a Natural Limestone from Tura, and a Man-made (Geopolymeric) Limestone

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## ABSTRACT

Contrary to the well-known hypothesis of construction of the Great Pyramids at Giza by carving and hoisting quarried limestone blocks, in 1974 a French research chemist, Joseph Davidovits, proposed a radically different hypothesis that the pyramid blocks are not quarried stone but cast-in-place "concrete" prepared with the soft, marly kaolinitic limestone of Giza that was readily disintegrated in water and mixed with locally available lime and natron. The lime-natron combination, according to Davidovits, dissociates the kaolinitic clay from the limestone and forms an alkali-aluminosilicate (zeolitic) "glue", which he termed "geopolymer". The "man-made" hypothesis was proposed as an alternative explanation to the apparent mysteries associated with the "carve-and-hoist" hypothesis in regard to the methods of construction and observations of some "unusual" minerals in pyramid samples that are rare in natural limestone.

The purposes of the present study are to investigate: (a) evidence of microchemical signatures of the proposed lime-natron-clay-based geopolymeric chemistry in the binder phases of the pyramid samples; (b) textural, mineralogical, microstructural, and binder-microchemical comparisons among pyramid samples, natural limestone from Tura, and geopolymeric limestone; and (c) the reported "unusual" constituents in the pyramid samples, if any, and their possible sources.

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[1] The Great Pyramid of Giza was the world's tallest building from c. 2570 BC to c. 1300 AD (from http://en.wikipedia.org/wiki/Great_Pyramid_of_Giza, with permission).

To achieve these goals, detailed petrographic examinations by optical and scanning electron microscopy, x-ray diffraction, and x-ray microanalysis were done on: (a) two pyramid samples, reportedly from the casing stones of the Great Pyramid of Khufu (EA-491 from the British Museum, and the famous "Lauer sample" from J.P. Lauer); (b) a natural limestone from Tura (one of the reported sources of the casing stones); and (c) a geopolymeric limestone, prepared by Davidovits.

Optical and scanning electron microscopical examinations show overall textural and mineralogical similarities between the casing stones and the limestone from Tura; and significant textural and microstructural differences between these samples and the man-made geopolymeric limestone. Both casing stones and natural limestone are variably porous, particulate-textured, bioclastic microcrystalline limestone consisting of isolated fossil fragments (foraminifera, molluscs, echinoids) in a dominantly microcrystalline calcite matrix of micritic mud, microsparite calcite, and micritic lumps. The Lauer sample (an inner casing stone sample from the ascending passageway of the Khufu pyramid), previously described by the proponents of the man-made hypothesis to be "synthetic", shows startling microstructural and textural similarities to the other casing stone, EA-491, and the natural limestone from Tura. There is no textural or microstructural indication of a "reconstituted limestone" in the pyramid casing stones.

X-ray microanalysis of the binder phases in the casing stone samples show no evidence of alkali-aluminosilicate-based chemistry, which is so characteristically and distinctly detected in the geopolymeric limestone. The pyramid casing stones are similar to other limestones and have a microcrystalline calcite binder – a normal geologic component. Based on the absence of any alkali or especially alumina enrichment in the binder phases of the casing stones, which is the essence of the proposed lime-natron-clay-based recipe of the geopolymer hypothesis, the pyramid stones are determined to be far removed from a "geopolymeric" limestone.

Based on the detection of a calcium phosphate-based composition in the "synthetic" white coating on the Lauer sample, and its subsequent detection in the underlying limestone, Davidovits proposed a synthetic origin for the entire Lauer sample. Present x-ray microanalysis showed a distinct zone of phosphorous enrichment at only one edge of the Lauer sample, with progressively decreasing phosphorous contents towards the opposite end to a distance of approximately 5 mm, and thereafter negligible and uniform phosphorous contents throughout the bulk interior of the Lauer sample. This clear zone of phosphate contamination in limestone is situated directly adjacent to the phosphate-based coating, where the porous microstructure of the casing limestone was invaded by phosphates from the coating. Phosphorous concentrations in the interior, away from this coating-influenced "contaminated zone" are negligible and similar to those found in the other casing stone (EA-491) and in the limestone from Tura. Therefore, previous detection of phosphate phases in the Lauer sample (at significantly lesser amounts than that in the coating) merely represents an artifact of contamination from the coating and does not in any way indicate a "synthetic" origin of the Lauer sample. No such phosphate enrichment was found in the other casing stone sample (EA-491) from the Great Pyramid of Khufu.

Besides calcium phosphate phases, the Lauer sample also contains a silica-rich microconstituent, characteristically spherical in shape, which is mineralogically described as opal-CT (a transitional phase from amorphous opal to tridymite/cristobalite). Despite its occurrence in many natural limestones, based on its detection in the Lauer sample only and not in the quarry limestone from Tura, a synthetic (geopolymeric) origin of casing stones in the Khufu pyramid was suggested by Davidovits. The present study detected numerous less than 10µm-sized[2], silica-rich microconstituents characteristically near-spherical to spherical in shape (lepispheres) in both the casing stones (EA-491 and the Lauer sample) and in the natural limestone from Tura, but not in the geopolymeric limestone. Cristobalite is detected not only in the casing stones but also in the natural limestone from Tura. The previously reported “unusual” chemistries of these microconstituents are an artifact of various impurities (e.g., Ca, Mg, Al, Na), which these phases, like any other minerals, can accommodate. XRD studies of acid-insoluble residues determined the tridymite/cristobalite mineralogy, and SEM-EDS studies determined the minor-element compositions of these silica-rich microconstituents. Contrary to the occurrences of these silica-rich microconstituents as isolated, very fine (< 10µm in size), near-spherical, “interstitial” phases between calcite grains in casing stones and natural limestone, geopolymeric limestone shows an overall uniform (i.e., non-isolated), homogeneous silica-rich composition of the binder along with high alkalis and alumina and no indication of a separate silica-rich microconstituent. Therefore, occurrences and variable compositions of these silica-rich microspheres of opal-CT both in casing stones and in natural limestone do not in any way indicate a “synthetic” origin of the pyramid blocks.

This study conclusively demonstrates that there is absolutely no evidence of an alkali-aluminosilicate-based composition in the binder phases of the casing stones, nor is there any evidence of “unusual” constituents in the pristine, bulk uncontaminated interior of the casing stones to call for a “man-made” origin. Despite the detection of a man-made “coating” on the Lauer casing stone, the stone itself is determined to be nothing but a high-quality natural limestone mineralogically, texturally, and microstructurally similar to that found in the quarries at Tura-Masara.

Based on the present scientific proof of the absence of a “geopolymeric” signature or any “synthetic” composition in the same Lauer casing stone, originally used as a “smoking gun” to support the concrete-pyramid hypothesis, the proposed geopolymer hypotheses of Davidovits and others, or any “new” hypothesis for that matter really has no practical credibility (let alone their astounding extension to both core and casing blocks, and granite/granodiorite/basalt/travertine/quartzite blocks, columns, pavements, and other architectural artifacts associated with the Great Pyramids) unless detailed and systematic research is done by a diverse group of scientists on actual pyramid samples of known provenances. A valid hypothesis must rest upon a reliable set of unquestionable data.

Despite much reported evidence of the use of zeolitic (geopolymeric) chemistry in the ancient technologies, its promising future in the modern cast-stone technology and as innovative building materials for sustainable development, there is no evidence of use of geopolymeric cement in the pyramid stones. Based on unassailable field evidence in favor of a geologic origin for the pyramid stones, and equally convincing results of the present laboratory studies confirming the “geologic” origin of the casing stone samples from the Great Pyramid of Khufu (originally used as evidence for a man-made origin), the author is convinced that the Egyptian pyramids stand as testament to the unprecedented accuracy, craftsmanship, and engineering skills of the Old Kingdom (2500 BC) stone masons!

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[2] 1µm = 1 micron = 0.001 millimeter.

## THE GREAT PYRAMID DEBATE

For more than a century, many hypotheses have been proposed to unravel the enduring mysteries of how the Great Pyramids of Giza were built. Among these, the most popular and widely published hypothesis, accepted by Egyptologists, scientists, researchers, engineers, geologists, archeologists, historians and other professionals is the "carve and hoist" hypothesis, which postulates building the Great Pyramids by quarrying, carving, and hoisting blocks from the natural limestone quarries at Giza with unprecedented accuracy, craftsmanship, and engineering skill by the Old Kingdom (2500 B.C.) masons. The rectangular-shaped core blocks (constituting more than 80 percent by mass of the Great Pyramid of Khufu) were prepared from the local limestone bedrock at Giza, whereas the more precise inner and outer casing stones (estimated 115,000 blocks of the total 2.3 million blocks in the Great Pyramid of Khufu) were built with fine-grained, superior quality, massive-textured limestone from the Middle Eocene limestone of the Mokattam Formation found near the villages of Tura and Masara on the east side of the Nile (Lehner 1997). The limestone underlying the Giza Plateau also belongs to the Mokattam Formation, but represents a shallower-water marine facies than the Tura-Masara limestone.

Contrary to this popular "carve and hoist" hypothesis of building the Great Pyramids of Egypt with quarried blocks of natural limestone, in 1974 Joseph Davidovits, a French research chemist, proposed a man-made (geopolymeric) origin for the pyramid blocks (Davidovits 1983, 1984, 1986, 1987, Davidovits and Morris 1988, Morris 1991), arguing that they are poured, cast-in-place concrete. The "concrete" is suggested to have been prepared by mixing the soft, marly, kaolinitic, nummulitic limestone of Giza with Nile river water (where limestone reportedly easily disintegrates[3]), lime [$Ca(OH)_2$], and locally available natron [$Na_2CO_3.10H_2O$] (Davidovits and Morris 1988). The lime-natron combination produces sodium hydroxide, which dissociates the aluminosilicate component in the limestone, i.e., the kaolinitic clay, and reacts to form an alkali-aluminosilicate (zeolitic) type, or geopolymeric binder. Geopolymeric reactions, such as by the proposed alkali-activation of aluminosilicates, is indeed common and dates back to the ancient times in manufacturing many mortars and cast stones. Reportedly, with as little as 5 to 10 percent of such binder by volume a man-made limestone can be prepared, which a stunning visual resemblance and close correspondence in physical properties to a natural limestone.

The man-made cast-in-place (geopolymeric) concrete origin has been proposed (Davidovits and Morris 1988, Morris 2004) to explain many apparent difficulties in the carve-and-hoist hypothesis related to: (a) the mysteries of carving and hoisting of closely joined blocks, and building such magnificent monuments in a short period of time with stone and copper-based tools during the Old Kingdom; (b) many puzzling engineering aspects of pyramid construction; and (c) certain field evidence of a "geologic" origin (e.g., jumbled fossils, softened weathered spongy zone at top of many pyramid blocks, sedimentary stratification, cross bedding, continuation of sedimentary bedding across many blocks, blocks having vertical sedimentary bedding, calcite-filled tectonic fractures, tool marks on blocks, gypsum

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[3] In actuality, however, the limestone quarried at Giza is neither marly (i.e., clay-rich) nor kaolinitic, and it will not disintegrate in water (Harrell, personal communication, April 2007). Davidovits claimed that it is the soft, marly, nummulitic, kaolinitic limestone in the Mokattam formation (similar to the soft layers interbedded with hard limestone layers present beneath the Sphinx), which was used for the preparation of "concrete" (Morris 1993). The core blocks in the great pyramids, which are known to have carved by using locally available limestone from the Giza plateau cannot be prepared by his method since the bedrock is simply too hard to disintegrate in water.

mortars between stones, etc.). Despite having many reasonable scientific explanations to each of these, and published irrefutable field evidence of “geologic” origin of pyramid blocks (Folk and Campbell 1992, Campbell and Folk 1991), proponents of the man-made hypothesis continued to provide further support from laboratory examinations of a few samples of casing stones, and natural (quarry) limestones (Davidovits 1983, 1986, 1987). Based on the discovery of certain “unusual” minerals, compounds and features in the pyramid casing stones, reporting the absence of those in natural limestone, and providing alternative explanations to textures and features found in the casing stones, a geopolymeric origin is suggested.

Ever since the first proposition of this “man-made” origin of pyramid blocks by Davidovits, mainly through his book *The Pyramids: An Enigma Solved* (1988), a number of scientists have published a wealth of data fiercely challenging this hypothesis and providing evidence in favor of a “geologic” origin (Campbell and Folk, 1991, Folk and Campbell 1992, Freestone et al. 1984, Mehta 1988, Gauri 1984, 1988, Moores 1992, Schoch 1992, Bradley and Middleton 1988, Freestone and Middleton 1986, 2007; Harrell and Penrod 1993, Ingram et al. 1993, Klemm and Klemm 2001, Novokshchenov 1996, Parry 2000). Contrary to the original proposition of geopolymeric origin from Davidovits, an eminent chemist, the challenges in favor of the natural (i.e., geologic) origin of the blocks were mostly provided by both engineers and geologists with expertise in limestone petrology. Therefore, a lack of understanding of the geopolymer chemistry by the geologists and engineers is sometimes mentioned by Davidovits as his rebuttal.

In a recent article by Barsoum et al. (2006), a team of material scientists at Drexel University, USA gave a renewed attention to this debate from evidence suggesting a “man-made” origin of the casing stones. Their study, based on scanning electron microscopy and x-ray microanalysis (SEM-EDS) detected some microconstituents in the casing stones that are reported to have compositions not found in natural limestone. Their study demonstrated the absence of alkali or alumina enrichment in the pyramid casing stones, which are the essence of the lime-natron-based recipe of Davidovits’ geopolymer hypothesis. Barsoum et al. (2006) detected silica-rich microconstituents and sub-micron size silica-rich spheres in the casing stones with estimated compositions reportedly rare in natural limestone (due to their lack of occurrence with identical chemistry in the examined natural limestones) – therefore, the “man-made” origin of the casing stones was supported. Although Barsoum et al. (2006) did not propose an alternative recipe for their reconstituted limestone hypothesis, unlike Davidovits and the followers of the geopolymer hypothesis, who suggested both core and casing blocks to be man-made, however, Barsoum et al. (2006) mentioned that “a careful examination of the visible pyramid blocks on the Giza plateau suggests that most – especially in the core – appear to have been carved.”

The latest research by Davidovits’ team at the Geopolymer Institute in France continued to promote the old lime-natron-clay-based recipe to support a “man-made” origin for the entire pyramid of Khufu (Davidovits, J. and Demortier, G. 1999, Demortier, G. 2004, Davidovits 2005). Their research, along with Davidovits’ latest demonstration on reproduction of his experimental pyramid with the proposed geopolymer recipe, and the recent claim by Barsoum et al. (2006) steered public interest and enquiry about this alternative hypothesis of pyramid construction (Bremner 2006, Wilford 2006). The present study is a result of this renewed debate on the natural versus man-made controversy of the Great Pyramids.

## PURPOSE OF THIS STUDY

This article provides a fresh look at this debate through detailed petrographic examinations of two previously examined samples from the casing stones of the Great Pyramid of Khufu, a natural limestone from Tura, and a geopolymeric limestone reportedly prepared and supplied by Davidovits for the purpose of chemical comparisons with the pyramid blocks. All samples were studied by optical microscopy, scanning electron microscopy with associated energy-dispersive x-ray elemental analysis, and wherever possible, x-ray diffraction.

The main purposes of this investigation are to:

(a) Characterize the texture, microstructure, and mineralogy of the limestone in these samples and search for evidence of 'reconstituted' stone in the pyramid samples. For detailed characterization, the samples were studied by *petrography*, which includes not only the commonly interpreted aspects of microscopy but indeed the detailed realm of classical petrography including, of course, microscopy, associated chemical analysis, x-ray diffraction, and all other methods applied to these samples in all previous studies and in the present study that are necessary for detailed characterization.

(b) Characterize the "binder" phases in these samples through microstructural and especially microchemical analyses, and search for evidence of any "extraneous" components, or alkali-aluminosilicate based geopolymeric binder in the pyramid samples. Extensive x-ray microanalysis of the binder phases were done for detailed characterization.

(c) Emphasize the importance of a *comprehensive* study encompassing optical microscopy, chemical analysis, x-ray diffraction, scanning electron microscopy, x-ray microanalysis, and other relevant methods to understand and explain the pyramid limestone. Several examples of 'misinterpretations' of results from previous *isolated* studies are presented to explain the root of this debate.

## SAMPLES, PREVIOUS WORK, AND METHODS OF EXAMINATIONS

**Pyramid Samples** – The pyramid samples received for this study constitute (Figure 1): (a) a casing stone sample of the Great Pyramid of Khufu, identified as EA-491, generously provided by the British Museum, and (b) an inner casing stone sample from the Khufu Pyramid, identified as the Lauer Sample, which as the name implies, was originally given to Davidovits in 1982 by the eminent Egyptologist Jean-Philippe Lauer.

EA-491 – Several small chips of **EA-491** were originally provided to Donald Campbell by M.S. Tite and A. Middleton of the British Museum (BM) on November 1987. The sample was previously studied by Campbell and the researchers at the British Museum, whose results are published elsewhere (Campbell and Folk 1991, British Museum Report by Freestone et al 1984, Middleton and Bradley 1989, Freestone and Middleton 2007). A precise sampling location was not reported.

The BM research on EA-491 includes: (a) optical microscopy and SEM-EDS studies of a polished thin section, (b) XRD analysis of powder, and (c) optical microscopy-SEM-XRD-IR studies of the hydrochloric acid-insoluble residue of EA-491. The Campbell and Folk (1991) research on EA-491 includes: (a) optical microscopical examinations of chips in a stereomicroscope, an epoxy-impregnated thin section, crushed powders, hydrochloride acid-insoluble residues of chips, and small stained areas of powders and acid-insoluble residues in thin sections under a petrographic microscope, (b) bulk chemical analysis of powder by AA spectroscopy, (c) differential thermal analysis of the crushed sample, and (d) XRD analysis of a pulverized chip not used for thin section.

Portions of EA-491 received for the present study from Campbell include (Figure 1): (a) half of a 27 × 46 mm epoxy-impregnated polished thin section with a cover slip originally prepared by the British Museum, (b) half of an epoxy encapsulated disc thin section prepared by Campbell, (c) a 27 × 46 mm thin section of crushed sample on an epoxy substrate, and (d) a 27 × 46 mm powder mount of hydrochloric acid soluble residue of the sample.

> The present research on EA-491 included optical microscopical examinations of the British Museum and Campbell thin sections, as received at magnifications of 6.3 to 100X in a stereo microscope and at 40 to 1000X in a petrographic microscope. The British Museum thin section had a cover slip mounted on the sample. The slip was partially removed to expose the thin section for SEM-EDS study. Campbell's epoxy-substrate thin section was polished for SEM-EDS study. The crushed sample (mounted on epoxy) and acid-insoluble residue of EA-491 were also examined by SEM-EDS. The British Museum thin section was used primarily for mineralogical, textural, and microstructural studies by optical microscopy and the Campbell thin section was used for the microchemical (SEM-EDS) study.

The Lauer Sample – The famous **Lauer Sample** reportedly **came from the surface of a wall of inner casing stones in the Ascending Passageway of the Great Pyramid of Khufu leading to the Grand Gallery (Davidovits 1983, 1986, Davidovits and Morris 1988)**. Perhaps among the most studied pyramid samples, various results on analysis of the Lauer sample were extensively published by the researchers from both sides of this debate (Davidovits 1983, 1986, 1987, Davidovits and Morris 1988, Morris 1991, Harrell and Penrod 1993). The sample reportedly contained a white coating with a red-colored surface (Davidovits 1983, 1986).

Two pieces of the Lauer sample were separately received by the present author from Campbell (hereafter 'Lauer-Campbell') and James A. Harrell (hereafter 'Lauer-Harrell'). In 1992, Harrell received a hand specimen and a thin section from Ms. Margie Morris.

The Lauer-Campbell sample was a polished section of a small wedge-shaped, blue epoxy impregnated piece (9 × 15 mm maximum dimensions on the polished section), apparently a remnant piece left over from a previous thin section preparation, which was further encapsulated in a 15-mm diameter × 5-mm thick clear epoxy disc and polished (Figure 1). The Lauer-Harrell was a solid 25 × 45 mm sized, blue epoxy impregnated saw-cut section of a piece, larger than the Lauer-Campbell sample, which was cut from the hand specimen supplied by Morris (Figure 1). Neither piece contained the white coating or the red paint that was originally mentioned by Davidovits, which was reportedly (by Harrell) accidentally removed during preparation of the thin section. Campbell received his piece from R. L. Folk via Harrell. Therefore, both pieces of the Lauer sample that the present author received from Campbell and Harrell apparently came from Morris, who, in turn, reportedly received it from Davidovits.

> The following preparations and studies were done on the Lauer sample:
> (a) Visual and low-power stereomicroscopical examinations (up to 100X) of the solid sectioned piece in Lauer-Harrell sample and of the polished section in Lauer-Campbell sample;

(b) Preparation of two uncovered thin sections from the Lauer-Harrell sample - one used for detailed petrographic examinations under Nikon-Optiphot 2 POL and Olympus BX-40 petrographic microscopes at magnification ranges from 40X to 1000X; the other used for acid-etching and x-ray diffraction study of the acetic acid-insoluble residue of the thin section;
(c) Preparation of a polished section of the Lauer-Harrell sample for x-ray diffraction study of the bulk sample, followed by scanning electron microscopical examinations with ancillary energy-dispersive x-ray microanalytical (SEM-EDS) studies; and
(d) Detailed SEM-EDS studies of both the Lauer-Campbell and Lauer-Harrell polished sections.

**Natural Limestone Sample** – The natural limestone sample, identified as "T-1", was received from James A Harrell, and reportedly came from one of the ancient limestone quarries on Gebel Tura, on the property of the Tura Portland Cement Co. A small pristine sample, approximately 70 × 80 × 150 mm in size, with saw-cut edges was received (Figure 1).

The sample was first examined visually with a stereomicroscope at magnifications of 10 to 100X. Multiple thin slices were then removed by using an ultra-thin continuous rim diamond wafering blade (less than 1 mm thick) in a precision sectioning saw (Buehler's Isomet Low Speed Saw) using glycol as cutting fluid. After cleaning the slices ultrasonically in alcohol, one piece was impregnated in epoxy mixed with blue-dye to prepare a 27 × 46 mm thin section. Two other slices were used (one with and another without epoxy impregnation) for preparation of polished sections for SEM-EDS study. Two other slices were pulverized to fine powders - one (pulverized down to 75μm size particles) for a hydrochloric acid-insoluble study, and the other (pulverized down to 10 to 15μm size particles) for an XRD study. The insoluble residue obtained was used directly for oil immersion mount examination, and SEM-EDS study; and an aliquot of residue was further pulverized down to 10 to 15μm size for XRD analysis. Bulk chemical analysis of this sample by XRF was provided in Harrell and Penrod (1993).

**Geopolymer Samples** – Of the two geopolymer samples received (Figure 1), the first one is a thin section of a hardened geopolymeric "limestone" and the second one is light cream-colored, small, angular chips of a hardened pure geopolymer. The former was half of a 27 × 46 mm thin section. Both samples came from Campbell, originally given to him by Davidovits. In a letter to Campbell, dated February 1988, Davidovits described these samples as:

> "(a) Pure Geopolymer, type K-PSS (Kaliophilite backbone ?)
> (b) Geopolymeric Limestone (made July 1982) comprising: limestone 70 percent by weight, Geopolymer 30 percent by weight (analcime type Na-PSS). X-ray datas are shown in the paper Science in Egyptology. The sample was produced from a clay-like plaster paste, this explains the high amount of air bubbles. We know now how to produce in the lab bubble-free geopolymeric limestone".

In the same letter Davidovits also mentioned a natural limestone from the Tura quarry, Sample HD, which he described in his Science in Egyptology paper (Davidovits 1986) and which was also petrographically described in Campbell and Folk (1991). The published results on Sample HD will be compared with the Tura Limestone received for this study.

The thin section of the hardened geopolymeric limestone was examined under a stereomicroscope (Mag. 6.3 to 100X) and petrographic microscope (Mag. 40 to 1000X). The section was studied in detail by optical microscopy and numerous photomicrographs were taken prior to the following next step. The hardened geopolymeric limestone slide had a cover slip mounted on the sample. The slip was partially removed and an SEM-EDS study was done on the freshly exposed surface to analyze the geopolymeric binder phase present in this limestone. The hardened kaliophilic-type pure geopolymer was studied in SEM-EDS to determine the microstructure and microchemistry.

**Instrumentation** – Instruments used in petrographic examinations include: (a) research-grade stereomicroscopes (Olympus SZH, SZX12, Mag. 6.3 to 100X); (b) petrographic microscopes (Nikon Optiphot 2 Pol, Olympus BX 40, Mag. 40-1000X); (c) Cambridge Scanning Electron Microscope's CamScan Series II SEM with EDS-BSE-SE detectors and 4Pi "Revolution" image capture and analysis modules (acceleration voltages used were 10 to 20 kV); and (d) Siemens D 5000 x-ray diffractometer with θ-2θ geometry and copper K-alpha radiation (30 mA, 40 KV). XRD scan rates varied from very slow at 0.5 degree/minute for insoluble residue analysis on an off-axis quartz plate to 2 degrees/minute for bulk sample analysis, or for search for a specific phase at a desired peak location.

**Sample Preparation** – All samples received for this study were examined and photographed, as received, to the extent possible prior to any sample preparation. The various sample preparation techniques used, e.g., impregnation, sectioning, lapping, polishing, thin sectioning, conductive coating, pulverization, etc. are described in detail in Jana (2006). Every precaution was taken to minimize any abrasive or other contaminations during sample preparation, and to reduce any accidental damage or loss (especially of thin sections) during further processing. The conductive coating for the SEM-EDS analysis was varied from no coating to very thin carbon coating or very thin gold coating, depending on the purpose of the study.

## VISUAL APPEARANCES OF PYRAMID CASING STONES, NATURAL LIMESTONE, AND GEOPOLYMER SAMPLES USED IN THIS STUDY

### The British Museum Sample EA-491: A Casing Stone Sample from the Great Pyramid of Khufu

Since EA-491 received for the present study does not include any original hand specimen, the following description is a summary of previous reports of British Museum on visual appearance of this casing stone sample.

> In hand specimen, BM report (Freestone et al. 1984) describes EA-491 as a "pale, dense, fine-grained rock, with few heterogeneities visible to the naked eye. There are no marked planes of weakness, so that from the point of view of the sculpture, this would have been a high quality material."

EA-491 is described by Campbell and Folk (1991) as "porous cream-colored massive stone" and "very light tan, lighter than the color of a Manila file folder."

### The Lauer Sample: An Inner Casing Stone Sample from the Great Pyramid of Khufu

Since two pieces of the Lauer sample received for this study do not include any "untreated" pristine hand specimen, the following description is a summary of previous reports on this sample from both sides of the debate (Davidovits 1983, 1986, 1987; Morris 1991 quoting Lauer Sample descriptions by Zeller, and McKinney; Harrell and Penrod 1993). The following descriptions highlight only the observations that are apparently consistent in all views and did not received any fierce criticisms.

> "Light gray, fine grained, dense calcareous rock containing oval to spherical voids and laminations along hair-line fractures filled with calcite. There is no apparent bedding, and one side of the specimen appears to have been painted (or enameled) with a resinous ochre-colored material. The rock underneath the coating exhibits a texture similar to wood grain." (McKinney, mentioned in Morris 1991)
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> "One side of the specimen is coated with a dark reddish brown material (probably a kind of paint) that was applied to the original surface. The matrix is generally compact, light yellowish in color and mottled. It is relatively fine grained, and has the megascopic appearance of a carbonate rock." (Zeller, mentioned in Morris 1991).
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> "The Lauer sample is a highly porous, recrystallized, fine-grained bioclastic limestone." (Harrell and Penrod 1993). This study also identified the coating mentioned in previous studies and gave a thickness of approximately 1 mm.

## A Natural Limestone from Tura

Since a hand specimen of the natural limestone from Tura was received (Figure 1), the following description is based on the present study.

The limestone sample is a dense, fine-grained, light cream to yellow colored, massive-textured, limestone with no visual fracture or bedding plane. The sample does not show any large voids, pores, or fossils in unaided eye.

The sample is homogeneous in appearance, similar to a typical bioclastic limestone. The overall appearance is similar to the descriptions of casing stones.

> In the description of Tura Limestone sample "HD" (provided by Davidovits) Campbell stated "a particulate texture virtually identical to that seen in the British Museum sample from the casing stone sample of the Khufu pyramid (i.e., EA-491). The quarry rock (i.e., the limestone from Tura), however, is considerably harder, with less porosity and permeability. The color of the quarry rock on a freshly broken surface is clearly lighter (off white) than that of the Cheops stone (very light tan, lighter than the color of a Manila file folder)."

## Geopolymer Samples of Davidovits

Of the two samples, only hardened pure geopolymer was received as chips; the geopolymeric limestone was received in thin section. Therefore, the following description for the chips is from the present study, and for the limestone is from previous reports by Davidovits, and Campbell and Folk (1991).

The hardened chips of pure Geopolymer (described by Davidovits as kaliophilite-type) are hard, angular, freshly fractured pieces, very fine-grained, dense, massive-textured, light yellow to cream colored. Fractured surfaces have conchoidal fractures. Some chips have a freshly fractured surface on one side with matted-appearance whereas shiny, polished appearance on the opposite side. The surfaces of the chips are very homogeneous with no evidence of any mineral, extraneous materials, cracks, voids, etc.

The geopolymeric limestone is reported by Campbell and Folk (1991) as follows - "to the untrained observer, Davidovits' geopolymeric limestone that he made in France appears much like many limestones, being light colored and hard, but that is where the close similarity ends when viewed microscopically." According to Morris (1991) the geopolymeric limestone was prepared for comparison on chemical composition to the pyramid limestones and was not intended as an imitation of pyramid stone.

## OPTICAL MICROSCOPICAL EXAMINATIONS

### The British Museum Sample "EA-491": A Casing Stone Sample from the Great Pyramid of Khufu

In thin section, EA-491 has a very typical particulate texture of a bioclastic microcrystalline limestone (Figures 2, 3, and 4) containing more than 90 percent calcite, a few minor constituents, approximately 7 percent acid-insoluble residue, and occasional pores and voids. The following paragraphs provide the textural and mineralogical characteristics of this casing stone:

Bioclasts – Bioclasts constitute very fine calcite fossil fragments, i.e., major amounts of foraminifera (e.g., nummulitids and globogerinids), and minor amounts of molluscan (pelecypod) and echinoid fragments that are large, whole or broken, circular, oval-shaped, lenticular, elongated, angular, from less than 20µm to 80µm in size, sporadically scattered and recrystallized throughout the microcrystalline calcite (Figure 2). There is no evidence of any coarse aggregate particles of fractured or incompletely disaggregated limestone, or any evidence of reconstituted limestone present among the allochems.

Microcrystalline Calcite Matrix – The microcrystalline calcite "mud" matrix is the major textural component containing an intimate association of ultra-fine-grained near-spherical micritic lumps in a particulate-textured mosaic of fine-grained micritic (i.e., clay-sized), silt-sized (less than 50µm in size), microsparitic (i.e., recrystallized micritic) calcite grains, and remnants of many complete or broken micro-fossils (Figures 2, 3, and 4). Patches of coarser, sparry calcite also occur and, along with the microspar, are the result of recrystallization of the original micritic mud matrix.

The calcite matrix, however, is distinctly different from an alkali-aluminosilicate type geopolymeric binder - both in composition (calcite-based versus alkali-aluminosilicate based) and in optical properties. The geopolymeric binder has a distinctly low negative relief, near-isotropic to very weak birefringence (up to 0.002), and low refractive index, which can be identified and distinguished from a calcite-based cement in limestone at 400X magnifications in the ultra-thin (~15µm) areas of the thin section. Based on optical microscopical examinations of both EA-491 thin sections, no evidence of a geopolymeric binder was found.

Pores – Non-uniformly scattered throughout the section are many irregularly shaped very fine intergranular pores and voids having sizes from less than 10µm to 50µm that are all empty (Figure 3). Amounts vary from less than 5 percent in some areas to as high as 20 percent in others. There is no evidence of any circular or spherical air bubbles present.

Other Minor Constituents – Sparsely distributed throughout the thin sections received in this study are: (a) small (less than 20µm size), angular, terrigenous quartz grains, (b) microscopic near-spherical to spherical silica-rich phases (described in the acid-insoluble residue section as lepispheres) amongst the calcite grains within the matrix; (c) a light brown stain due to ferruginous impurities at a few isolated locations within the matrix; and (d) a trace amount of opaque grains.

Other minor constituents detected by the researchers at the British Museum (Freestone at al. 1984) and Campbell and Folk (1991) include: (a) gypsum (detected in XRD and in a stained powder mount and thin section by Campbell and volumetrically estimated to be approximately 1 percent); (b) approximately 7 percent by mass of hydrochloric acid-insoluble residue (described below); and (c) a few splintery-textured, light to dark brown plant fragments with various degrees of silicification and alteration to chalcedony (in Campbell's study). All these minor constituents are described by all researchers as not uncommon in a natural limestone.

Acid-Insoluble Residue – The acid-insoluble residue fraction contains:
(a) predominantly a silica-rich phase, which is identified in Campbell and Folk (1991) as relatively small spherical assemblages of tridymite (lepispheres), representing a possible transitional phase from opal to alpha-quartz (opal-CT), volumetrically amounts to no more than 2 percent with average sizes of 5 to 8μm (the BM report describes it as disordered cristobalite (opal-CT), occurring as spherical aggregates of bladed crystals 5 to 10μm in diameter);
(b) a small amount of angular quartz grains detected in all studies;
(c) a suite of opaque minerals (identified by SEM-EDS study of the British Museum as rutile, galena, cassiterite, zircon); and
(d) possibly some clay.

As previously reported by Campbell (unpublished, 1988), the Campbell thin section of EA-491 appears to be slightly different from that prepared by the BM. The latter has a higher abundance of micritic lumps with a few more angular grains of terrigenous quartz and feldspar, larger lepispheres, and iron oxide grains.

## The Lauer Sample: An Inner Casing Stone Sample from the Great Pyramid of Khufu

In the present thin section study, the Lauer sample appeared as a porous, recrystallized, fine-grained bioclastic limestone with overall broad similarity to the EA-491 sample (see Figures 2, 3, and 4 for textural comparison).

Bioclasts – Bioclasts constitute major amounts of fragmented or whole skeletons of foraminifera with minor amounts of molluscan shells (Figure 2), echinoids, and a trace amount of calcareous algae less than 200μm in size. Similar to EA-491, there is no evidence of any coarse aggregate particles of fractured or incompletely disaggregated limestone, or any evidence of reconstituted limestone.

Microcrystalline Calcite Matrix – Similar to EA-491, microcrystalline calcite matrix is the major textural component having a particulate texture and containing fine-grained micritic calcite to mostly silt-sized calcite grains (micritic silt), ultra-fine-grained near-spherical and irregular-shaped micritic lumps, microsparite, and remnants of many fragmented micro-fossils (Figures 2, 3, and 4).

A calcite-filled fracture cuts through one corner of the sample, which is approximately 10μm in maximum width with tapered ends, discontinuous and followed by another calcite-filled fracture in an en echelon pattern (Figure 3).

The observed fine calcite matrix is distinctly different from an alkali-aluminosilicate type geopolymeric binder - both in composition (calcite-based versus alkali-aluminosilicate based) and in optical properties. Similar to EA-491, this thin section shows no evidence of a geopolymeric binder.

According to Morris (1991, 1992), recrystallization, recarbonation (of the excess lime added in the "concrete mix"), and alkali-calcium exchange during prolonged periods can alter the ancient geopolymeric binder from that found in modern geopolymeric limestone, and, therefore, a direct comparison in optical and chemical properties of ancient versus modern geopolymeric binders may not be possible. Admittedly (by both Davidovits 1987, and Campbell and Folk 1991), prolonged carbonation of lime, if added in preparation of an ancient mortar or concrete, and micritic lumps in natural limestone are difficult to distinguish in thin sections. The micritic lumps observed in both EA-491 and Lauer sample, however, do not show certain textural features (e.g., differential degree of carbonation throughout the area of the lime or lump, occasional relict areas of less-carbonated lime, coarsely crystalline secondary calcite precipitates in air voids associated with a carbonated ancient masonry lime matrix, shrinkage microcracks) that are usually found in the carbonated lime lumps in ancient lime-pozzolana mortars[4]. These micritic lumps are very similar in texture to those seen in the natural limestone sample from Tura, described later. Nevertheless, additional analysis, especially by SEM-EDS, is undoubtedly needed to search for evidence of alkali activation and an alumina-rich composition in the original geopolymeric binder and its any subsequent alterations, if that is indeed present in the Lauer sample. The section on the SEM-EDS study of the binder phase will address this issue further.

<u>Intergranular Pores and Voids</u> – The Lauer sample is admitted by all to contain high intergranular porosity with many small irregular pores and voids. The high intergranular porosity is also revealed in the present study in a total three thin sections prepared from the Lauer-Harrell sample and highlighted by the blue-dyed epoxy used in the original impregnation. The distributions of irregularly-shaped voids are heterogeneous – some areas contain as much as 15 to 20 percent voids, whereas other areas have less then 2 percent voids. The calcite-filled fracture separates a void-rich area from a dense area at one location, which is followed by void-rich areas on both sides of the fracture. Harrell and Penrod (1993) described some of these as solution vugs less than 200μm in size and abundant large dissolved ovoid peloids (300 to 600 um) that were originally fecal pellets. There is no evidence of any circular or spherical air bubbles present. Davidovits (1983, 1986, and 1987) mentioned the presence of air bubbles that are not spherical but oval. Both the present study and the observation by Harrell and Penrod (1991) found oval shaped “voids” that are clear indication of oval-shaped foraminiferal casts.

Regarding voids in the Lauer sample, the results of a previous thin-section analysis by Robert G. McKinney, mentioned in Morris (1992) is highly controversial and erroneous. The oval-shaped voids shown in thin-section photomicrographs are undoubtedly fossil casts and are not uncommon in the natural limestone of either Giza or Tura-Masara. The characteristic oval-shape and its startling resemblance to oval-shaped fossils in the Lauer sample should lead to a common-sense interpretation even without any background on limestone petrography. Speculating that these voids are “air pockets” resulting from geopolymeric reaction is clearly a spoon-fed interpretation, which is not supported by textural studies of natural limestone.

<u>Other Minor Constituents</u> – Sparsely scattered throughout the section are fine-grained angular detrital quartz grains. Such quartz grains are also observed by Harrell and Penrod (1993), which is contrary to the original description of Davidovits (1986, 1987), who did not detect quartz in the XRD studies of the Lauer sample (but he did find quartz in the quarry samples). Probably, the amounts of detrital quartz grains that are positively identified in the Lauer sample thin section studies are below the detection limit of XRD in Davidovits’ study, and less than the amount present in his quarry samples.

In sharp contrast to the thin section description of Robert G. McKinney (mentioned in Morris 1991, 1992), the present study, as shown in numerous photomicrographs of the Lauer thin section (Figures 2, 3, and 4) did not detect any evidence whatsoever of volcanic

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[4] “Lime lumps, even though carbonated, normally retain some of their original microstructure pseudomorphically in modern samples. Nothing like this has been observed in the pyramid samples.” (Campbell, personal communication, 10th April 2007).

glass fragments, fibrous laths of partially devitrified to completely devitrified glass, sericite, opaque ferromagnesian minerals, or dipyramidal crystals of phosphatic carbonates! This conclusion, derived from textural interpretation, is further supported by a detailed SEM-EDS study of both pieces of the Lauer sample examined in this study. The sample is undoubtedly not a "tuffaceous limestone" as described by McKinney but a porous, bioclastic microcrystalline limestone. As criticized by Campbell and Folk (1992) and mentioned by Harrell and Penrod (1993), McKinney probably misidentified some lath and shard-like calcitic echinoid and pelecypod fossils as glass, highly birefringent calcite as sericite, opaque pyrite and iron oxide as opaque ferromagnesian minerals, and calcitic nummulitic foraminifera as phosphatic carbonate crystals and concretions. Such significant differences in mineralogical and textural interpretations of the Lauer sample thin section by the present study, Campbell and Folk (1992), Harrell and Penrod (1993), and many other limestone petrologists' described in their criticisms versus the observation of McKinney on the very same sample casts serious doubt on McKinney's ability of textural interpretation, which, apparently, carried significant weight as evidence in support of the "man-made" origin of the Lauer sample in a series of publications by Morris (1991, 1992). Additional opinions from limestone petrographers as well as additional observations (such as by either SEM-EDS or thin sections) are certainly welcome to settle this issue if there is still any doubt of McKinney's unfortunate textural misinterpretation.

A similar debate arose over the claim of "a fragment of a gold-colored mineral, which appeared to be a native gold" by the late Edward J. Zeller (mentioned in Morris 1991) on one side of the Lauer sample (the one opposite from the coating, Morris 1993), and its interpretation by Harrell and Penrod (1993) as pyrite, or "fool's gold" (reportedly a common occurrence in Mokattam limestone). This could have been easily settled by a direct analysis of the grains in question by, for example, SEM-EDS. Any suggestion of a "man-made" origin for the pyramid stones must be accompanied by careful, detailed studies that document the presence of any unnatural constituents.

Surprisingly, based on a stereo-microscopical examination of the Lauer sample at only 6X to 80X magnification, Zeller's observation of a dark reddish brown coating on one side, compact light yellowish colored, relatively fine-grained matrix, macroscopical appearance of the rock, numerous small sub-spherical and oval shaped randomly distributed bubbles, a shell fragment, and a fragment of what appeared to be native gold led him to conclude without any doubt that the Lauer sample is an example of a synthetic stone (as reported in Morris 1991)! Indeed, unlike McKinney's erroneous thin section interpretation, nothing in the published description of the sample by Zeller indicate its synthetic origin.

<u>Acid-Insoluble Residue</u> – Previous studies on the Lauer sample detected a silica-rich phase, identified as opal-CT (Davidovits 1983, 1986, Campbell and Folk 1991, Harrell and Penrod 1993), and a calcium phosphate-rich phase identical to that found in the coating of the sample (Davidovits 1983, 1986). Davidovits' XRD scan of the insoluble residue of the Lauer sample did not detect any of the quartz grains that he found in the Tura quarry samples (Davidovits 1986). This last observation was one piece of the evidence that Davidovits used to conclude that the Lauer sample is not similar to the quarry samples. As mentioned before, the present thin section analysis of the Lauer sample clearly shows the presence of detrital quartz grains, which is inconsistent with Davidovits' conclusion based on XRD results.

A 30-µm thin section of the Lauer sample prepared in this study was lightly etched with diluted acetic acid to remove the calcite component from the rock and highlight the acid-insoluble residue. The etched section was scanned at a slow rate (0.5 degrees per minute) in a Siemens D 5000 diffractometer to examine the acetic acid-insoluble residue and to compare the result with a XRD scan of the bulk polished section. Neither the diffraction pattern of the residue nor the bulk sample conclusively detected any silica-rich phase (e.g., opal-CT) as found in Davidovits' XRD study (1986). The epoxy substrate used to bond the thin section to the glass slide (which became exposed after acid etching) masked the diffraction pattern. A XRD scan of a finely pulverized sample would have been more appropriate than that of a polished section from the residue of thin section preparation. As described in the SEM-EDS study below, the Lauer sample did show a clear indication of the presence of many interstitial near-spherical and spherical silica-rich phases (consistent with an impure opal-CT) in between the calcite grains, which are texturally and compositionally similar to the similar-rich phases detected in EA-491 and the natural limestone from Tura. Clearly, the XRD scan of the thin section failed to detect the silica-rich phases, which were probably removed along with the soluble materials during acid digestion of the thin section. Nevertheless, they were conclusively detected in the SEM-EDS study of the "bulk" sample. This exercise demonstrates the importance of multiple methods (XRD and SEM-EDS) of analysis for the confirmative detection of low-abundance, microconstituents in limestone.

## A Natural Limestone from Tura

The quarry sample from Tura is a very dense, fine-grained bioclastic limestone with fossil fragments similar to those found in the casing stones sporadically scattered through microcrystalline calcite matrix. The sample has a particulate texture and predominance of microcrystalline calcite grains that are virtually identical to those find in the casing stones samples (see Figures 2, 3, and 4 for comparison). Compared to the casing stones, this limestone has experienced more recrystallization and consequently is somewhat harder and also has a lower porosity.

Bioclasts – Sporadically distributed are fine, whole or broken nummulites and other foraminifera, mollusc fragments, less than 10 to 50µm in size. A predominance of foraminiferal bioclasts, as in casing stone samples is noticed.

Microcrystalline Calcite Matrix – Similar to the casing stone samples, the limestone from Tura is also a bioclastic microcrystalline limestone consisting of small microcrystalline (micritic) calcite grains, micritic calcite lumps, silt-sized calcite particles, microsparite, and fine broken fossil fragments. No sparry calcite cement is present in this limestone.

Pores and Voids – Fine, irregularly shaped voids sporadically distributed, mostly detected at high magnifications; the sample is relatively dense with a lower porosity than that found in the casing stone samples.

Acid-Insoluble Residue – The acid-insoluble residue content is determined to be 7.0 percent. The residue shows overall very fine-grained clay-sized particles as well as very fine cristobalite, near-spherical to irregularly shaped grains, and occasional angular silt-sized, detrital quartz grains.

The overall texture and mineralogy of the limestone from Tura is virtually identical to those in the casing stones, the differences being no more than ordinary geologic variation observed in limestones from same or different stratigraphic layers.

## Geopolymeric Limestone

According to Davidovits, geopolymeric limestones can have startling similarities in visual appearance to a natural limestone. In spite of this pronouncement, looking at the thin section of the present geopolymeric limestone under a petrographic microscope at a magnification of 100X quickly reveals an entirely different texture, which is very unlike that found in the casing stones, or in natural limestone (see Figures 2, 3, and 4 for textural differences). The sample, originally prepared by Davidovits for chemical comparison purposes to pyramid stones, shows a texture that is very typical of a “reconstituted” limestone.

> First, the sample shows many broken fossil fragments that contain very fine-grained calcite ‘dust’ within their internal pore spaces. Such calcite dust within broken fossil fragments is an indication of accidental inclusions of disaggregated calcite particles into the fossils, and this is something not found in the casing stones or natural limestones. The textural components of a “geopolymeric limestone” are limestone fragments (sand to silt size, largely calcite and dolomite), limestone dust (largely calcite and dolomite), fossil fragments, clay and other acid-insoluble residues, and, of course, a “geopolymeric” cement.
>
> Second, in contrast to the casing stones and natural limestones, where the overall microcrystalline calcite framework has a typical particulate texture consisting of micritic to microsparitic calcite grains and micritic lumps, geopolymeric limestone has a much finer-grained “dusty” appearance with the calcite particles uniformly dispersed in a geopolymer binder. Limestone, being an inherently soft rock, will produce a lot of “fines” during the Davidovits’ hypothesis of disaggregation in water and subsequent mixing and molding, which will be scattered throughout the matrix of a “reconstituted” limestone.
>
> Third, contrary to the highly birefringent calcitic matrix phases in the casing stones, the geopolymer (zeolitic) binder phase in the “man-made” limestone has a low negative relief, very weak birefringence to isotropic nature, and low refractive index (well below 1.54). These aspects are best identified in ultra-thin sections (<10μm) at high magnifications (at least 400X), after gentle etching with HCl to remove the calcite fraction.
>
> Fourth, geopolymeric limestone shows many spherical and elliptical “lumps” of dusty calcite agglomerates (Figures 3 and 4) that are significantly larger in size (some up to 1 mm in diameter) than the micritic calcite lumps found within the matrix of the casing stones. These dusty calcite agglomerates are similar in appearance to aggregates in concrete and contain many irregularly shaped voids.
>
> Fifth, distributed throughout the limestone are numerous very fine irregularly-shaped, near-spherical to spherical voids (0.05-1.5 mm) that are different in character from the interstitial pores and voids in the casing stones and natural limestone, and represent leftover voids from the mixing process (Figure 4). Spherical air voids in the sample are characteristic of reconstituted limestone, an artifact of mixing solid particles in a polymer binder, which are not found in either the casing stones or in natural limestone.

Admittedly, Davidovits’ geopolymeric limestone was prepared only for the demonstration purposes and chemical comparison to pyramid stones with no intention to “imitate” pyramid stones. Based on the observed textural differences, however, an exact reproduction of micro-texture of pyramid casing stones with close textural similarities to natural limestone by a “reconstituted” limestone is a major challenge, and one which is yet to be achieved and experimentally demonstrated by the proponents of geopolymer hypothesis.

## X-RAY DIFFRACTION STUDIES

Figure 6 shows a reproduction of XRD patterns of the coating on the casing stone from the Khufu pyramid, the casing stone itself (the Lauer sample), and natural (quarry) limestones that Davidovits published (Davidovits 1986) and used as the major scientific evidence in favor of “man-made” origin of the casing stone (Davidovits 1983, 1986, 1987; Davidovits and Morris 1988).

A close examination of the pattern shows the following:

1. The "coating" contains major amounts of calcium phosphate (crystalline hydroxyapatite with characteristic diffraction peaks at 2.72, 2.78, 2.81, and 3.44A; and brushite with characteristic diffraction peaks at 7.58 and 7.62A), opal-CT (cristobalite and "volcanic" quartz[5] with characteristic diffraction peaks at 4.07 and 4.26A, respectively), a silico-aluminate phase similar to zeolite ZK-20 with characteristic diffraction peaks at 8.25 and 13.18A.
2. The "casing stone" contains major amounts of calcite from the limestone and *significantly lesser amounts* of calcium phosphates (hydroxyapatite and brushite) and silico-aluminate than that detected in the coating, and opal-CT.
3. The "quarry limestone" samples contain major amounts of calcite, minor amounts of quartz, and no calcium phosphate, silico-aluminate, or opal-CT phases.

Based on these observations, Davidovits proposed that the casing stone, like that of its coating, is synthetic. The conclusion came without an investigation of possible contamination of the coating components in the analyzed casing stone sample since the phosphate/zeolitic phases in the casing stone that are reportedly unknown in natural limestone (and not found in the quarry samples) are the *exact same phases* detected *at significantly greater amounts* in the coating on the sample. Instead, the "man-made" hypothesis postulated a possible migration of these components from the casing stone itself to form the coating.

To further support that pyramid stones are "synthetic", Davidovits prepared a geopolymeric limestone with disaggregated limestone and a phosphate-free synthetic zeolitic mineral binder added at 30 to 50 wt% and prepared by mixing soluble silica, aluminate, and caustic soda (Davidovits 1983). XRD pattern of this hardened stone reportedly reproduced a pattern similar to that of the casing stone having calcite as the predominant phase and geopolymeric ingredients (synthetic zeolites, silica) in very small quantities.

First, his experiment has failed to demonstrate the detection of phosphate phases (along with synthetic zeolite) in the casing stone at significantly lesser amounts than that detected in the coating, and nor did his synthetic stone form a coating with similar mineralogies detected in the casing stone.

Second, the silica-alumina-caustic soda mixture used for the mineral binder will undoubtedly leave an inescapable signature of alkali-aluminosilicate composition in the binder phase (consistent with its detection as synthetic zeolite in minor quantities in the XRD pattern), which could be easily detected by detailed x-ray elemental analysis (SEM-EDS) of the binder phase in the casing stone. The present SEM-EDS investigation of the same casing stone sample show no evidence whatsoever of an alkali-activated binder.

The present SEM-EDS study conclusively demonstrates that the coating on the casing stone is an external application of a synthetic material, and not a by-product of geopolymerization in a synthetic casing stone because no signature of the reported composition of the coating is found in the bulk interior of the same casing stone, away from the zone of coating contamination.

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[5] Although Davidovits described quartz in the Lauer sample as "volcanic", the more appropriate term might be "terrigenous" or "detrital" quartz. Volcanic quartz is characteristically bipyramidal, clear, with straight extinction. The quartz in the Lauer sample is more likely to be "magmatic" or "metamorphic" in origin (Campbell, personal communication, April 2007).

Figure 7 is another reproduction of Davidovits' XRD patterns related to the reported discovery of opal-CT in the casing stone, its absence in the quarry limestones, and therefore, a synthetic origin of the casing stone.

Figure 7 shows clear detection of opal-CT phases (consisting of low cristobalite and "volcanic" quartz with characteristic diffraction peaks at 4.07 and 4.26A, respectively) in the casing stone from the Khufu pyramid. Opal-CT phases became distinct in the XRD patterns of acid-insoluble residue of the casing stone. Based on its presence in the casing stone and not in the natural limestones, a synthetic origin of the stone was proposed. To further support this synthetic origin, the casing stone sample was reported containing practically no detrital quartz, which is characteristically present in the quarry limestones (Davidovits 1983, 1986).

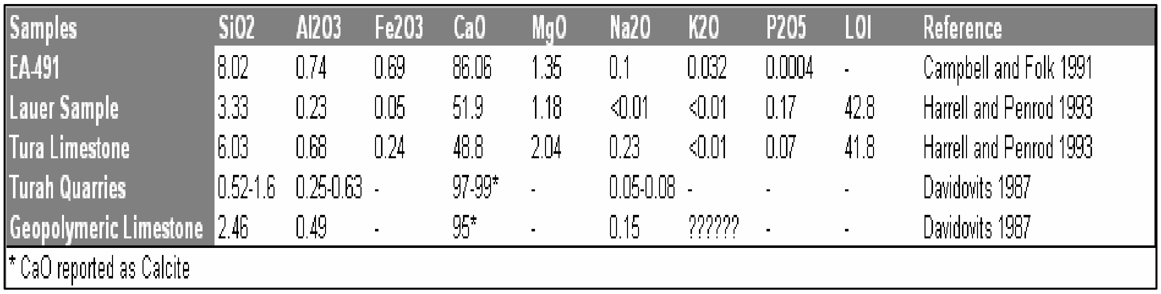
Contrary to these: (a) a small peak of opal-CT is indeed detected in the Tura limestone XRD pattern at a significantly lesser intensity than that in the casing stone (circled in the Figure 7); (b) detrital quartz grains are indeed detected in the casing stone both in his XRD pattern and by the present optical microscopical examinations of the same casing stone sample; (c) XRD pattern of the acid-insoluble residue fraction of the Tura limestone in the present study clearly show the presence of cristobalite (opal-CT) similar to that found in the casing stone; (d) detrital quartz and opal-CT are detected to be the common minor constituents not only in the two casing stones studied in this present report (including the casing stone of Davidovits) but also in the Tura limestone.

Figure 8 presents an XRD attempt to determine the minor phases in the Lauer-Harrell sample. The epoxy-impregnated polished section of the sample as received and used for SEM-EDS study was scanned in Siemens D5000 x-ray diffractometer (Cu-Kα radiation, 30 mA, 40 KV) at 2°/min for the bulk mineralogy and at a slow scan rate of 0.5°/min at regions of characteristic diffraction peaks of calcium phosphate and opal-CT phases. The pattern did show the expected dominance of calcite but virtually undetectable calcium phosphate or opal-CT. Possible reasons for their absence are: (a) use of an epoxy-impregnated polished section of the Lauer sample, rather than the conventional pulverized sample; (b) the presence of minor amounts of opal-CT probably below the detection level of XRD (unless concentrated by acid-insoluble residue); and (c) the absence of calcium phosphate phase in the "bulk" sample without a coating. Another XRD analysis of the Lauer sample by Harrell and Penrod (1993) also showed more than 95 percent calcite and no traces of calcium phosphate or zeolite cement.

Unlike the Lauer sample, since a bulk sample of natural limestone from Tura was received from Harrell, the sample, along with its hydrochloric acid-insoluble residue were pulverized to ~10μm size powder, analyzed, and results reproduced in Figure 9. The results show major amounts of calcite and minor amounts of dolomite among the carbonate fractions in the bulk sample and the presence of sodium montmorillonite, cristobalite, and quartz as the minor non-carbonate fractions. The acid-insoluble residue clearly shows the presence of sodium montmorillonite clay, cristobalite, and quartz. Contrary to the reported absence of opal-CT phase in natural limestone, the present limestone sample from Tura clearly shows this phase, which could have been easily verified by Davidovits in the acid-insoluble XRD study of his quarry samples like the present one, or his similar study for the casing stone.

## REPORTS ON BULK CHEMICAL COMPOSITIONS

The following Table shows published bulk chemical analysis of the samples of this study analyzed by x-ray fluorescence (the "Lauer" sample and the limestone from Tura by Harrell and Penrod 1993), EA-491 (atomic absorption spectroscopy by Campbell by Folk 1991). Also included are published analyses of geopolymeric limestone by Davidovits (1987) and its apparent reported resemblance in major oxide chemistry to natural limestones from the quarries at Tura-Masara.



| Samples | SiO2 | Al2O3 | Fe2O3 | CaO | MgO | Na2O | K2O | P2O5 | LOI | Reference |
|---|---|---|---|---|---|---|---|---|---|---|
| EA-491 | 8.02 | 0.74 | 0.69 | 86.06 | 1.35 | 0.1 | 0.032 | 0.0004 | - | Campbell and Folk 1991 |
| Lauer Sample | 3.33 | 0.23 | 0.05 | 51.9 | 1.18 | <0.01 | <0.01 | 0.17 | 42.8 | Harrell and Penrod 1993 |
| Tura Limestone | 6.03 | 0.68 | 0.24 | 48.8 | 2.04 | 0.23 | <0.01 | 0.07 | 41.8 | Harrell and Penrod 1993 |
| Turah Quarries | 0.52-1.6 | 0.25-0.63 | - | 97-99* | - | 0.05-0.08 | - | - | - | Davidovits 1987 |
| Geopolymeric Limestone | 2.46 | 0.49 | - | 95* | - | 0.15 | ?????? | - | - | Davidovits 1987 |

* CaO reported as Calcite

Contrary to the overall resemblance in calcium-silica-alumina-sodium oxide compositions of geopolymeric limestone and natural limestone, both Campbell and Folk (1991), and Harrell and Penrod (1993) mentioned the low alkali contents (total sodium and potassium oxide) in the casing stones as evidence against an alkali-activated geopolymeric chemistry. Although a published result of total alkalis in geopolymeric limestone ($Na_2O+K_2O$) could have settled this issue, in author's opinion, however, due to the reported possible use of geopolymeric binder at a very low concentration (as low as 5 percent by weight), and minor amounts of alkalis needed for the activation, the bulk major element chemistry may not necessarily show a geopolymeric signature, or any difference from the natural limestone. It is the "binder phase" in the limestone where alkali-aluminosilicate based geopolymeric signature will be best evident. Therefore, SEM-EDS analysis, as shown in the following section will settle this issue of the absence of such a signature in the casing stones.

## SEM-EDS STUDIES

**[1] <u>Microstructures Revealed through SE & BSE Imaging</u>** – Consistent with optical microscopical observations (thin-section photomicrographs in Figures 2, 3, and 4), back-scatter electron images of casing stones, natural limestone and geopolymeric limestone (Figure 5) reveal: (a) the basic microstructural similarities of casing stone and natural limestone, and (b) their significant difference with the microstructure of a geopolymeric limestone. Both casing stone and the limestone from Tura show a particulate microstructure with calcite fossils, microcrystalline calcite matrix[6] and other binder phases; and interstitial

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[6] The term "matrix" should not be confused with "cement" or "binder" in limestone. The framework or mosaic in a limestone within which fossil fragments and other allochems are embedded constitutes: (a) the microcrystalline calcite "matrix" or "calcitic mud" including micrite (i.e., clay-sized calcite), silt-sized calcite, micritic lumps, and microsparite (i.e., calcite crystals less than 30μm) and (b) microcrystalline, coarse-grained pore-filling calcite cement (spar). "Microspar" is recrystallized micrite and so is not cement. Sparry calcite is almost always pore-filling cement but rarely can also be produced by recrystallization of a micritic matrix (Harrell, personal communication, April 2007). The difference between micritic calcite and microspar is often difficult, partly due to recrystallization. The term "binder" in pyramid samples encompasses microcrystalline calcite matrix, microspar, and very little or no sparry calcite cement.

pores (the casing stones having higher overall porosities than the limestone from Tura). By contrast, the geopolymeric limestone has a much smoother appearance (almost invisible intergranular porosity) with occasional large spherical air voids and a very different overall microstructure than the pyramid stones.

**[2]** **Elemental Maps** – The difference between natural and geopolymeric limestones is best detected in the microchemistry from SEM-EDS analyses, which is represented as a series of x-ray elemental maps in Figures 10 and 11. These figures are the "representative" results of numerous similar maps reproduced from over the entire area of the samples to diagnose any compositional variation across the examined surfaces. Each elemental map represents an approximately 300μm$^2$ area.

First, x-ray elemental mapping of geopolymeric limestone shows clear and distinct uniform, homogeneous enrichment of alkalis (sodium and potassium), alumina, and silica over the entire examined surface (Figure 11), which is consistent with the alkali-aluminosilicate based composition of geopolymeric binder. No such uniform enrichment of silica, and especially alumina and alkalis are found either in the casing stones (Figure 10) or in the natural limestone (Figure 11). A similar complete absence of any alkali or alumina enrichment was noticed in both the casing stone and natural limestone when the samples were scanned at higher magnifications than the ones used for the reported maps. The elemental maps in Figures 10 and 11 are representative maps of several similar ones reproduced from each sample at variable SEM magnifications from 20X to 100,000X. The binder phases in the casing stones and interstitial areas between the calcite framework grains do not show any evidence of alkali or alumina enrichment at any level of magnification, which is the essence of the lime-natron-clay based geopolymer hypothesis.

Second, both casing stones and natural limestone show very fine (less than 10μm in size), isolated, characteristically near-spherical to spherical or irregularly shaped areas of silica enrichment in areas between the calcite-rich portions, indicating the presence of silica-rich microconstituents in the interstitial spaces between the calcite grains. The "phase maps" in Figures 10 and 11 and Si-maps in Figure 16 clearly show these results. EA-491, the Lauer sample, and the limestone from Tura – all show very similar silica-rich, near-spherical fine "spots" in the interstitial spaces of Ca-rich (calcite) areas. Figure 16 shows representative Si-maps of all samples to highlight similarities in Si-signals among the casing stones and the limestone from Tura, and their sharp differences from the uniform Si-signal in geopolymeric limestone. In EA-491, some of these Si-rich spots also contain less enriched Ca-Al signals. In the Lauer sample, some of these Si-rich signals are also superposed with highlighted Ca-Mg-rich ones. In the limestone from Tura, some of these Si-rich spots are also superposed with lesser enriched Ca-Al-Na signals. All these silica-rich microconstituents contain variable but minor amounts of Ca, Mg, Al, and Na, presumably, the result of simple geologic variation.

Similar to the present study, the previous EDS study of the Lauer sample by Barsoum et al. (2006) also detected Ca and Mg in the silica-rich microconstituents and these authors stated that their occurrence and concentrations (ratios) are unknown in natural limestones. The present study, however, clearly shows occurrences of silica-rich microconstituents in all samples except the geopolymeric limestone, and their variable chemistry is due to trace amounts of impurities that these phases can accommodate.

The Ca-rich areas, corresponding to calcite grains in limestone also show an overall similarity in casing stones and natural limestone with a uniform "density" of elemental concentration (represented by uniform brightness of the highlighted spots) and their sharp contrast in appearance to the Ca-map of the geopolymeric limestone; in the latter, the density of the Ca-signal is highly variable from place to place and clearly shows a "concrete-looking" appearance of Ca-rich, subangular to subrounded areas (corresponding to calcite-lumps or limestone fragments) sporadically scattered in a matrix of lower density Ca-signals (corresponding to very fine calcite "dust" in the matrix).

**[3] <u>Silica-rich Microconstituents in the Casing Stones and Natural Limestone</u>** – After determining the silica-rich microconstituents in the elemental maps (Figure 16), individual areas of high silica concentrations were separately analyzed at high magnifications for detailed compositions. Each phase to be analyzed was detected in the backscatter and secondary electron images; then a homogeneous area at the center of the phase of interest was chosen by a raster mode (from less than 5μm to 10μm raster spacing depending on the area's size) and selectively analyzed by excluding everything else around the chosen raster. Accelerating voltage of electron beams varied from 10 to 20 Kv. Larger-size rasters and diffused beams (for bigger "spot size") were used for bulk analysis of a region of interest including multiple phases (e.g., for detecting phosphorus contamination in the Lauer sample).

Several different analytical approaches were practiced to determine the best possible results. Samples were analyzed with no conductive coating, with both carbon and gold coatings, and with different coating thicknesses (sputtering times). The results were compared with and without coatings. The approach of using calcite as an internal standard and directly analyzing light elements such as carbon and oxygen in these microconstituents (similar to those practiced by Barsoum et al. 2006) was unrealistic due to the intimate association and, hence, interference of epoxy in the epoxy-impregnated casing stone samples (both EA-491 and the Lauer sample, when received were already impregnated with epoxy). Instead, bulk chemical analyses of silica-rich microconstituents in the epoxy-impregnated interstitial areas were done in terms of atomic and oxide proportions of Si, Ca, Al, Mg, and Na from raster scans of homogeneous areas of these phases and comparing these results with concentrations of the same elements in a mid-ocean ridge basalt standard from the U. S. Geological Survey. The purpose was to characterize the major element compositions of these silica-rich phases and determine any difference among similar phases in the casing stones and natural limestone. Other elements, e.g., Fe, S[7], and others were not measured due to their complete absence in the elemental maps studied prior to the phase-analysis step, and absence in the elemental spectra of analyzed phases.

Backscatter and secondary electron images of both casing stones and natural limestone show spectacular occurrences of silica-rich microconstituents as lepispheres (XRD-detected opal-CT, Figure 17 for EA-491, Figures 19 and 20 for the Lauer sample, and Figures 21 and 22 for the limestone from Tura) having a characteristic silica-rich composition and minor to trace amounts of variable impurities such as Ca>Mg>>Al in the Lauer sample, Ca>>Al>Mg in EA-491, and Ca>>Na>Al>Mg in the limestone from Tura. The Na-signal in the lepispheres of the limestone from Tura could come from the presence of sodium montmorillonite clay on

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[7] In author's opinion, detection of "S-rich", "Ca-rich", and "Si-rich" microconstituents in the Lauer sample by Barsoum et al. 2006 correspond to the presence of gypsum, calcite, and opal-CT, respectively, as minor constituents in limestone. Gypsum was not detected in the present Lauer sample. Barsoum et al.'s detection of gypsum as a S-rich, fully hydrated phase that oozed out on a freshly prepared polished surface after exposure to air for a few weeks is indicative of its occurrence as an efflorescent salt, which is a common salt and minor constituent in limestones, especially in pyramid stones that are placed with lime-gypsum jointing mortars (Ghorab et al. 1986, Ragai 1988) and have a high moisture content (Dolphin and Brown 1975). Gypsum was also detected in the other casing stone, EA-491, by Campbell and Folk (1991). Detection of gypsum as "S-rich microconstituent" does not indicate "synthetic" origin of pyramid limestone. Gypsum is a common minor constituent in natural limestones as well, especially in Egypt.

the analyzed surface, which was detected in XRD study. All these lepispheres are less than 5µm to 10µm in size.

A critical evaluation of major element oxide compositions of all silica-rich microspheres show a clear enrichment of these spheres with calcium and magnesium in the Lauer sample, as previously reported by Barsoum et al. (2006). Contrary to their results, however, the present study clearly shows: (a) the presence of these silica-rich microconstituents not only in both casing stone samples but also in the natural limestone, and hence the ubiquitous occurrences as a common microconstituent in the studied samples from Giza; and (b) their variable minor element oxide compositions, indicative of incorporation of impurities by the lepispheres. The occurrence of these "impurities" in the silica-rich microconstituents (lepispheres) are quite "natural" and do not indicate a "synthetic" nature of limestone.

The acid-insoluble fraction of the limestone from Tura (Figure 23) shows many distorted silica-rich microspheres with surfaces rougher than the spheres in the bulk sample (due to acid etching). The high-silica regions contain minor amounts of alumina and trace amounts of magnesia (from montmorillonite clay residue detected by XRD; the sodium content of clay, however, was dissolved by the acid-treatment and so absent from the insoluble residue).

**[4] Evidence of a "coating-influenced phosphate-rich zone" in the Lauer sample directly adjacent to the "coating"** – The major discoveries of the present SEM-EDS studies of casing stones are:

- The detection of a clear zone of phosphate enrichment at one side of the Lauer sample adjacent to the coating where the porous microstructure of the limestone was invaded by phosphates from the coating,
- A progressive and systematic decrease in phosphorous-concentration within the porous "coating-influenced or contaminated zone" in the limestone to a maximum distance of approximately 5 mm towards the opposite end of the sample,
- A negligible but uniform phosphorous concentration in the bulk uncontaminated interior of the Lauer sample, which has a similar low phosphorous content as in the other casing stone (EA-491) and the natural limestone from Tura; and
- A complete absence of such a phosphorus profile or any evidence of phosphate-enrichment in the other casing stone, EA-491.

All these evidence as clearly demonstrated in Figures 12 through 15, indicate beyond a shadow of a doubt that the calcium phosphate signature that was previously detected in the XRD studies of the Lauer casing stone sample from the Khufu pyramid by Davidovits (1983, 1986, 1987) is a clear artifact of contamination of the limestone by the coating material, which is not present in the bulk unaltered interior of the Lauer sample well away from the influence of the coating (i.e., more than ~5 mm from the zone of contamination adjacent to the coating) or in the other casing stone (EA-491). Therefore, the detection of phosphate phases in a casing stone is not an indication of a "synthetic" origin.

Figure 12 is a phosphorous-map of the Lauer sample (at low magnification with a very slow scan) showing enriched P at one corner and its decrease towards the opposite sides. Figure 13 shows area scans across three vertical columns spaced over the entire surface at equal distances (five 300µm$^2$ size areas per column positioned from the coating side to the interior, a total of 15 scanned areas across the entire surface) where P-concentration shows a clear increase at the top 5 mm and then more or less uniformly low concentrations in the unaltered interior. Figure 14 shows elemental maps of three areas at high magnifications, one placed right at the P-enriched zone where a high P-signal was noticed in areas that also have high-Ca signals (consistent with a calcium phosphate-based chemistry), another placed directly opposite to the first in the bulk uncontaminated interior where literally no P-signal was found; the third area was placed somewhere in between the first two where P-signals were detected at intermediate intensities between the first two. Figure 15 shows a thin section photomicrograph of the Lauer sample from James A. Harrell where the coating is clearly visible as a dark isotropic zone (in crossed polarized light) – also shown are EDS analyses of different areas, one within the coating (determined by Harrell) showing calcium phosphate composition, another in the coating-contaminated or invaded zone in the limestone with minor P-concentration, and the third in the unaltered bulk interior with negligible and uniform P-concentration.

Although the actual "coating" was not present in the Lauer sample of this study (reportedly accidentally removed when the rock chip was trimmed during previous thin section preparation), based on the published composition of the coating, clear evidence of contamination of the limestone at the coating side of the Lauer sample was detected by the present EDS study. The textural and mineralogical characteristics of the "coating" that was present on this particular Lauer sample were described by Harrell and Penrod (1993). Consistent with Davidovits' XRD detection of calcium phosphate phases in the coating, Harrell and Penrod (1993) also detected calcium phosphate in the coating but also found four successive zones in the coating by optical microscopy [i.e., 5 to 10μm thick zone of clay and iron oxide, 20 to 40μm thick zone of isotropic to weakly birefringent submicroscopic calcium phosphate, 40 to 80μm thick zone of calcite, iron oxide, calcium phosphate; and 400 to 800μm thick zone of submicroscopic to finely crystalline (< 20μm) calcium phosphate with scattered <5μm size calcite and occasional silt-sized detrital quartz, the last being towards the limestone side]. Davidovits' XRD pattern of the red coating also showed calcite, which he described as "coating polluted with calcite from the core". Based on the present study, it is the limestone, which is polluted with calcium phosphate from the coating for a distance of approximately ~5 mm.

Contrary to the detected phosphate influence in limestone from the calcium phosphate-rich coating, a silicoaluminate (zeolite ZK-20) phase reportedly detected in the red paint, coating, and underlying limestone by Davidovits' XRD study did not show any corresponding Al-Si influence in the EDS study of the contaminated zone. Due to the significantly higher concentration of phosphate in the phosphate-based coating, its signature was clearly detected in the coating-contaminated zone in the limestone but due to the reported much lower concentration of a zeolitic phase (compared to phosphates) in the coating, its signature was not indicated in the EDS analysis of the contaminated zone in limestone.

It is important to mention that unlike the Lauer sample, EA-491 (the other casing stone sample studied) does not show any indication of a phosphate phase in the limestone. Certainly, the "coating phases" in the Lauer sample are not indicative of a "synthetic" origin of the stone but a mere alteration as a result of the synthetic coating (probably red paint with an egg-based binder) applied on the casing stone surfaces.

**[5]** **Geopolymeric Limestone and Pure Geopolymer** – Figure 24 shows the bulk chemical analysis of Davidovits' geopolymeric limestone. As expected, besides calcium from the calcite grains, the sample shows significant silica, alumina, sodium, and potassium concentrations with Al, Na, and K being higher than that detected in the casing stones and natural limestone. The alkali and alumina enrichment are characteristically significant, and their concentrations in the interstitial phases are even higher than in the bulk compositions determined from broad areas by raster scans at low magnifications. The binder shows both sodium and potassium enrichment indicative of a possible use of mixed analcime/kaliophilite-type components in preparing this reconstituented limestone. Figure 25 shows the elemental analysis of a pure hardened geopolymer prepared by Davidovits, which, consistent with his original description of a kaliophilite base, shows a potassium-alumina-silica based composition.

## AN EVALUATION OF “THE HARD SCIENTIFIC PROOF” OF DAVIDOVITS IN LIGHT OF THIS PRESENT STUDY

In Chapter 7 of his book “*The Pyramids: An Enigma Solved,*” Davidovits laid down “the hard scientific proof”, mostly from his study of two casing stone samples (the Lauer sample from the Khufu Pyramid in Giza and a sample from the Teti Pyramid in Saqqara) and quarry limestones from Tura to propose the “man-made” origin of the casing stones. His hypothesis is based upon: (a) the reported discovery of unusual minerals in the red paint on the Lauer sample, (b) detection of calcium phosphate (hydroxyapatite and brushite) and zeolite phases in the white coating on the Lauer sample, (c) detection of similar phosphate phases in the casing stone samples, (d) detection of opal-CT in the casing stone, and (e) the absence of these “unusual” phosphate/silicate phases in the natural (quarry) limestone samples that he studied.

The following is an excerpt from his Chapter 7. He started the chapter with an example of Le Chatelier’s study on enameled funerary statuettes:

> “Though I am the first to reproduce the synthetic pyramid stone and apply the technology to the construction theory, another French chemist, Henry le Chatelier (1850-1936), was the first to discover that the ancient Egyptians produced man-made stone. Le Chatelier was also a metallurgist and ceramist. He worked with newly developed micrographic techniques, glass slides, thin section analysis, and photography in combination with the microscope. He was the first to examine enameled funerary statuettes from Egypt’s Thinite epoch (c.3000 BC) with these techniques and saw them as they had never been seen before.
>
> As Le Chatelier studied enameled funerary statuettes, he found that his observation methods enabled him to notice that the enamel was not a coating applied to the surface of the statuettes. Instead, the enamel was the result of minerals which migrated from within the stone itself. He cut thin sections with a diamond-tipped saw and observed a gradually increasing concentration of minerals that had migrated to or near the surface of the stone to form enamel. The process is like that which occurs with Egyptian faience, a self-glazing ceramic. Le Chatelier was astonished to realize that the statuettes were man-made stone.”

The implication of beginning his chapter, “The Hard Scientific Proof” with Le Chatelier’s example is to lay down a foundation for the reader in order to propose that the mineral assemblages in the “coating” on the Lauer sample, which are unquestionably determined to be “man-made” and not minerals of a natural limestone, are actually a “geopolymeric coat” that *migrated out of the man-made limestone itself* and is present on the surface as a “skin”, similar to the enamel coat that LeChatelier found in what he thought was a statuette of man-made stone. It should be noted that no other scientist, apart from Davidovits, has ever agreed with Le Chatelier’s interpretation of reported artifacts of synthetic stone[8].

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[8] Harrell, personal communication, April 2007.

Unfortunately, no hard scientific "proof" was given to support that hypothesis, such as detailed thin section textural characteristics of the Lauer sample itself in relation to its coating, similar to that mentioned in the study of Le Chatelier, which could have shown, beyond a shadow of a doubt, that there is absolutely no such elemental migration of coating materials from within the stone itself. The present study determined that the bulk interior of the casing stones is as pristine as a natural limestone can be with a distinct zone of infiltration of the coating materials down to a distance of ~5 mm into the porous structure of the limestone situated immediately adjacent to the coating, and that most of the stone itself is absolutely free of any "unusual" signatures (i.e., of calcium phosphate from the coating). There is nothing to imply a derivation of the coating from within a man-made stone itself. Figures 12 through 15 in the present study illustrate "hard scientific proof" where the coating, the contaminated zone, and the pristine uncontaminated limestone are marked on a thin section photomicrograph of the Lauer sample. The three zones have very different optical characteristics allowing their differentiation even with the help of only an antique petrographic microscope.

Without using the modern technology of SEM-EDS (which was unavailable to Le Chatelier), a similar hands-on detailed petrographic study of the Lauer sample thin section could have established that the coating, which is definitely man-made, is nothing but a layer applied on a natural limestone and certainly not derived from within the stone.

Modern technology, i.e., SEM-EDS, undoubtedly provides even harder scientific proof that there is no variation in concentration of the primary coating ingredient, phosphorous, within the "bulk uncontaminated zone" of the Lauer sample. Its presence is not sufficient to propose an elemental migration of coating materials from within the interior of the stone, or to postulate a man-made origin of the stone. Within the contaminated zone of the limestone, phosphorus from the coating shows a clear, distinct, and systematic decrease from the side adjacent to the coating towards the interior. The porous microstructure of the limestone itself was receptive to the coating materials. After about 5 mm, phosphorous concentrations show uniform negligible values for the rest of the sample with no indication of any decrease or change (or an amount suggestive as unusual) over the entire thin section of the Lauer sample. Phosphorous concentration in the bulk uncontaminated zone of the Lauer sample is similar to that found in many natural limestones, including the one from Tura and the other casing stone studied, EA-491.

Based on the detection of brushite (a calcium phosphate phase) in the Lauer sample, Davidovits proposed possibilities of use of: (a) bird droppings from a nearby Ostrich Farm at Giza in preparing this man-made stone (similar to its use along with urine, animal dung with straw and mud in mud brick by the ancient Egyptians); or (b) bone as the source in preparing this "man-made" stone related to mysterious sacrificial rites of antiquity practiced by the ancient Egyptians.

Davidovits (1983, 1986), surprisingly, made no mention of the possibility of a simple man-made coating on limestone, such as paint, and failed to recognized that the "coating" was a possible source of the brushite in the casing stone even after knowing that: (a) brushite is one of the main phases detected in the coating, (b) brushite was reported by Andre Pochan (1934) as part of a "paint" – a red coating on the Giza pyramids; (c) the coating was applied directly to the limestone, (d) ingredients from the coating migrated into the stone, and (e) the coating is indeed a "man-made" material.

Another excerpt from Chapter 7 states:

> "The pyramid samples also contain a mineral known as opal CT, a siliceous material. ……Whereas a geological explanation for the presence of opal CT is valid, the presence of opal CT (detected by X-ray diffraction or microscopy) could also imply the addition of silicate materials during stone manufacture. The presence of opal CT in the pyramid stone might result from an addition of ashes from burnt offerings of such siliceous materials as cereal husks, straw, and certain types of reeds.
>
> To my knowledge, the only other researcher who performed a comparative chemical analysis on stone from Egyptian quarries and pyramid stone is Klemm, whose project was described previously. Thanks to help from colleagues, especially Hisham Gaber, a geology graduate of Ain Shams University in Cairo, I obtained samples from the quarries of Tura and Mokattam in the Arabian Mountains, where it is believed that the casing blocks originated. Gaber collected more than thirty samples from various sites. X-ray diffraction and microscopical analyses of the quarry samples indicates that they are pure calcite, sometimes containing a trace of dolomite. None of the quarry samples contains any of the unusual minerals found in the pyramid samples."

Based on the present investigation, the following points can be made against the above statements:

1. In the original XRD work of Davidovits (Davidovits 1986), opal-CT was detected not only in the casing stone of the Khufu pyramid but also in a limestone sample from the Tura quarry (though at a lower concentration in the latter than in the casing stone). An XRD study of the acid-insoluble residue of the quarry sample (Tura limestone), similar to that provided for the casing stone, was indeed needed to get a clear detection of opal-CT in the natural limestone. Unfortunately, that was not provided in his original research.
2. The present XRD study of the limestone from Tura shows a clear presence of opal-CT in the natural limestone samples from Tura. Thus, detection of opal-CT in the casing stone does not at all suggest the stone is "man-made". Opal-CT is indeed a natural microconstituent of limestone from the Tura quarries.
3. EA-491, a casing stone sample from the Khufu pyramid also contains opal-CT, which is detected both by Campbell and Folk (1991) and the researchers at the British Museum (Freestone et al. 1984), and described as tridymite and cristobalite, respectively.
4. Silica-rich microspheres (lepispheres), the reported form of occurrences of opal-CT in these limestones, are indeed common microconstituents in all casing and natural limestone samples studied in this study, indicating a "geologic" origin for the casing stone samples. Opal-CT is not detected in the geopolymeric limestone.
5. Gaber's XRD analysis of quarry samples correctly determined the major amounts of calcite and trace amounts of dolomite in the Tura limestone, which is consistent with the present XRD results of the limestone sample from Tura. His study, however, did not find cristobalite (opal-CT), quartz, and sodium montmorillonite that have been detected in the XRD pattern of acid-insoluble residue from the Tura limestone in the present study.
6. Finally, contrary to the Davidovits' claim, the Lauer casing stone sample examined by him does not contain any "unusual" minerals (except for the ones from the man-made coating), which are not present in the quarry samples, to call for a "synthetic" origin for the casing stone.

Another excerpt of the same chapter of Davidovits' book states:

> "The samples from the Great Pyramid provided by Lauer is topped with a white coating overlaid with a brownish-red surface coloration. Such coloration appears also on a few remaining outer casing blocks of this pyramid and varies from brownish red to grayish black. There has been long debate about whether the coloration is a type of paint or a patina, the latter resulting gradually from desert weather conditions.
>
> Attempting to show that the casing block coloration of the Khufu and Khafra pyramids is a paint, Andre Pochan, in 1934, analyzed the coloration appearing on these pyramids. His tests revealed the presence of minerals highly uncommon in limestone, leading him to conclude that the coloration could not be a patina because that would require a migration of minerals from within the stone itself. He therefore proposed that some type of hard, siliceous binder was applied and painted over with a pigment of red ochre."

SEM-EDS analysis of the present Lauer sample provides additional support in favor of Pochan's finding that there is no evidence of any unusual materials in the bulk limestone body of the Lauer sample which can create a surface patina by elemental migration. Based on the present study of the interior of the Lauer sample, the reported red layer is judged to be paint, which is consistent with Davidovits' observation of filling of a crack in the sample by the paint.

> "Because Pochan had already analyzed the red coloration, I analyzed only the underlying white coating appearing on the sample from the Great Pyramid. I submitted Lauer's sample to two different laboratories employing experts with diverse backgrounds in geology and mineralogy. Combining our expertise, I was amazed to find a tremendously complex geopolymeric chemical system in the white coating. Its principal ingredients are two calcium phosphates, brushite and crystalline hydroxyapatite, both found in bone, and a zeolite called ZK-20. The coating is pure geopolymeric cement. It is the key to the composition of the pyramid stone. This binder is infinitely more sophisticated than the simple gypsum and lime cement by which scholars have characterized Egyptian cement technology. Indeed, the binder is more sophisticated than I had expected."

Based on the published XRD data of the coating and its above-mentioned mineralogy, the present author is in concurrence with the statement that such composition is unusual in natural limestones and is indicative of a "synthetic" origin. The present study, however, sharply disputes Davidovits' conclusion that the coating is "the key to the composition of the pyramid stone" because beyond a zone of "contaminated" limestone directly adjacent to the coating, no evidence of the coating chemistry, mineralogy, or elemental signature could be found in the body of the Lauer sample. The interior is clearly a normal limestone with nothing unusual in its composition.

Unlike the red paint (whose unusual chemical signature was not reportedly detected in the "limestone" component of the Lauer sample), based on the detection of calcium phosphate from the white "coating" within the Lauer sample, Davidovits extended the hypothesis that this synthetic "coating" is the key to the proposed geopolymeric composition of the pyramid stone. The paper-thin pyramid cement, mistakenly assumed by others to be an ordinary lime-gypsum plaster, is reported as a by-product of geopolymerization that forms as a skin when there is excess water in the geopolymeric concrete slurry. No study or evidence was provided by Davidovits to examine the possibility that: (a) the coating-signature within the limestone is indeed an artifact of contamination or infiltration of coating materials into the limestone, and not an inherent chemistry of the limestone; and (b) the paper-thin pyramid cement is compositionally very different from the interior limestone. Hopefully, the results of the present study will put an end to this controversy.

The present optical and SEM-EDS studies provide the hard scientific proof that: (a) the bulk limestone of the Lauer sample away from the coating does not show the calcium phosphate chemical signature of the coating, and (b) the opal-CT phase, reportedly discovered in the pyramid stones only by Davidovits and Barsoum et al. (2006), is indeed a common siliceous microconstituent in the limestone from Tura as well. The red paint and the underlying white coating on the Lauer sample are synthetic but the limestone beneath it is certainly not.

Finally, Davidovits' lime-natron-clay-based recipe of geopolymeric limestone for the pyramid stone cannot explain the phosphate phases in the Lauer sample, which he used as his hard scientific proof to propose the man-made origin of the casing stones. Only contamination from the adjacent phosphate-based coating can explain the detection of phosphate phases in the Lauer sample, and this contamination is not present in the other casing stone or in the Tura limestone.

## SUMMARY

The present study, based on detailed textural, mineralogical, microstructural, and microchemical analyses of pyramid casing stones, a natural limestone from Tura, and a geopolymeric limestone from Davidovits conclusively justifies the following statements:

(1) **<u>Basic Textural and Microstructural Differences Between Casing stones and Reconstituted (Geopolymeric) Limestone</u>** – There is no textural or microstructural evidence of a "reconstituted" limestone in the examined pyramid casing stones. The overall texture of a man-made geopolymeric limestone shows: (a) fine-grained limestone "lumps" and incompletely and variably disaggregated limestone fragments (similar to "aggregates" in a concrete) sporadically distributed in a (b) fine-grained calcite-geopolymer cement-based matrix (similar to paste or mortar-fraction in concrete), and (c) many irregularly shaped to spherical "air voids" produced in the mixing process. Optical microscopical examinations of the geopolymeric limestone clearly show many of these characteristics, which are in sharp contrast to the textural appearances of the pyramid stones and quarried limestones. Both pyramid casing stones and the limestone from Tura show a normal, geologic particulate texture of variably porous to dense bioclastic microcrystalline limestone consisting of: (a) a dominantly microcrystalline calcite 'mud' matrix (micrite to microspar calcite grains, intimately associated with micritic lumps), (b) occasional bioclasts (shell fragments of foraminifera, mollusks and echinoids), (c) occasional calcite-filled fractures, and (d) characteristic intergranular porosity comprised of irregularly-shaped (i.e., mostly non-spherical) pores with overall porosities from relatively low in the limestone from Tura to high in the casing stone samples.

Despite the reported "visual" resemblance of pyramid stones to a "reconstituted" limestone with the unaided eye or even with a hand lens (Morris 1991), significant textural differences revealed from optical microscopy (i.e., examinations of thin sections in a petrographic microscope at magnifications of 100 to 1000X) are further supported by striking differences in microstructures between the pyramid stones and geopolymer limestone in the secondary and backscatter electron images from the SEM. Despite the reported broad visual and bulk chemical compositional similarities, duplicating the intricate textural and microstructural similarities of pyramid stones and natural limestone by a "reconstituted" limestone is a challenge that far from being fulfilled.

Jumbled fossils, oval-shaped air bubbles, organic fibers, native gold, etc. previously reported in the field and in the hand specimen of the Lauer sample by the followers of the geopolymer hypothesis (Davidovits, Morris, Zeller, McKinney), and used as evidence in favor of a "man-made" origin, are not found in the "bulk interior" of the same Lauer sample studied here (neither by optical microscopy nor by SEM analyses), or in the other casing stone sample, EA-491. Those features are, therefore, indicative of preexisting features in the field (e.g. jumbled fossils as detected in the Giza bedrock), or accidental inclusions in the sample (e.g., fibers) and do not indicate a "man-made" origin of the entire stone. A few oval-shaped voids previously detected in the thin section photomicrographs of the Lauer sample are also found in the present study, but these are undoubtedly fossil casts with the characteristic shapes of nummulites and other foraminifera. The casing stone samples contain many irregularly shaped voids but no spherical voids, which are characteristically present in the reconstituted geopolymeric limestone (due to the mixing action of the ingredients).

(2) **Absence of Geopolymeric (Alkali-Aluminosilicate) Chemistry in the "Binder Phase" of Casing Stones** – Perhaps the most important finding in this study is the lack of evidence of an alkali and/or aluminosilicate-based composition of the binder phase in the casing stone samples of the Khufu pyramid, which is the essence of the lime-natron-clay-based recipe of the geopolymer hypothesis proposed by Davidovits (1983, 1986, 1987, 1988). SEM-EDS analyses of both casing stone samples, "EA-491" and the "Lauer" sample, from the Khufu pyramid do not show any evidence of alkali or alumina in the binder phase in limestone. Contrary to the geopolymeric limestone, where the entire binder phase is uniformly enriched in Si, Al, Na, and K, the casing stones literally show no noticeable Na, K, or especially Al signature in either the binder or the interstitial areas between the calcite grains.

Proponents of the geopolymer hypothesis may suggest that detection of alkalis in the ancient geopolymeric cement is difficult due to its possible use at a very low concentration for activation of clays or pozzolans (as little as one percent NaOH, equivalent to $0.64Na_2O$, can activate the setting of pozzolana-lime cement), which, along with lime-alkali exchange, alkali leaching, and recarbonation of excess lime after alkali-activation can "mask" the alkali-signature. However, the basic aluminosilicate structure, the building block of geopolymeric cement, must be preserved and so detectable by SEM-EDS. No such evidence of an alumina-based composition was found in the casing stone matrix. The most recent studies on pyramid casing stones (e.g., Davidovits, J. and Demortier, G. 1999, Demortier, G. 2004) should have, in their attempts at detecting aluminosilicates, done the analysis on the pristine uncontaminated interior of the casing stones away from the silico-aluminate (zeolitic) component in the coating and its invaded zone within limestone, and should have been confirmed by independent SEM-EDS analysis. The present SEM-EDS study conclusively demonstrated the absence of any such signature either in the EA-491 sample, or in the interior of the Lauer sample.

(3) **No "Synthetic" Phases, e.g., Calcium Phosphate, in the Bulk Uncontaminated Interior of the Casing Stone** – Contrary to the previous reports on the presence of calcium phosphate and silicoaluminate phases in the casing stone sample from the

Khufu pyramid, and, therefore, the notion of its synthetic origin, the present study determined a zone of contamination in the casing stone adjacent to the coating where the porous microstructure of the limestone was invaded by phosphates from the coating. The phosphorous concentration in the contaminated zone in limestone showed a progressive decrease towards the interior for an approximate distance of 5 mm from one edge of the sample, and thereafter the phosphorous concentration was uniformly negligible (and similar to that in EA-491 and the limestone from Tura) in the bulk interior. Beyond this contaminated (or coating-influenced) zone, the bulk interior limestone in the Lauer sample is as pristine and as natural in its origin as EA-491 and the limestone from Tura.

(4) **Lepispheres – Geologically Normal Silica-rich Microconstituents in the Casing Stones and the Limestone from Tura** – Spherical and near-spherical Si-rich microconstituents, previously described as opal-CT (lepispheres) are confirmed by the present SEM-EDS study as isolated, very fine (<10μm size), interstitial Si-rich constituents in both casing stones and in the limestone from Tura. The study also determined that these silica-rich microconstituents contain variable amounts of other elements such as Ca, Mg and Al as impurities. XRD studies of the acid-insoluble fraction of the limestone from Tura detected cristobalite. Detection of opal-CT in casing stone, or the variable minor-element compositions of these silica-rich microconstituents does not suggest it has a "synthetic" origin. Minor element (e.g., Ca, Mg, Al, Na) compositional variations in opal-CT are normal and well-known geologic chemical variation[9].

The present study of a limited number of samples, mostly remains of previous samples provided by others, should serve as an example of the importance of detailed petrographic examinations of pyramid samples to evaluate all previous results, generate unquestionable data, and resolve any controversy. To settle this "natural" versus "man-made" controversy, the importance of a comprehensive examination encompassing microscopy (Optical & SEM), XRD, chemical (XRF, AA, IR), microstructural (SE-BSE), microchemical (EDS), and any other related analyses of limestones and their non-carbonate (acid-insoluble) constituents cannot be overemphasized.

The latest research by Barsoum et al. (2006) show two significant deviations from Davidovits' geopolymer hypothesis. First, similar to the present study, Barsoum et al. (2006) did not find any evidence of an alkali or alumina based binder in their casing stone samples, which is the mandatory requirement of lime-natron-clay based geopolymer hypothesis. Second, unlike Davidovits and others (Davidovits and Morris 1988, Morris 2004), who have extended the geopolymer hypothesis to not only the casing blocks but also to the core blocks of the great pyramids, Barsoum et al. (2006) have reported that the majority of the core blocks of the Khufu pyramid are "carved". Contrary to their evidence of so-called "synthetic" origin of silica-rich microconstituents in the casing stone (having reportedly "rare" Ca/Mg ratios), the present study found these microconstituents (with their normal geologic minor-element compositional variations) in both casing stone and limestone quarry samples.

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[9] There are two theories of formation of opal-CT (lepispheres) or silica-rich microconstituents in limestone – one is by normal diagenetic precipitation, and the other is by nanobacterial precipitation (Folk et al. 1995) – in both ways opal-CT can accommodate noticeable amounts of Ca, Mg, and other elements, having Ca/Mg ratios dependent on temperature, salinity, and other factors of the post-depositional environment.

A reliable set of data derived from comprehensive laboratory investigations by petrographers, materials scientists, and geochemists on a range of actual pyramid samples reveals the truth about "natural" versus "man-made" origin of pyramid blocks. We should refrain from postulating a hypothesis based on results from limited investigation with a single study, with no confirmative support from other studies. Selectively producing results in favor of a hypothesis on a limited number of samples with questionable provenance from third parties, or proposing the hypothesis first and then generating results in favor of it are not proper scientific procedures. The typical alkali-aluminosilicate-based geopolymeric chemistries in the binder phases of pyramid stones are yet to be discovered. There is no foreign or man-made constituent found in the "uncontaminated" portion of the Lauer casing stone, which is identical to the quarried limestone in Tura. Detailed results on the actual mineralogy, texture, composition, and binder chemistry of the limestone in the core blocks, constituting 80 percent of the mass of the Khufu Pyramid are yet to be published, and should be required before postulating them to be "man-made". Also yet to be demonstrated by the proponents of the "cast-in-place concrete" hypothesis is a synthetic geopolymeric limestone sample that is similar to the casing stone not only in visual appearance and bulk chemistry but also in texture, microstructure, minor constituent mineralogy, and especially in calcareous, *alkali-aluminosilicate-free binder microchemistry*. Based on a detailed literature survey on this debate and evaluation of all published results *in light of this present comprehensive study*, it is the author's opinion that we are far from accepting even as a remote possibility of a "man-made" origin of pyramid stones. It is indeed this absence of any geopolymeric signature in the pyramid stones, which should encourage re-evaluation of apparent "mysteries" in carving and hoisting large pyramid blocks, originally offered to support the "man-made" origin.

Undoubtedly, the future of the geopolymer technology is exciting, especially in the cast-stone technology, and as promising portland cement alternatives in the construction industry, or as blended geopolymer-portland cement combinations for sustainable development. Davidovits should be commended for his research in channeling this zeolite-cement technology toward future applications. Synthetic zeolites (geopolymers) have many similar pozzolanic applications in construction, as demonstrated by various researchers in the three international proceedings organized by Davidovits' Geopolymer Institute in France (Davidovits 2005). A companion paper of the present author in this proceeding also emphasizes the importance of natural zeolite as an excellent pozzolan in developing durable concrete products. Despite its many reported ancient routes, and unquestionable potential future applications of geopolymer technology, the Egyptian pyramids, in author's opinion, still stand as marvels and mysteries of ancient engineering technologies exercised by the Old Kingdom (2500 BC) stone masons.

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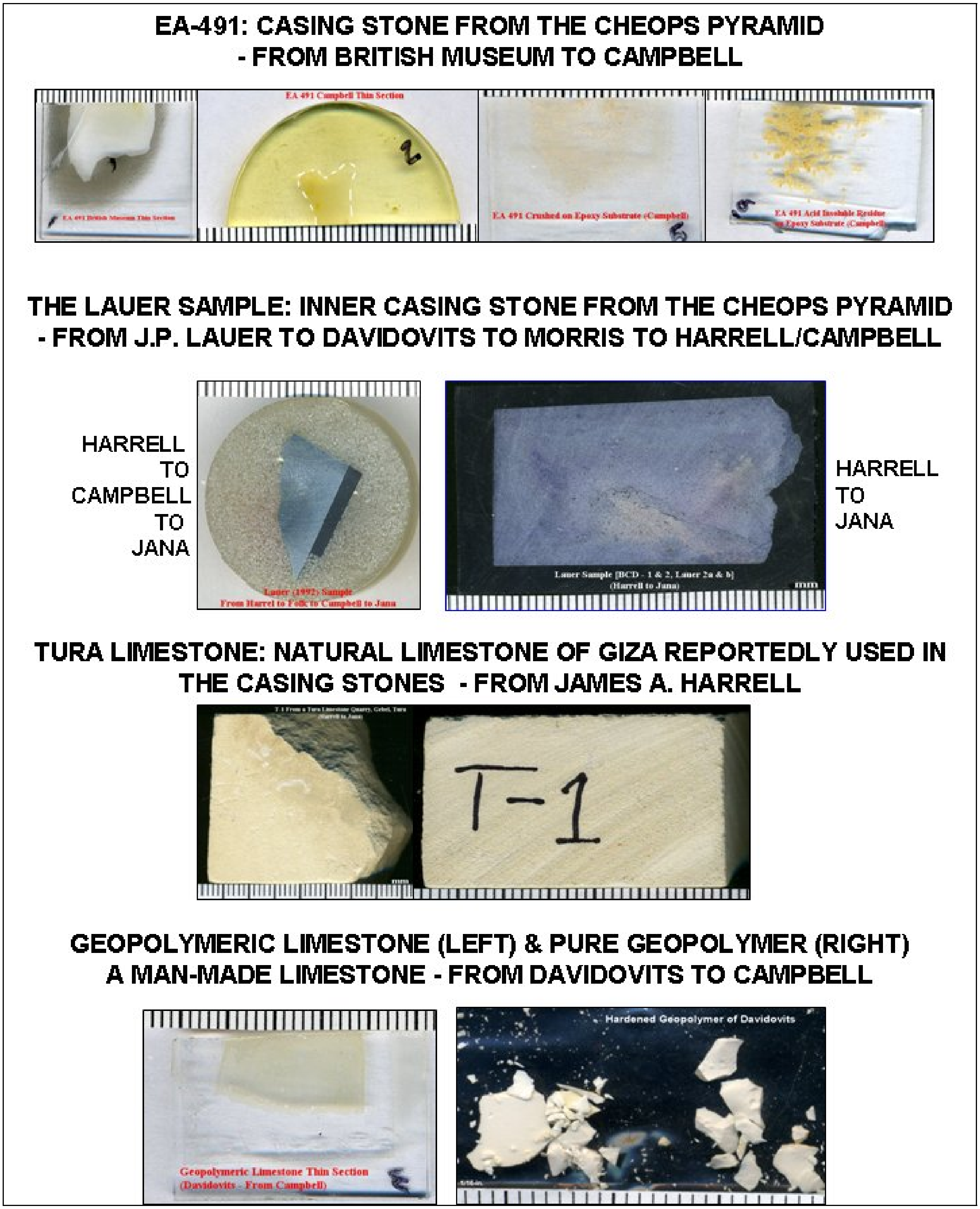


**Figure 1**: Shown are the thin sections, polished sections, solid samples, and fragments of the casing stone samples of the Khufu pyramid (EA-491 and the Lauer sample), a natural limestone (T-1) from Tura, and a geopolymeric limestone received for this study. Also given are the names of individuals and organizations through whom the samples came to the author.

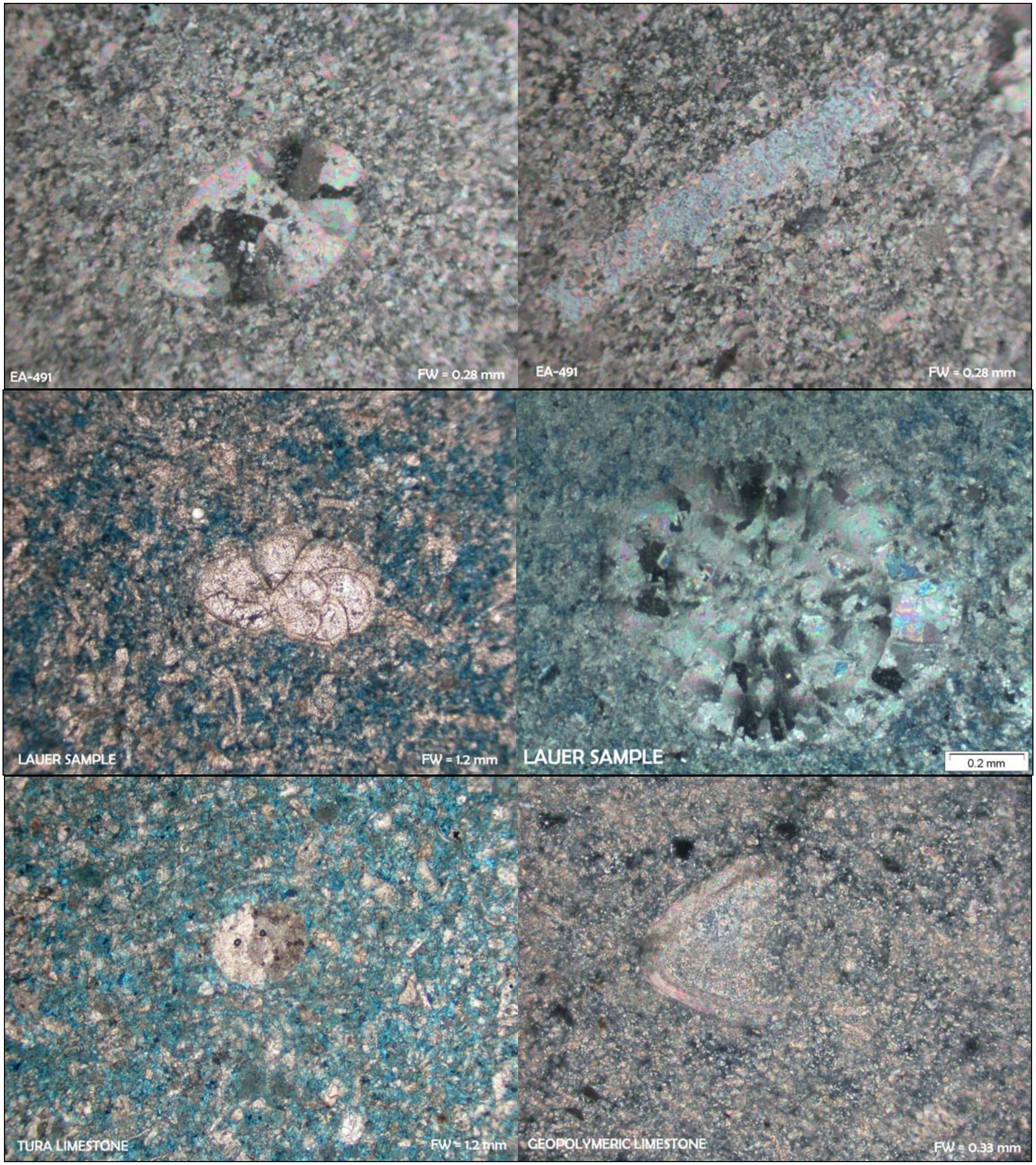


**Figure 2**: Photomicrographs of thin sections of casing stones (EA-491 and the Lauer sample), Tura limestone, and geopolymeric limestone showing some bioclast fragments (e.g., foraminifera, molluscs) and overall texture of the microcrystalline calcite grains in the surrounding areas. FW (Field Width) is the distance from left to right of a photo.

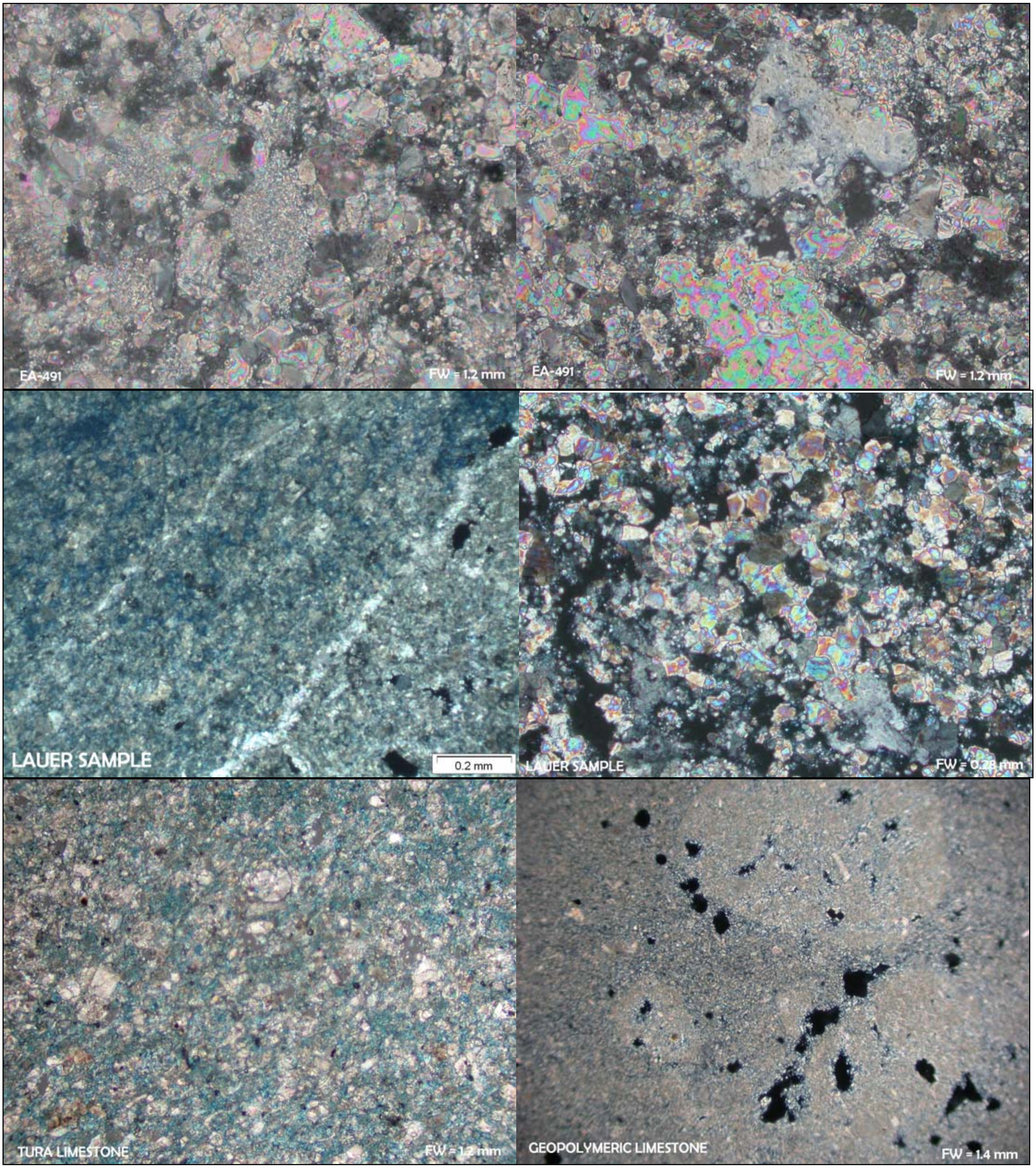


**Figure 3**: Photomicrographs of thin sections of casing stones (EA-491 and the Lauer sample), Tura limestone, and geopolymeric limestone showing the overall texture of micritic calcite grains, fine-grained micritic lumps in casing stones, spherical and elliptical lumps of calcite dust in geopolymeric limestone, and a calcite-filled fracture in the Lauer sample. FW (Field Width) is the distance from left to right of a photo.

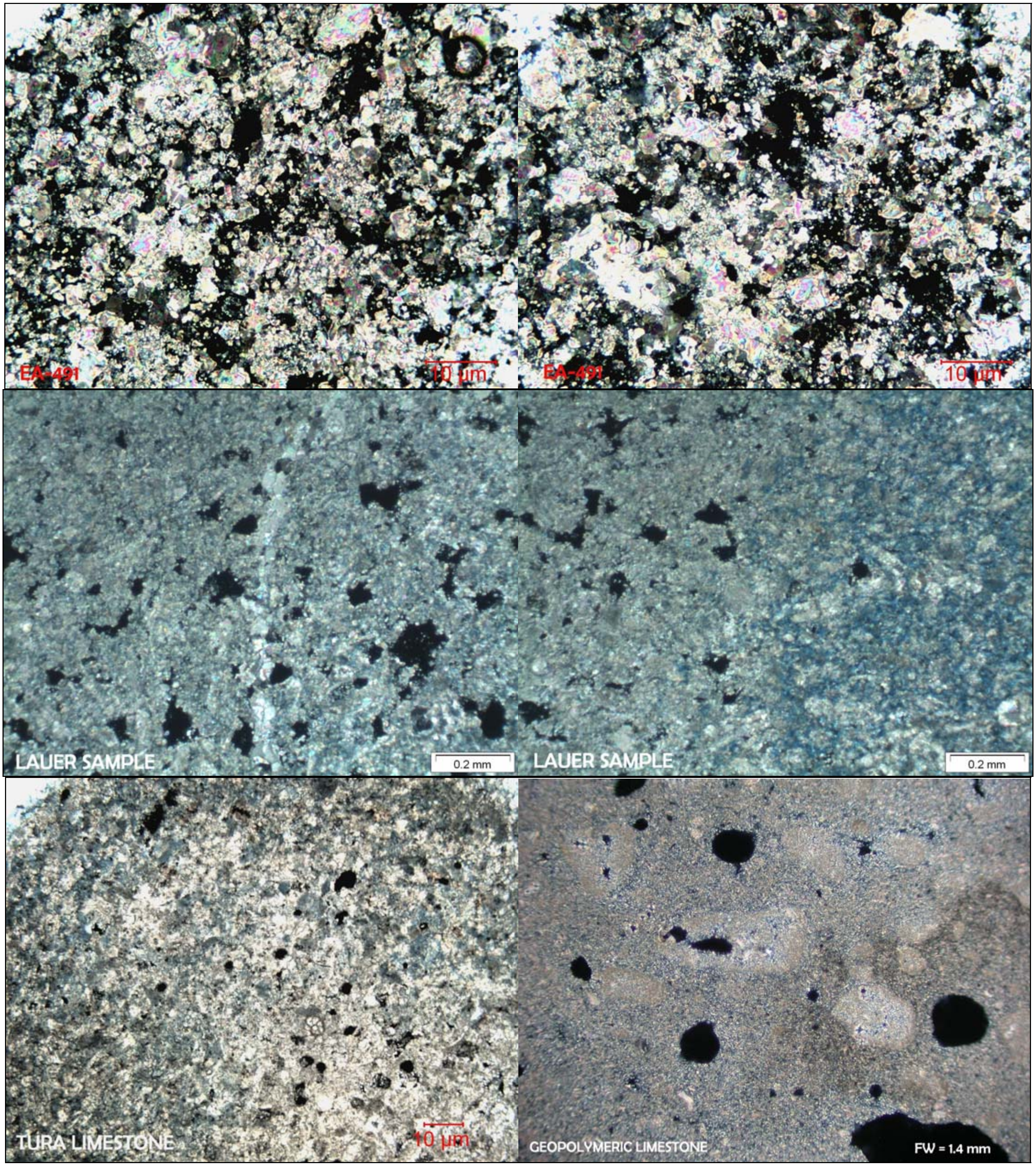


**Figure 4**: Photomicrographs of thin sections of casing stones (EA-491 and the Lauer sample), Tura limestone, and geopolymeric limestone showing intergranular pore spaces in EA-491, irregularly shaped voids in the Lauer sample, very fine voids and pores in Tura limestone and characteristic near-spherical and spherical voids in geopolymeric limestone. FW (Field Width) is the distance from left to right of a photo.

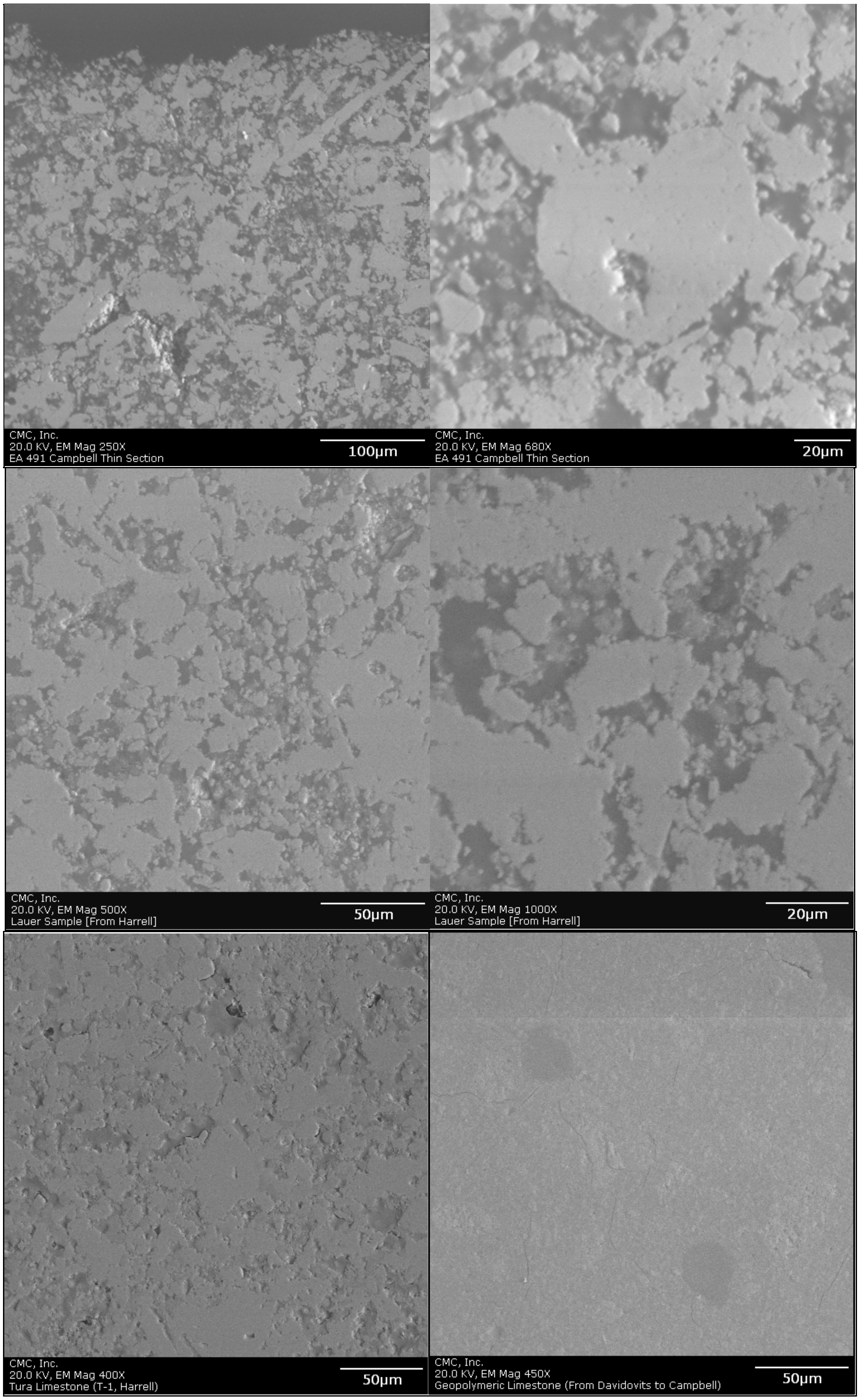
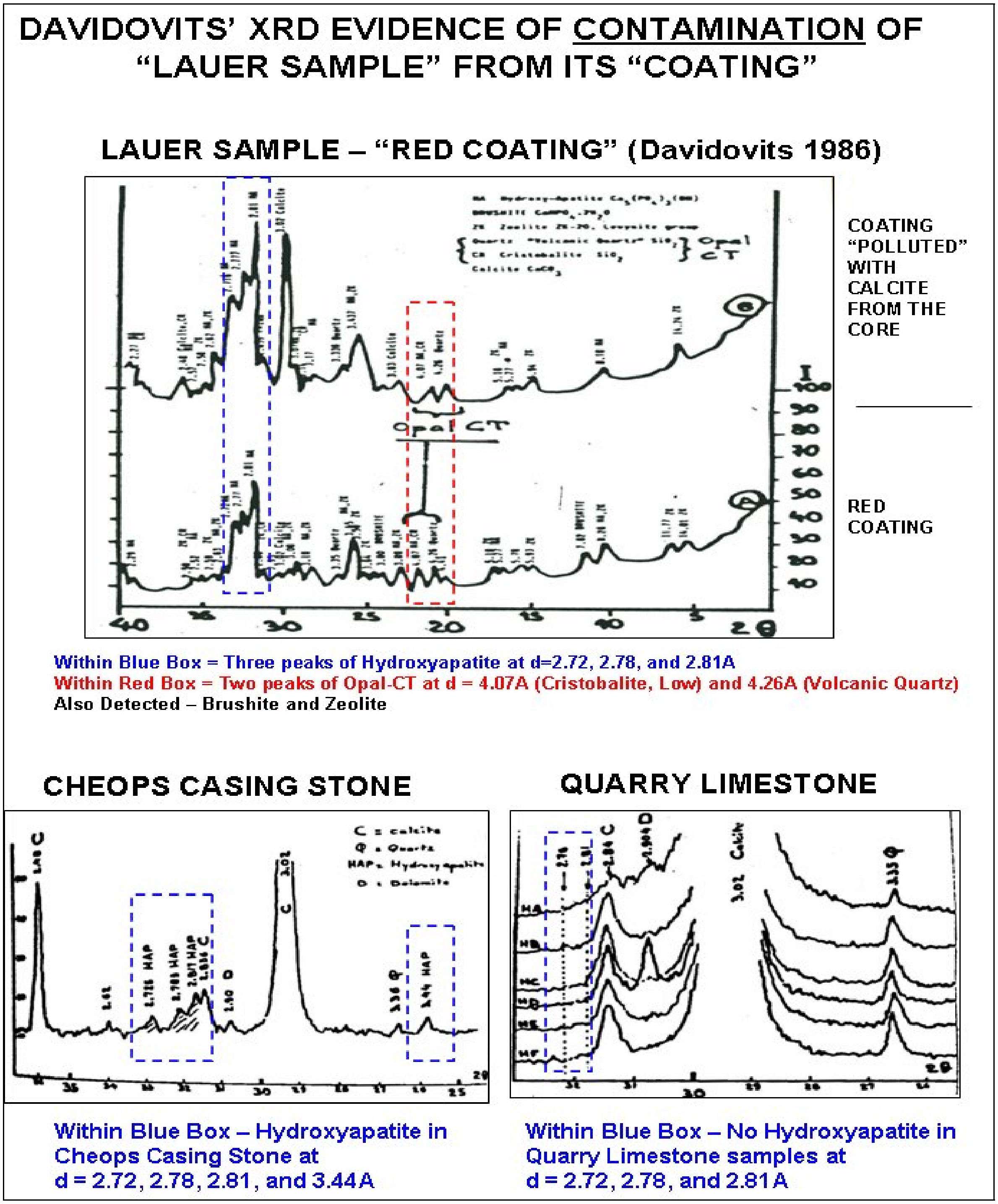


**Figure 5**: Backscatter electron images showing the overall particulate texture with intergranular pore spaces in the casing stones and Tura limestone, whereas relatively smooth texture with two spherical air voids in the geopolymeric limestone.



DAVIDOVITS' XRD EVIDENCE OF CONTAMINATION OF "LAUER SAMPLE" FROM ITS "COATING"

LAUER SAMPLE – "RED COATING" (Davidovits 1986)

Within Blue Box = Three peaks of Hydroxyapatite at d=2.72, 2.78, and 2.81A

Within Red Box = Two peaks of Opal-CT at d = 4.07A (Cristobalite, Low) and 4.26A (Volcanic Quartz)

Also Detected – Brushite and Zeolite

Within Blue Box – Hydroxyapatite in Cheops Casing Stone at d = 2.72, 2.78, 2.81, and 3.44A

Within Blue Box – No Hydroxyapatite in Quarry Limestone samples at d = 2.72, 2.78, and 2.81A

**Figure 6**: A reproduction of Davidovits' XRD patterns of: (a) the red coating on the casing stone of the Khufu pyramid, (b) the casing stone beneath the coating; and (c) natural (quarry) limestones. The patterns show the presence of a calcium phosphate phase (HAP, hydroxyapatite) in the coating (diagnosed within the blue boxed areas), its detection *in significantly less amount* in the casing stone beneath the coating, and its absence in the quarry limestone samples. The data itself indicates a possible contamination of the casing stone by the overlying coating materials, which is not present in the quarry limestones. Detection of HAP (and associated traces of coating materials) in the limestone, therefore, does not indicate a "man-made" origin of the casing stone. This statement is supported by the present study, where a clear zone of phosphate contamination is detected in the limestone beneath the coating to a distance of ~5 mm.

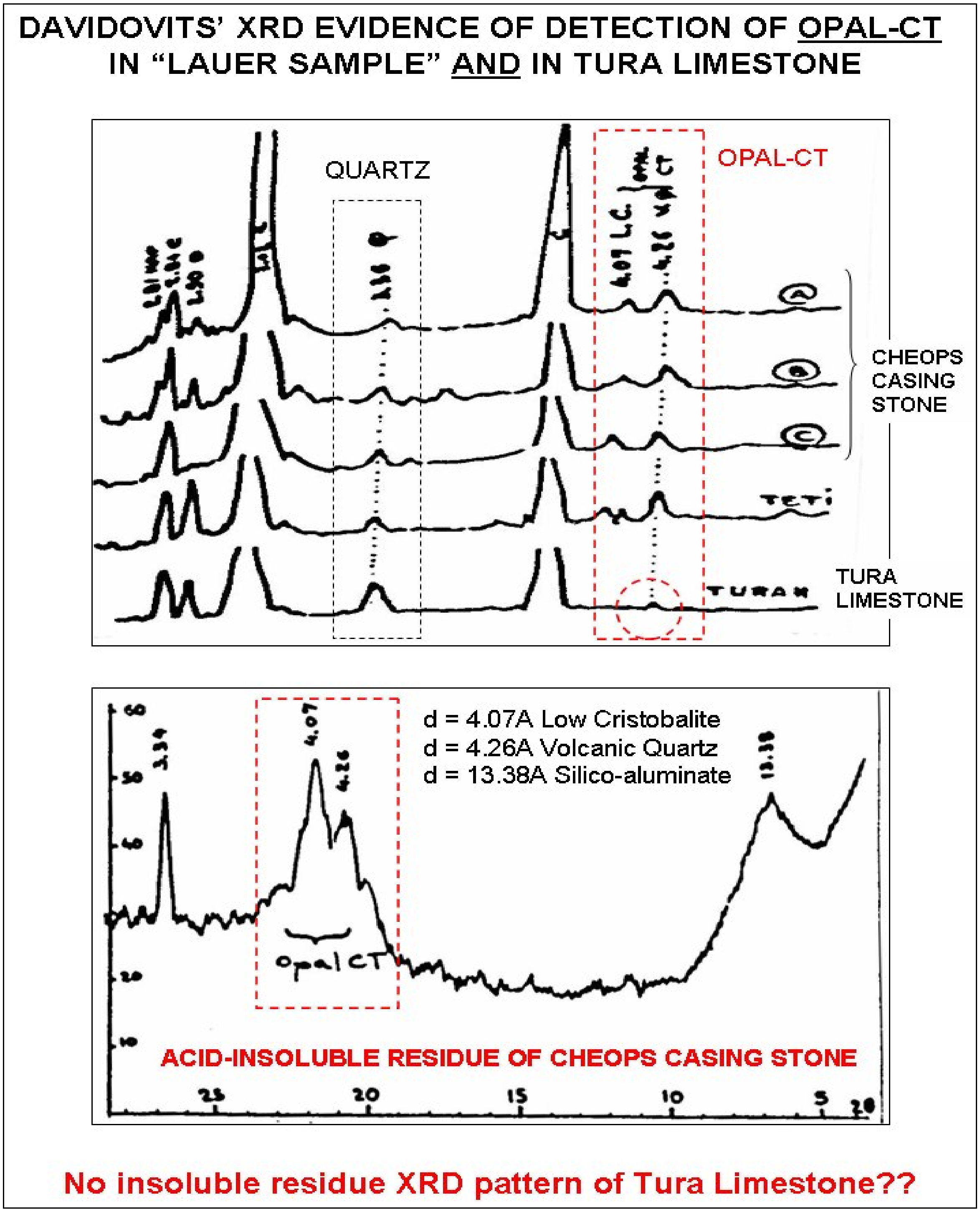


**Figure 7**: A reproduction of Davidovits' XRD patterns of: (a) casing stone samples from the Khufu pyramid and Tura limestone, and (b) acid-insoluble residue of a casing stone. The data itself indicates: (a) the presence of an opal-CT phase (boxed red) not only in the casing stone but also, in lesser amount, in the Tura limestone (circled), and detection of opal-CT in the acid-insoluble residue fraction of the casing stone; and (b) the presence of quartz (boxed black) not only in the quarry samples but also in the casing stone. The results, therefore, do not indicate any mineralogical difference to call for a "man-made" origin of the casing stone. Similar to the casing stone, an XRD analysis of insoluble residue fraction of Tura limestone should have provided a far better indication of the presence of opal-CT in natural limestone of Giza than the bulk analysis (which is provided in this study in Fig. 9 where opal-CT is indeed detected in the Tura Limestone).

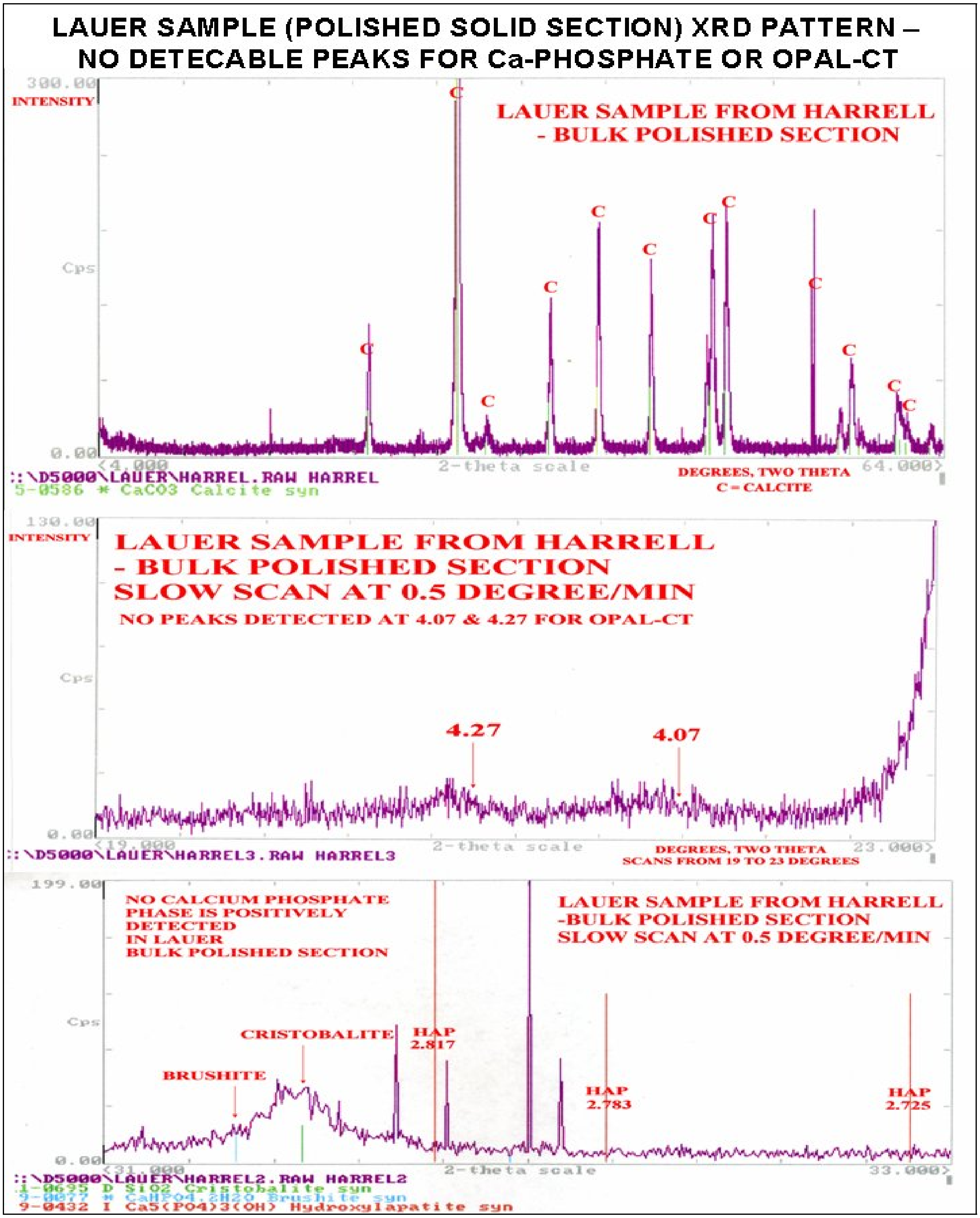


**Figure 8**: X-ray diffraction pattern of polished section of the Lauer-Harrell sample, which was used for the SEM work. The pattern shows the dominance of calcite, as expected; and an apparent absence of an opal-CT or a calcium phosphate phase *on a polished section* (during slow scans in 2θ ranges where characteristic diffraction peaks were detected in Davidovits' 1986 study). Optical and scanning electron microscopy, however, clearly detected silica-rich spherical microconstituents in this sample, which, therefore, indicates an integrated approach of optical-SEM-XRD work for definitive detection of microconstituents in these samples.

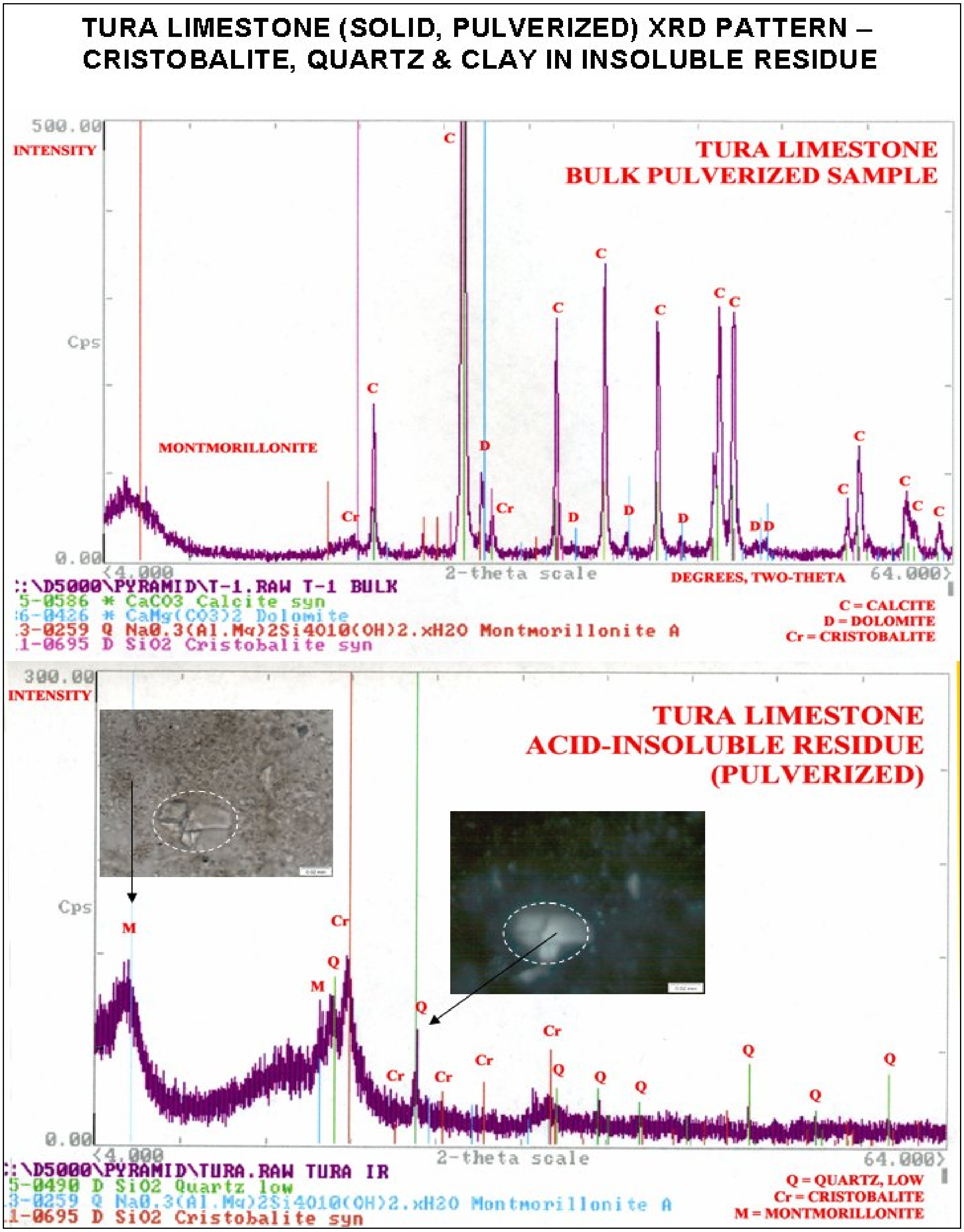


**Figure 9**: X-ray diffraction patterns of the Tura limestone (top), and its acid-insoluble residue (bottom) showing: (a) the dominance of calcite with a minor amount of dolomite in the limestone; and (b) the presence of quartz, cristobalite (opal-CT), and sodium montmorillonite clay in the insoluble residue. The inset optical micrographs of oil immersion mounts of the acid-insoluble residue in the bottom pattern shows clay and a quartz grain (circled).

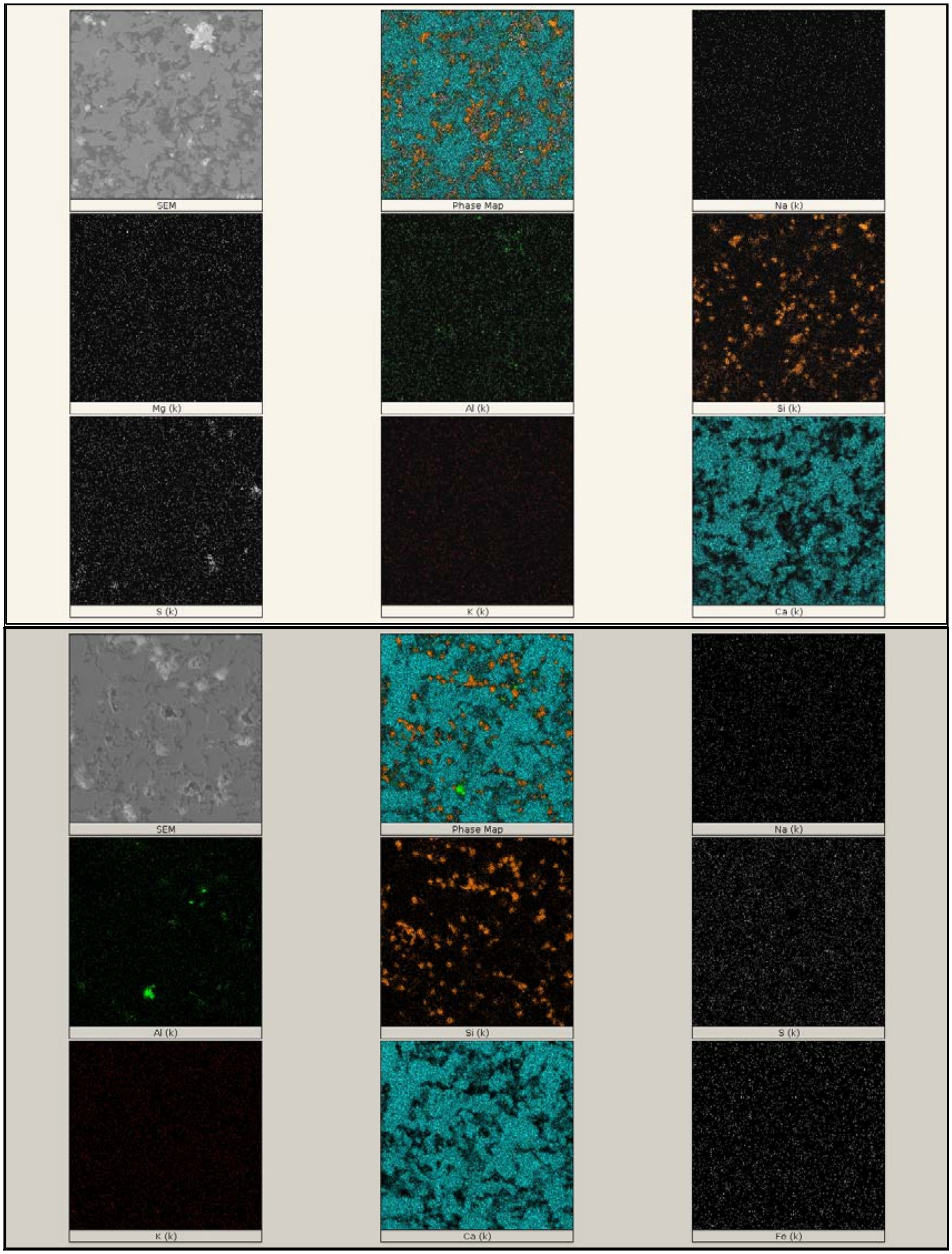


**Figure10**: X-ray elemental analysis (SEM-EDS) of the casing stone samples from the Khufu pyramid - EA-491 (top) and the Lauer sample (bottom) showing: (a) the dominance of Ca-rich areas (in blue) from their characteristic calcite-based mineralogies; (b) occurrences of Si-rich areas (in brown) as small, isolated, near-spherical or irregularly shaped interstitial phases; (c) a very few minor occurrences of S-rich spots in EA-491 (consistent with findings of gypsum in this sample by Campbell and Folk 1991), and one Al-rich "spot" in the Lauer sample; and, most noticeably, (d) complete absence of any indication of alkali (Na, K) or alumina (Al) enrichment in the *binder phases* (interstitial areas) or in grains, which Davidovits' lime-natron-clay-based geopolymeric chemistry produces (see Figure 11 for comparison). The absence of alkali or alumina enrichment in the interstitial areas is also verified in elemental maps at higher magnifications.

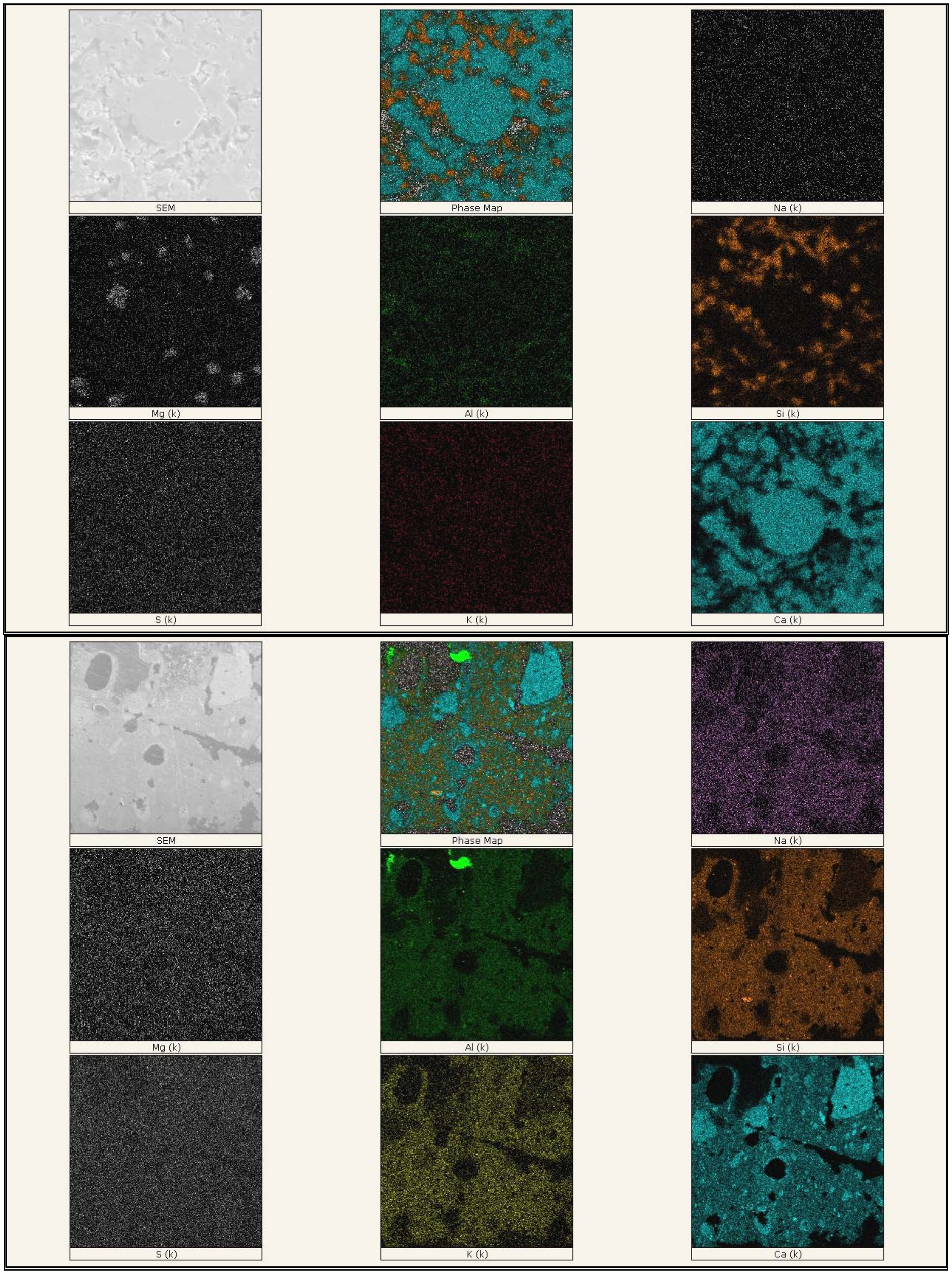


**Figure11**: X-ray elemental analysis (SEM-EDS) of Tura Limestone (top) and Davidovits' Geopolymeric Limestone (bottom). Similar to the patterns seen in the casing stones, Tura limestone shows: (a) the dominance of Ca-rich areas (in blue) corresponding to the calcite grains, (b) Si-rich areas (in brown) as isolated, mostly near-spherical to irregularly shaped interstitial areas, some of which correspond to the Mg-rich ones (in white); and (c) complete absence of any indication of alkali (Na, K) or alumina (Al) enrichment in the *binder phases* (interstitial areas) or in grains, which Davidovits' lime-natron-clay based geopolymeric chemistry produces in the bottom photo. Notice the uniform and distinct enrichment of Na (in purple), K (in yellow), Al (in green), and Si (in brown) in the geopolymer matrix, and occurrences of Si as uniform mass in a geopolymer matrix rather than interstitial, isolated "spots/grains" as in the pyramid samples and Tura limestone.

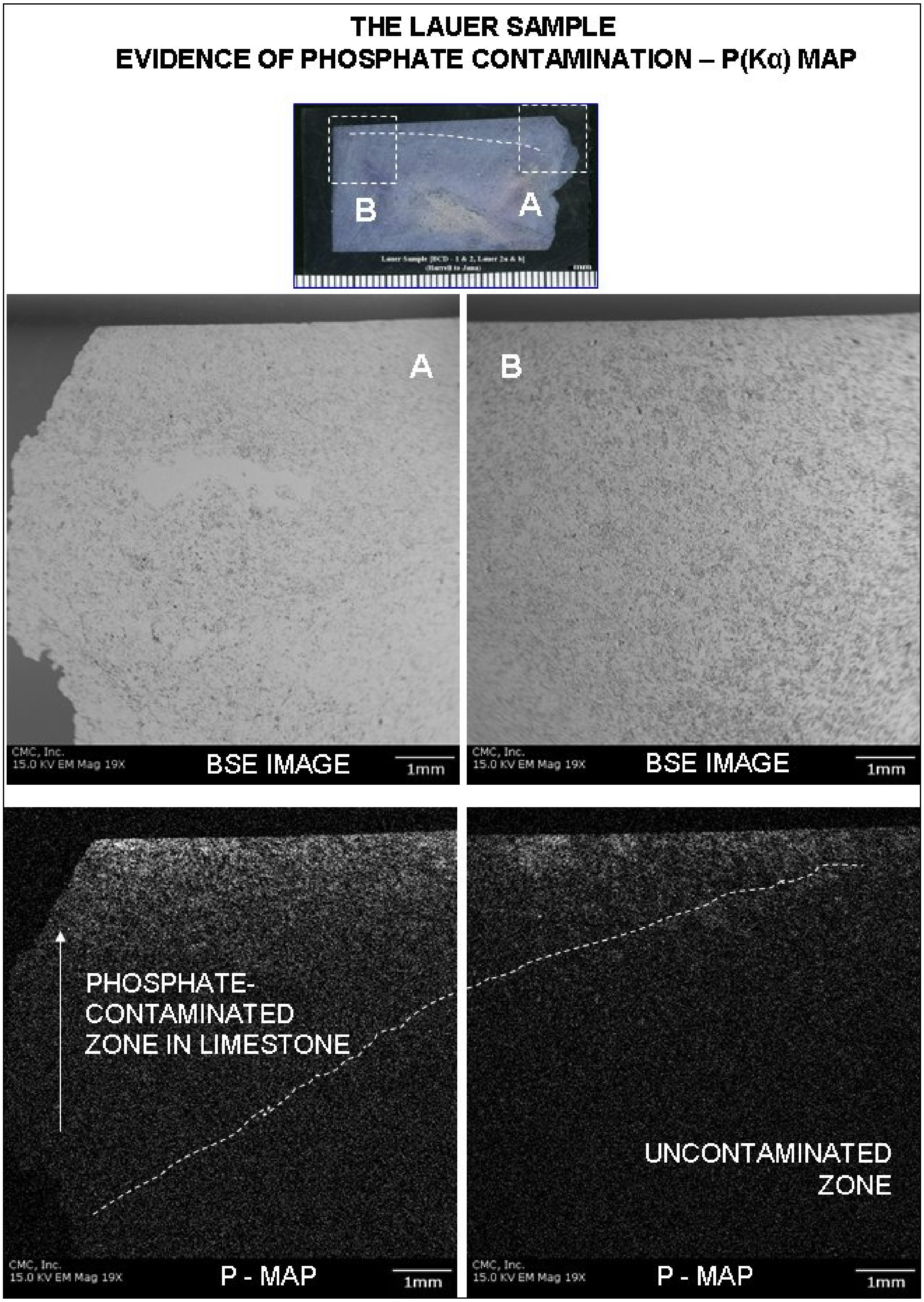
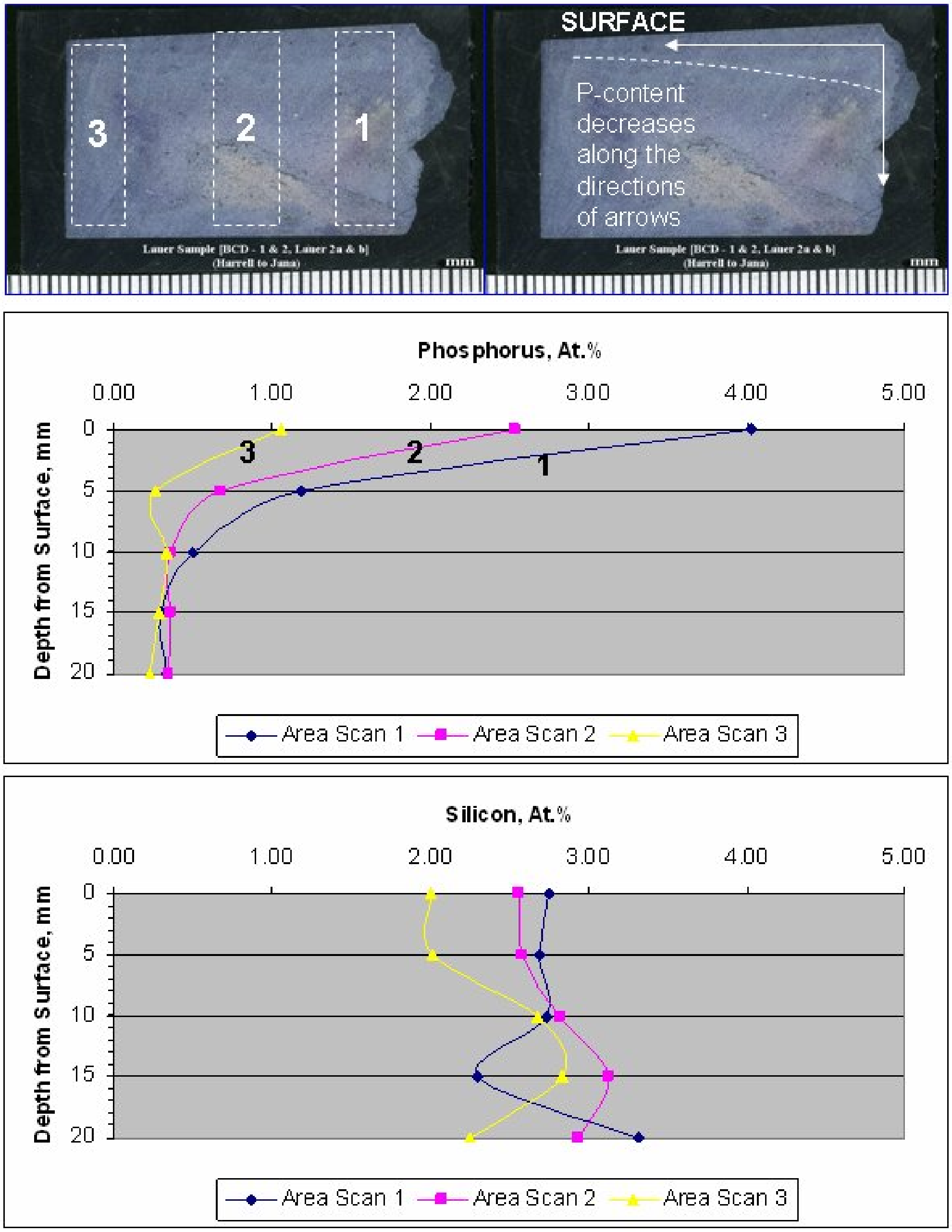


**Figure 12**: X-ray elemental (phosphorus) map of the Lauer sample over a broad area from one side of the sample (shown in the top photo) showing distinct P-enrichment at one corner on the top and its progressive decrease in concentration towards opposite ends (bottom photos). The middle photos are backscatter electron images of the boxed areas A and B on the sample (top photo); the lower photos are the P-scans over these areas. The P-contaminated zone is separated by a dashed line (bottom photo) from the interior uncontaminated limestone. The calcium phosphate phases that Davidovits detected in his XRD pattern of the Lauer casing stone sample most probably came from the contaminated zone.

**THE LAUER SAMPLE**
**EVIDENCE OF PHOSPHATE CONTAMINATION – AREAL SCANS**



Each "area scan" consists of five 300-micron square areas vertically arranged from one side of the sample to the opposite, scanned for Ca, Si, P, Mg, Fe, Na, K, S, O, C at slow rate. Except for P, all other elements show similar concentration from one end to the other. Ca = 28-35%, Mg = < 0.1%, K= < 0.20%, Fe = < 0.25%, others below the detection limit. The top inset photo of Lauer sample shows the polished section that was examined in three parallel area scan profiles (five areas per profile, 15 areas total). A systematic decrease of phosphorus concentration from one side of the surface to the other (from top to bottom side and left to right direction in the photo marked with arrows) was noticed.

**Figure 13**: Further evidence of phosphorus contamination in the Lauer sample. Notice the decrease in P concentrations along three area profiles 1, 2, and 3 on the top photo whereas more or less consistent concentration of silicon (and other elements) in these areas. Based on this analysis, the maximum depth of phosphorus contamination is judged to be ~5 mm from the sectioned edge.

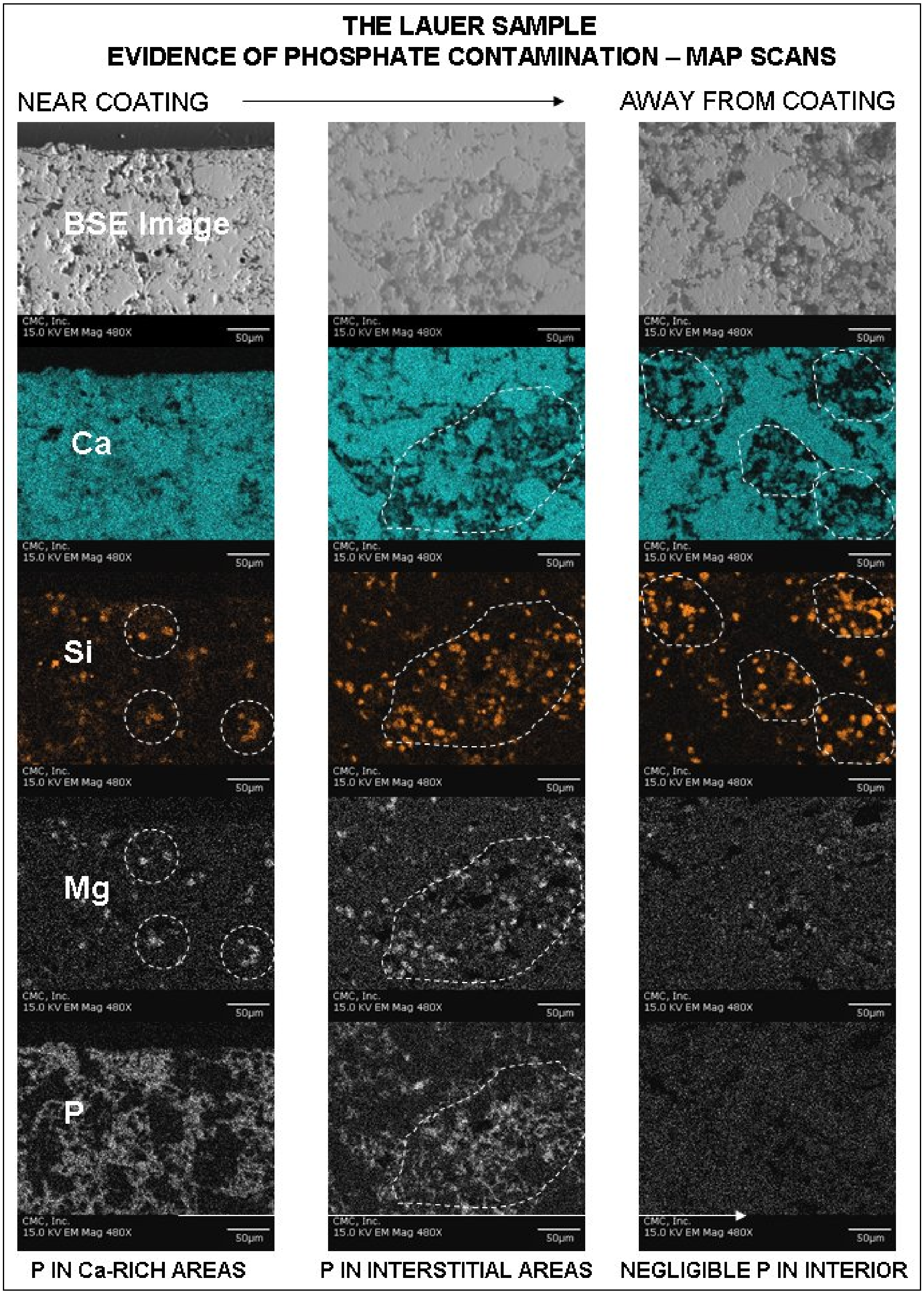
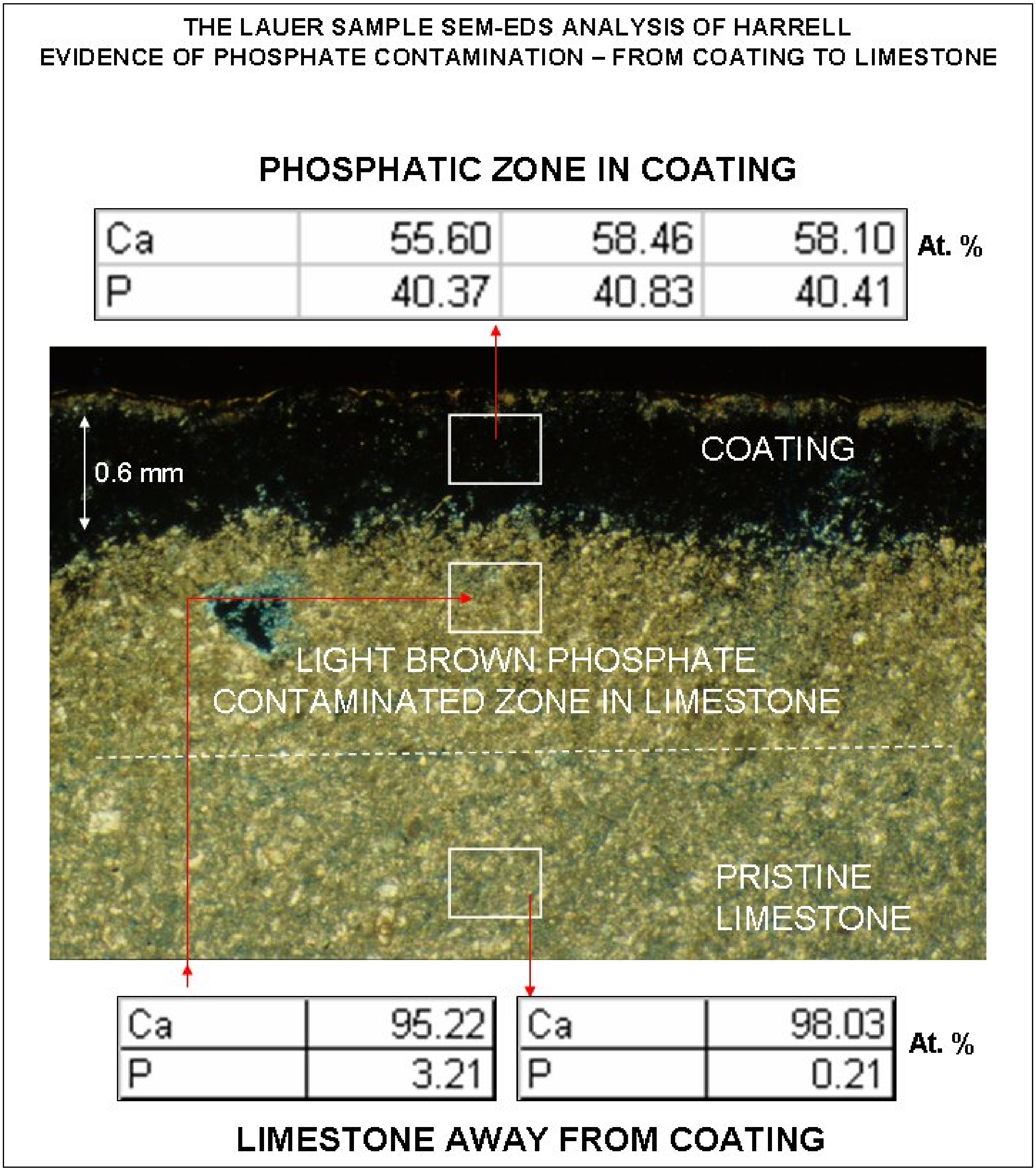


**Figure 14**: Further evidence of P-contamination - Elemental mapping of polished section of the Lauer sample in three 300µm$^2$ areas located diagonally across the section from the most contaminated zone at the top corner (shown by the left column of analyses with the maximum P) to the uncontaminated interior at the opposite corner (shown by the right column of analyses with negligible P). Notice in the contaminated zone P occurs mostly in the areas of Ca, indicating a possible calcium-phosphate based chemistry, whereas away from this zone, in the middle column, P occurs in the interstitial and in Ca-rich areas. The Si-rich interstitial phases are also enriched in Ca and Mg.



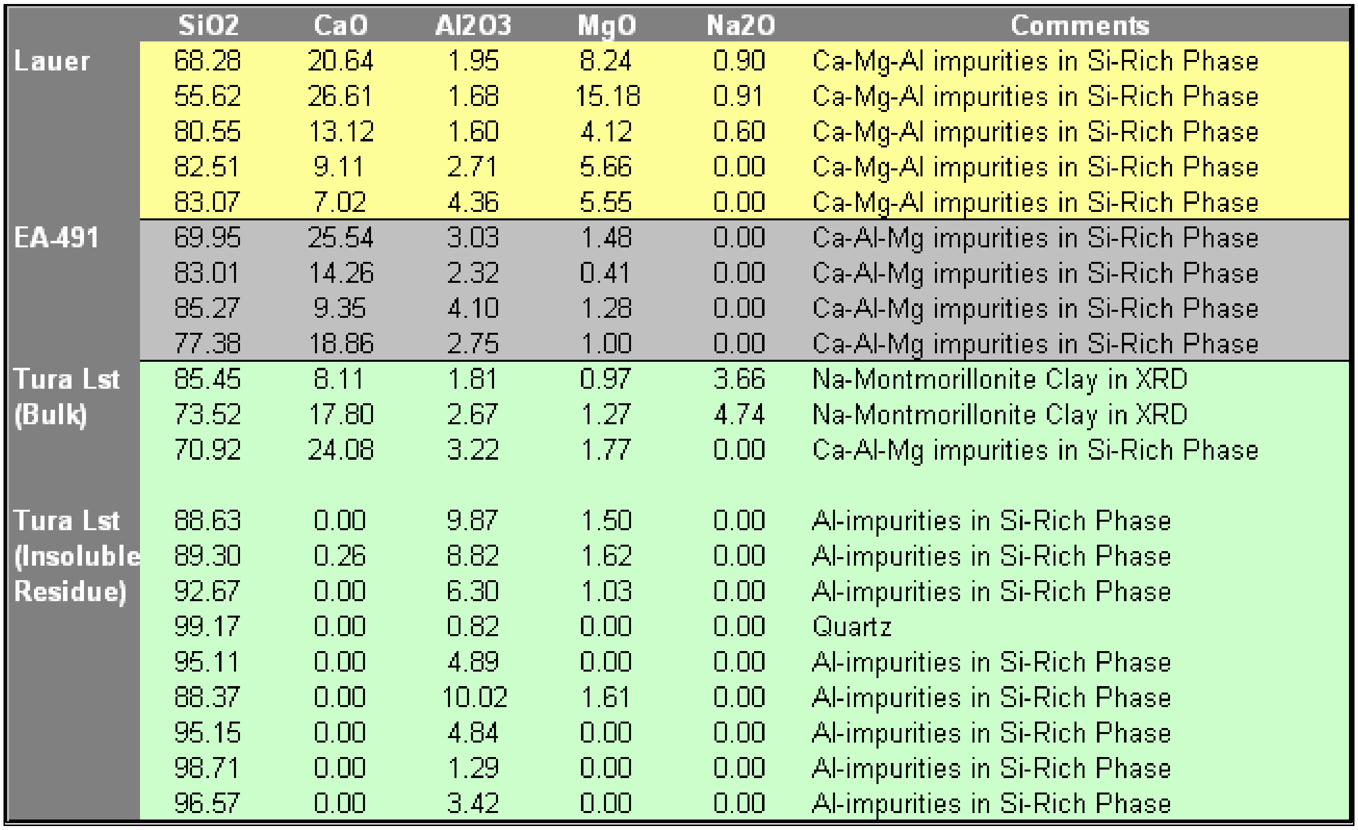
| | | | |
|---|---|---|---|
| Ca | 55.60 | 58.46 | 58.10 |
| P | 40.37 | 40.83 | 40.41 |

| | |
|---|---|
| Ca | 95.22 |
| P | 3.21 |

| | |
|---|---|
| Ca | 98.03 |
| P | 0.21 |

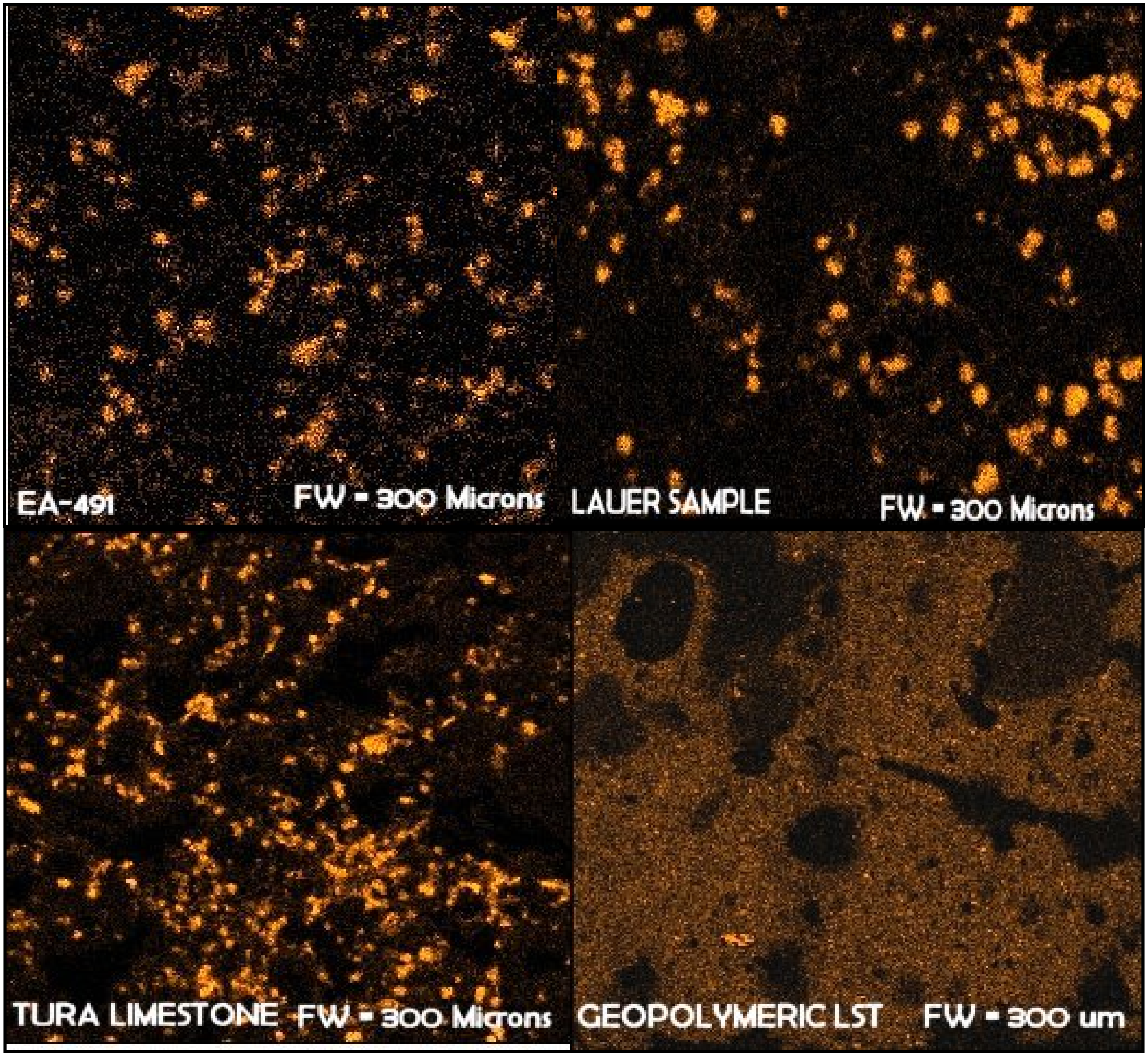
**Figure 15**: Photomicrograph of thin section of the Lauer sample studied by Harrell (Harrell and Penrod 1993), which contained a dark isotropic coating layer (approximately 1 mm in maximum thickness) on top of limestone, which is followed by a light brown contaminated zone in the limestone, and then the uncontaminated interior. Inset EDS analyses of the coating and the interior limestone show the calcium phosphate composition of coating (consistent with Davidovits' XRD results) and the absence of a phosphate-phase in the interior limestone. Despite the absence of this "coating", Figures 12 through 14 in this present study clearly detected evidence of phosphorus invasion in limestone presumably from this coating, extension of contamination to a distance of approximately 5 mm, and the existence of bulk interior "uncontaminated" limestone devoid of any phosphate phase. The coating layer is described in detail in Harrell and Penrod (1993). Photo courtesy of James A. Harrell.

# TABLE - SEM-EDS X-RAY ELEMENTAL ANALYSES OF SILICA-RICH MICROCONSTITUENTS IN THE CASING STONES OF THE GREAT PYRAMID OF KHUFU & THE LIMESTONE FROM TURA

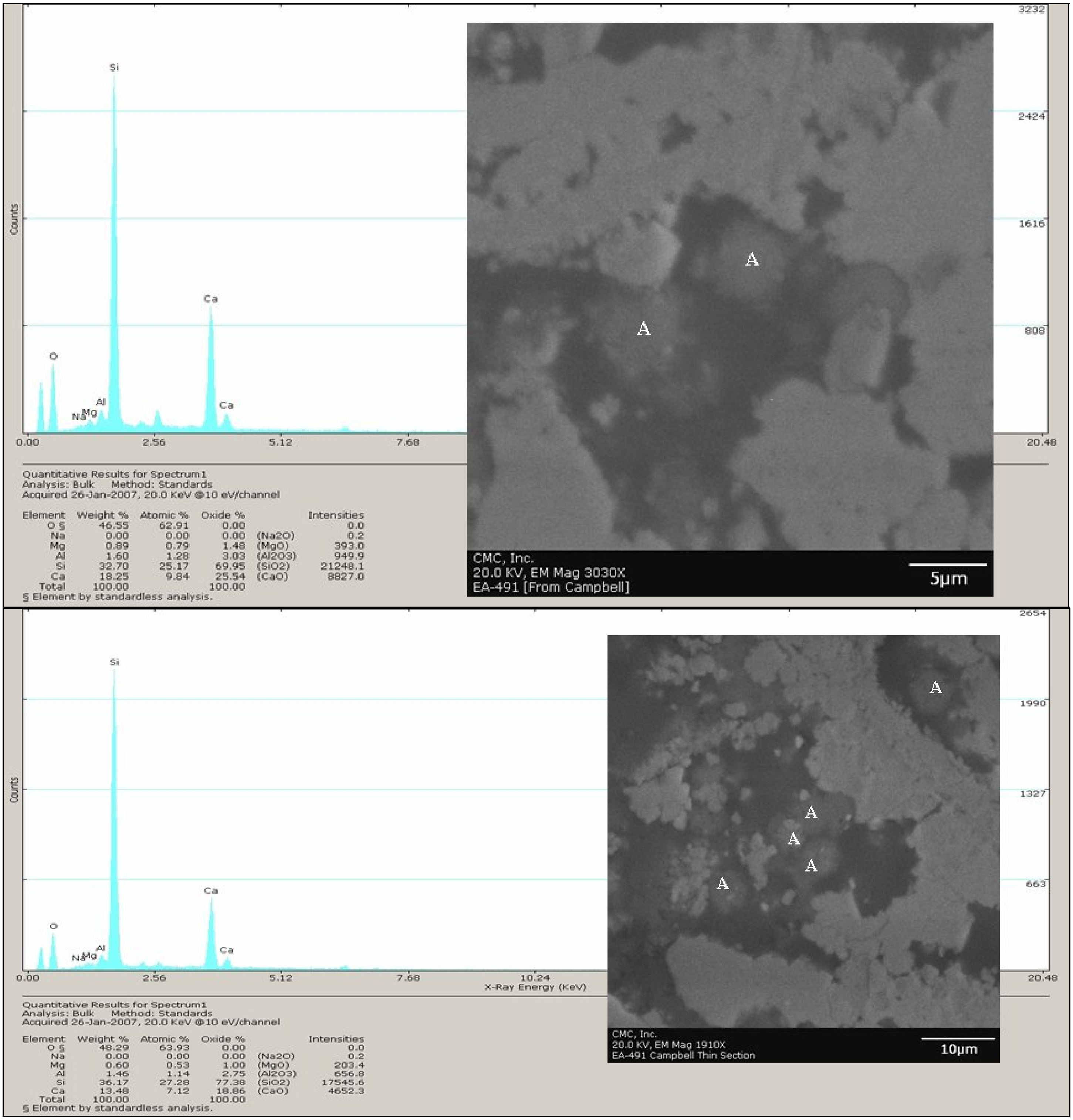


| | SiO2 | CaO | Al2O3 | MgO | Na2O | Comments |
|---|---|---|---|---|---|---|
| **Lauer** | 68.28 | 20.64 | 1.95 | 8.24 | 0.90 | Ca-Mg-Al impurities in Si-Rich Phase |
| | 55.62 | 26.61 | 1.68 | 15.18 | 0.91 | Ca-Mg-Al impurities in Si-Rich Phase |
| | 80.55 | 13.12 | 1.60 | 4.12 | 0.60 | Ca-Mg-Al impurities in Si-Rich Phase |
| | 82.51 | 9.11 | 2.71 | 5.66 | 0.00 | Ca-Mg-Al impurities in Si-Rich Phase |
| | 83.07 | 7.02 | 4.36 | 5.55 | 0.00 | Ca-Mg-Al impurities in Si-Rich Phase |
| **EA-491** | 69.95 | 25.54 | 3.03 | 1.48 | 0.00 | Ca-Al-Mg impurities in Si-Rich Phase |
| | 83.01 | 14.26 | 2.32 | 0.41 | 0.00 | Ca-Al-Mg impurities in Si-Rich Phase |
| | 85.27 | 9.35 | 4.10 | 1.28 | 0.00 | Ca-Al-Mg impurities in Si-Rich Phase |
| | 77.38 | 18.86 | 2.75 | 1.00 | 0.00 | Ca-Al-Mg impurities in Si-Rich Phase |
| **Tura Lst (Bulk)** | 85.45 | 8.11 | 1.81 | 0.97 | 3.66 | Na-Montmorillonite Clay in XRD |
| | 73.52 | 17.80 | 2.67 | 1.27 | 4.74 | Na-Montmorillonite Clay in XRD |
| | 70.92 | 24.08 | 3.22 | 1.77 | 0.00 | Ca-Al-Mg impurities in Si-Rich Phase |
| | | | | | | |
| **Tura Lst (Insoluble Residue)** | 88.63 | 0.00 | 9.87 | 1.50 | 0.00 | Al-impurities in Si-Rich Phase |
| | 89.30 | 0.26 | 8.82 | 1.62 | 0.00 | Al-impurities in Si-Rich Phase |
| | 92.67 | 0.00 | 6.30 | 1.03 | 0.00 | Al-impurities in Si-Rich Phase |
| | 99.17 | 0.00 | 0.82 | 0.00 | 0.00 | Quartz |
| | 95.11 | 0.00 | 4.89 | 0.00 | 0.00 | Al-impurities in Si-Rich Phase |
| | 88.37 | 0.00 | 10.02 | 1.61 | 0.00 | Al-impurities in Si-Rich Phase |
| | 95.15 | 0.00 | 4.84 | 0.00 | 0.00 | Al-impurities in Si-Rich Phase |
| | 98.71 | 0.00 | 1.29 | 0.00 | 0.00 | Al-impurities in Si-Rich Phase |
| | 96.57 | 0.00 | 3.42 | 0.00 | 0.00 | Al-impurities in Si-Rich Phase |

NOTE: X-ray elemental spectra of many of these compositions are shown in Figures 17 through 23. All silica-rich near-spherical and spherical microconstituents (less than 10μm in size) contain Ca, Mg, Al, and trace amounts of Na as impurities. Unlike Barsoum et al. (2006) proposition, their presence in both casing stone and natural limestone do not indicate a synthetic or geopolymeric origin of these constituents. Quartz grains in the acid-insoluble residue of Tura limestone are angular and less than 1 mm in size. The high sodium content in some spherical silica-microconstituents in Tura limestone may contain traces of sodium montmorillonite clay on their surfaces, which was detected in the XRD analysis.



<u>Figure 16</u>: **X-ray elemental maps of silicon (Si-Kα)** in EA-491, Lauer sample, Tura limestone, and geopolymeric limestone. Contrary to the geopolymeric limestone chemistry, where silica occurs uniformly over the entire alkali-aluminosilicate based geopolymeric binder (the bottom-right image), in casing stone and Tura limestone samples, silica occurs as isolated, small (less than 10μm in diameter), spherical, near-spherical, or irregularly shaped, interstitial areas in between the calcite grains that are distinctly highlighted by the Si "spots" in these elemental maps. Notice the near-spherical shapes of these Si-spots in casing stone samples and in many areas in the Tura limestone, which correlate well with spherical silica-rich phases that are detected in SE-BSE images of these samples (see Figures 17-23). An image analysis of these "dot maps" by Image Pro Plus software (www.mediacybernatics.com) detected approximately 10 to 15 volumetric percentages of silica rich areas in these samples (taken from 10 to 15 different area scans like these in each sample). Occurrences of these silica-rich phases do not indicate a "man-made" origin of limestone. They are common constituents in many natural limestones, including the ones at Giza and have been described by many as "lepispheres" of opal-CT mineralogy (Bradley and Middleton 1988; Campbell and Folk 1991).



Quantitative Results for Spectrum1
Analysis: Bulk Method: Standards
Acquired 26-Jan-2007, 20.0 KeV @10 eV/channel

| Element | Weight % | Atomic % | Oxide % | | Intensities |
|---|---|---|---|---|---|
| O § | 46.55 | 62.91 | 0.00 | | 0.0 |
| Na | 0.00 | 0.00 | 0.00 | (Na2O) | 0.2 |
| Mg | 0.89 | 0.79 | 1.48 | (MgO) | 393.0 |
| Al | 1.60 | 1.28 | 3.03 | (Al2O3) | 949.9 |
| Si | 32.70 | 25.17 | 69.95 | (SiO2) | 21248.1 |
| Ca | 18.25 | 9.84 | 25.54 | (CaO) | 8827.0 |
| Total | 100.00 | | 100.00 | | |

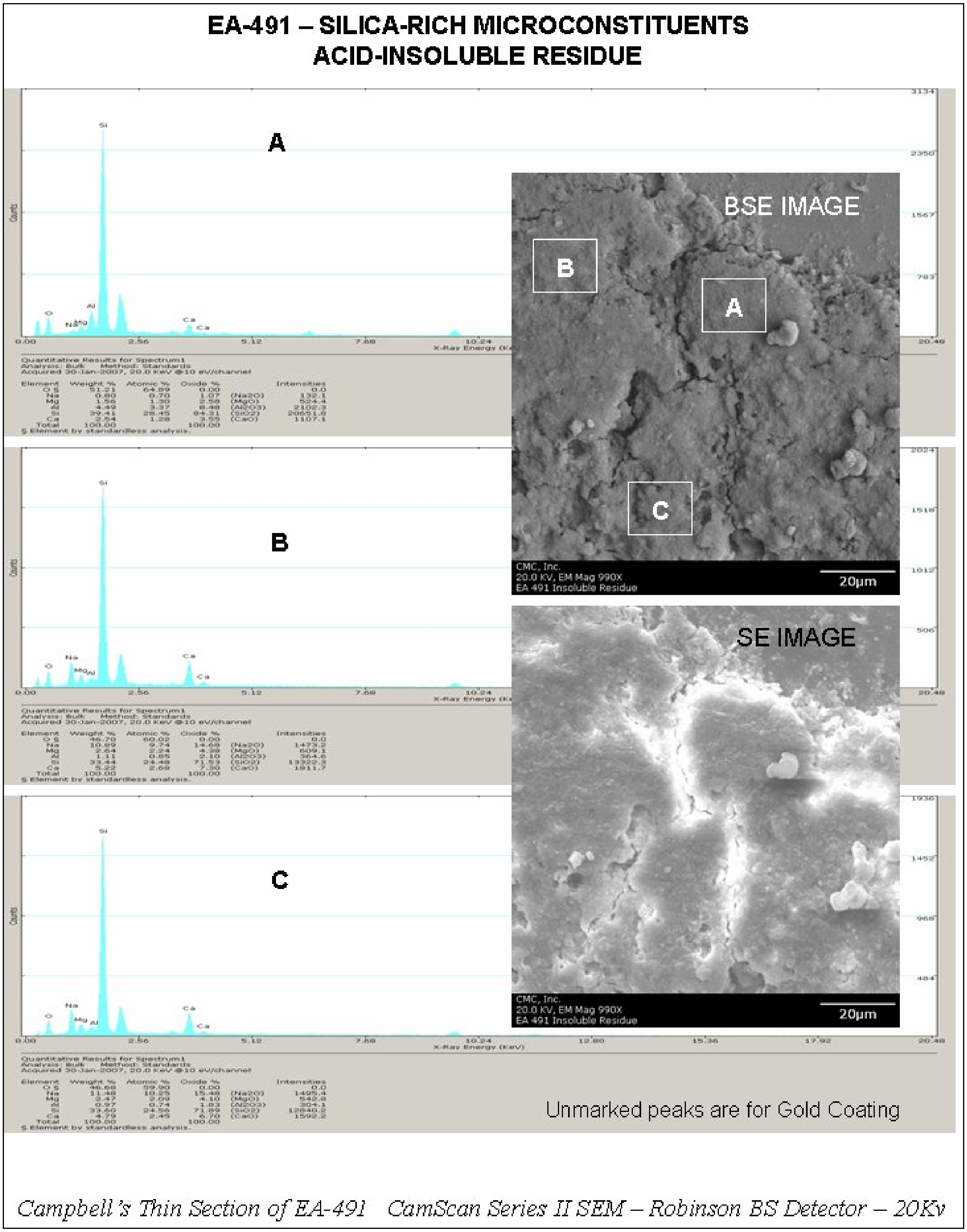
§ Element by standardless analysis.

Quantitative Results for Spectrum1
Analysis: Bulk Method: Standards
Acquired 26-Jan-2007, 20.0 KeV @10 eV/channel

| Element | Weight % | Atomic % | Oxide % | | Intensities |
|---|---|---|---|---|---|
| O § | 48.29 | 63.93 | 0.00 | | 0.0 |
| Na | 0.00 | 0.00 | 0.00 | (Na2O) | 0.2 |
| Mg | 0.60 | 0.53 | 1.00 | (MgO) | 203.4 |
| Al | 1.46 | 1.14 | 2.75 | (Al2O3) | 656.8 |
| Si | 36.17 | 27.28 | 77.38 | (SiO2) | 17545.6 |
| Ca | 13.48 | 7.12 | 18.86 | (CaO) | 4652.3 |
| Total | 100.00 | | 100.00 | | |

§ Element by standardless analysis.

**Figure 17**: Backscatter electron images and x-ray elemental analyses of near-spherical silica-rich microconstituents (areas marked as “A”) in EA-491 that are described as “lepispheres” in Campbell and Folk (1991) and Bradley and Middleton (1988). All silica-rich areas have more or less similar compositions (Si>>Ca>Mg>Al); two representative ones are shown here. Lepispheres are dark gray spheres in these BSE images located in the interstitial spaces, in between the relatively brighter calcite grains.



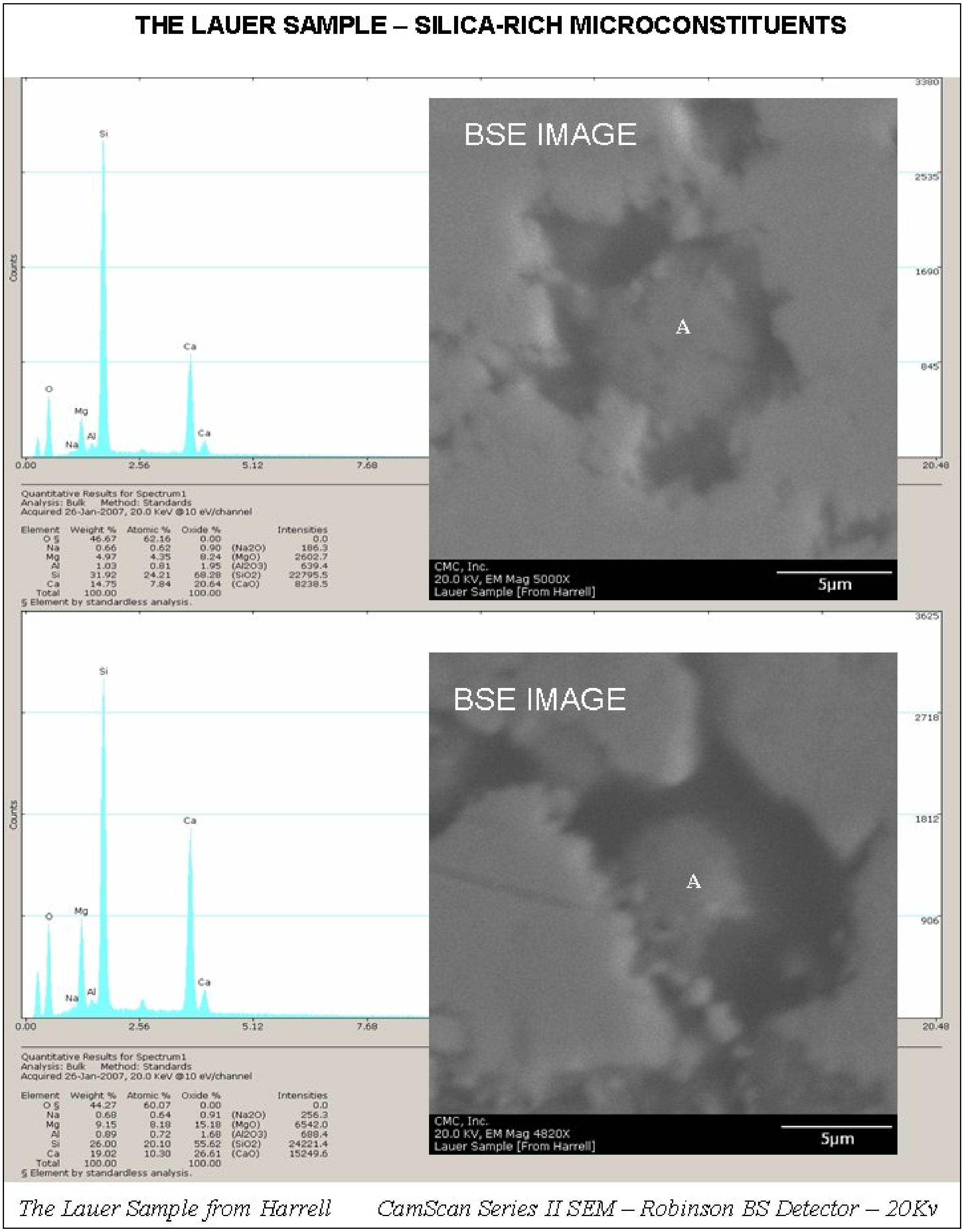
```
Quantitative Results for Spectrum1
Analysis: Bulk    Method: Standards
Acquired 30-Jan-2007, 20.0 KeV @10 eV/channel

Element   Weight %   Atomic %   Oxide %            Intensities
    O §      51.21      64.89      0.00                    0.0
     Na       0.80       0.70      1.07  (Na2O)          132.1
     Mg       1.56       1.30      2.58  (MgO)           524.4
     Al       4.49       3.37      8.48  (Al2O3)        2102.3
     Si      39.41      28.45     84.31  (SiO2)        20651.8
     Ca       2.54       1.28      3.55  (CaO)          1107.1
  Total     100.00               100.00
§ Element by standardless analysis.
```

```
Quantitative Results for Spectrum1
Analysis: Bulk    Method: Standards
Acquired 30-Jan-2007, 20.0 KeV @10 eV/channel

Element   Weight %   Atomic %   Oxide %            Intensities
    O §      46.70      60.02      0.00                    0.0
     Na      10.89       9.74     14.68  (Na2O)         1473.2
     Mg       2.64       2.24      4.38  (MgO)           609.1
     Al       1.11       0.85      2.10  (Al2O3)         364.6
     Si      33.44      24.48     71.53  (SiO2)        13322.3
     Ca       5.22       2.68      7.30  (CaO)          1811.7
  Total     100.00               100.00
§ Element by standardless analysis.
```

```
Quantitative Results for Spectrum1
Analysis: Bulk    Method: Standards
Acquired 30-Jan-2007, 20.0 KeV @10 eV/channel

Element   Weight %   Atomic %   Oxide %            Intensities
    O §      46.68      59.90      0.00                    0.0
     Na      11.48      10.25     15.48  (Na2O)         1495.4
     Mg       2.47       2.09      4.10  (MgO)           542.8
     Al       0.97       0.74      1.83  (Al2O3)         304.1
     Si      33.60      24.56     71.89  (SiO2)        12840.2
     Ca       4.79       2.45      6.70  (CaO)          1592.2
  Total     100.00               100.00
§ Element by standardless analysis.
```

*Campbell's Thin Section of EA-491   CamScan Series II SEM – Robinson BS Detector – 20Kv*

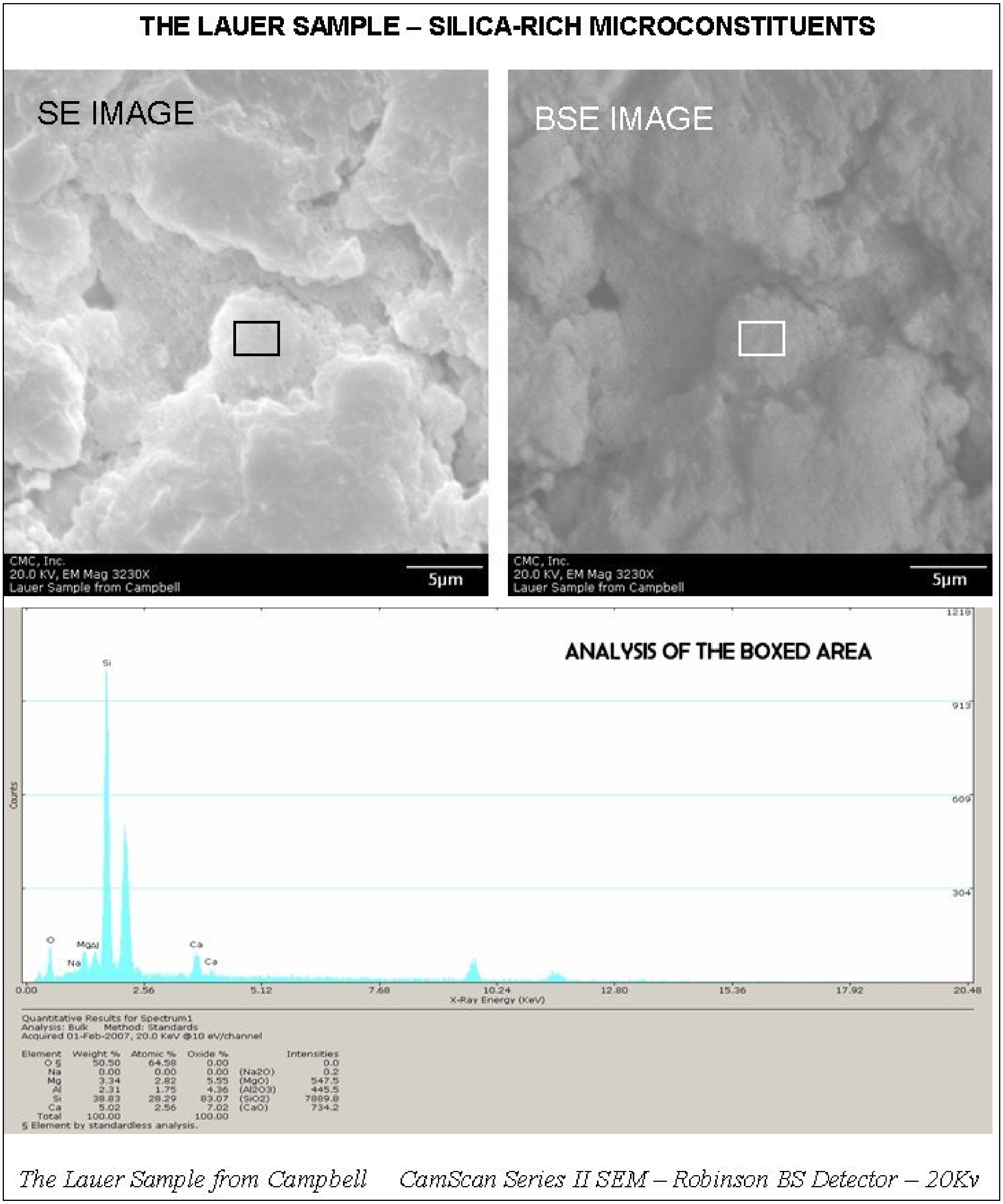
**Figure 18**: Backscatter electron image (inset top right), secondary electron image (inset bottom right) and x-ray elemental analyses (left photos) of hydrochloric acid-insoluble residue in EA-491. The residue is silica-rich with minor amounts of Ca, Na, Mg, and Al. Analyses of the boxed areas marked as A, B, and C in the BSE image are given in the left. Optical microscopy determined the presence of quartz, opal-CT, clay, and iron oxide in the residue (this study, Campbell and Folk 1991, Freestone et al. 1984).



```
Quantitative Results for Spectrum1
Analysis: Bulk    Method: Standards
Acquired 26-Jan-2007, 20.0 KeV @10 eV/channel

Element  Weight %  Atomic %  Oxide %            Intensities
    O §     46.67     62.16     0.00                    0.0
     Na      0.66      0.62     0.90  (Na2O)          186.3
     Mg      4.97      4.35     8.24  (MgO)          2602.7
     Al      1.03      0.81     1.95  (Al2O3)         639.4
     Si     31.92     24.21    68.28  (SiO2)        22795.5
     Ca     14.75      7.84    20.64  (CaO)          8238.5
  Total    100.00             100.00
§ Element by standardless analysis.
```

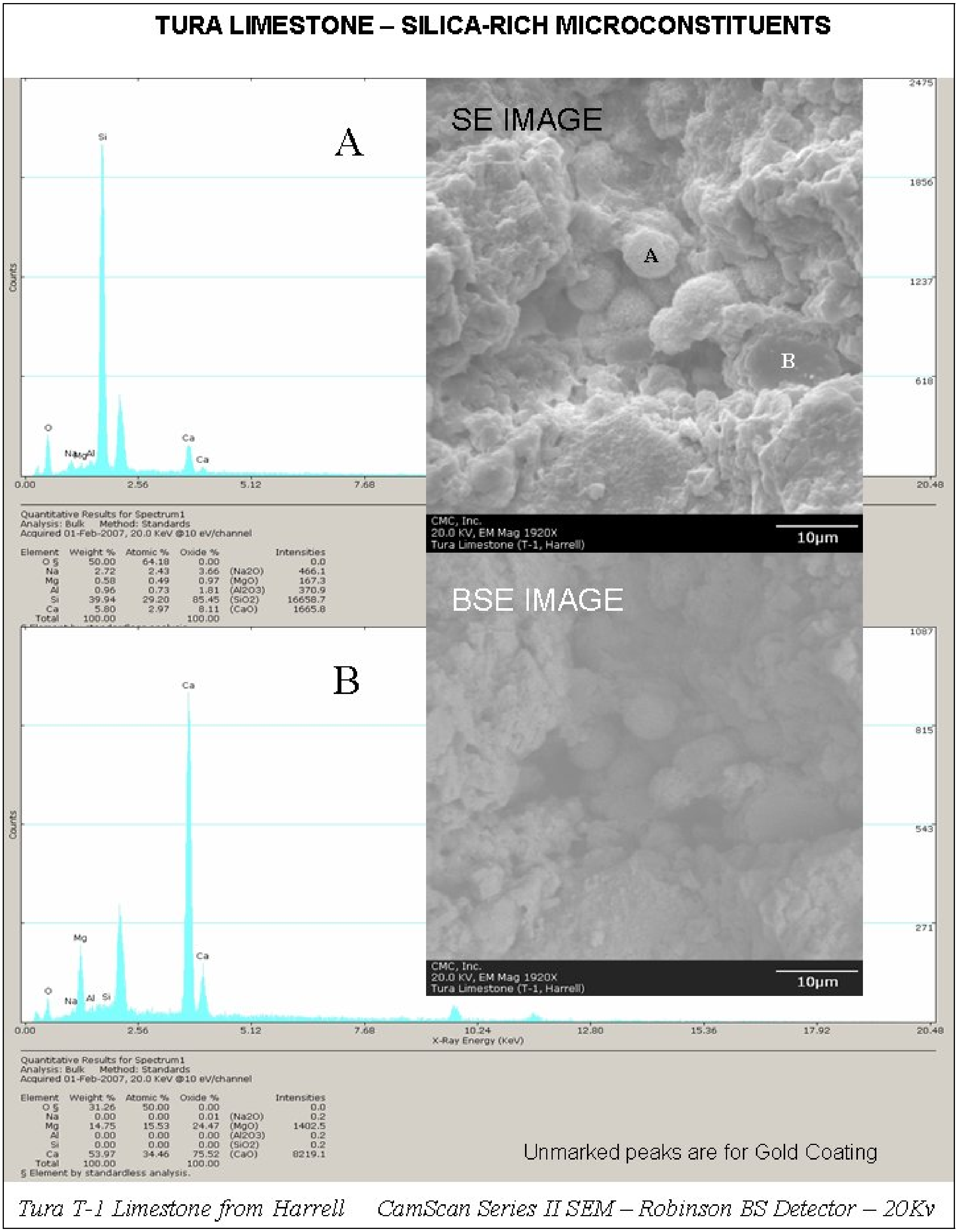
```
Quantitative Results for Spectrum1
Analysis: Bulk    Method: Standards
Acquired 26-Jan-2007, 20.0 KeV @10 eV/channel

Element  Weight %  Atomic %  Oxide %            Intensities
    O §     44.27     60.07     0.00                    0.0
     Na      0.68      0.64     0.91  (Na2O)          256.3
     Mg      9.15      8.18    15.18  (MgO)          6542.0
     Al      0.89      0.72     1.68  (Al2O3)         688.4
     Si     26.00     20.10    55.62  (SiO2)        24221.4
     Ca     19.02     10.30    26.61  (CaO)         15249.6
  Total    100.00             100.00
§ Element by standardless analysis.
```

**Figure 19**: Backscatter electron images (inset top and bottom right) and x-ray elemental analyses (left photos) of spherical silica-rich microconstituents in the Lauer sample. The silica-rich spherical phases, presumably described as lepispheres or opal-CT also contain subordinate amounts of Ca and Mg and minor amounts of Al, and Na. Two different areas are analyzed. The sample contains many such areas with similar compositions. These silica-rich spheres correspond to Si-rich spots on dot maps shown in Figure 16.



```
Quantitative Results for Spectrum1
Analysis: Bulk     Method: Standards
Acquired 01-Feb-2007, 20.0 KeV @10 eV/channel

Element  Weight %  Atomic %  Oxide %            Intensities
    O §     50.50     64.58     0.00                    0.0
     Na      0.00      0.00     0.00  (Na2O)            0.2
     Mg      3.34      2.82     5.55  (MgO)           547.5
     Al      2.31      1.75     4.36  (Al2O3)         445.5
     Si     38.83     28.29    83.07  (SiO2)         7889.8
     Ca      5.02      2.56     7.02  (CaO)           734.2
  Total    100.00             100.00
§ Element by standardless analysis.
```

**Figure 20**: A silica-rich microsphere in the Lauer sample with greater than 80 percent $SiO_2$ and 4 to 7 percent CaO, $Al_2O_3$, and MgO - a typical example of “impure” lepispheres, a common microconstituent in these limestones. The sphere in this example is approximately 5µm in diameter (lepispheres are 5 to 10µm in size, some are finer than 5µm).



Quantitative Results for Spectrum1
Analysis: Bulk Method: Standards
Acquired 01-Feb-2007, 20.0 KeV @10 eV/channel

| Element | Weight % | Atomic % | Oxide % | | Intensities |
|---|---|---|---|---|---|
| O § | 50.00 | 64.18 | 0.00 | | 0.0 |
| Na | 2.72 | 2.43 | 3.66 | (Na2O) | 466.1 |
| Mg | 0.58 | 0.49 | 0.97 | (MgO) | 167.3 |
| Al | 0.96 | 0.73 | 1.81 | (Al2O3) | 370.9 |
| Si | 39.94 | 29.20 | 85.45 | (SiO2) | 16658.7 |
| Ca | 5.80 | 2.97 | 8.11 | (CaO) | 1665.8 |
| Total | 100.00 | | 100.00 | | |

Quantitative Results for Spectrum1
Analysis: Bulk Method: Standards
Acquired 01-Feb-2007, 20.0 KeV @10 eV/channel

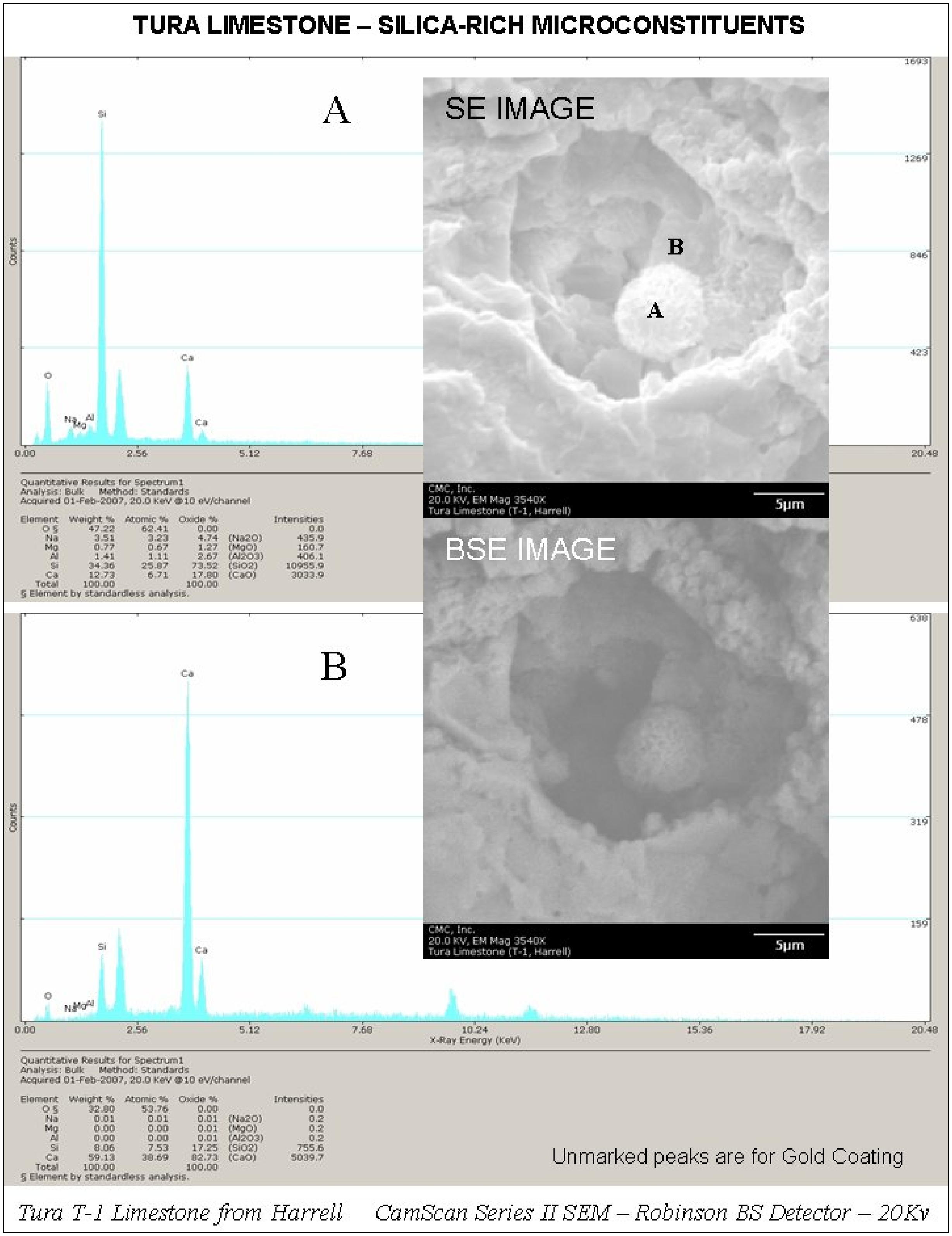
| Element | Weight % | Atomic % | Oxide % | | Intensities |
|---|---|---|---|---|---|
| O § | 31.26 | 50.00 | 0.00 | | 0.0 |
| Na | 0.00 | 0.00 | 0.01 | (Na2O) | 0.2 |
| Mg | 14.75 | 15.53 | 24.47 | (MgO) | 1402.5 |
| Al | 0.00 | 0.00 | 0.00 | (Al2O3) | 0.2 |
| Si | 0.00 | 0.00 | 0.00 | (SiO2) | 0.2 |
| Ca | 53.97 | 34.46 | 75.52 | (CaO) | 8219.1 |
| Total | 100.00 | | 100.00 | | |

§ Element by standardless analysis.

Unmarked peaks are for Gold Coating

*Tura T-1 Limestone from Harrell CamScan Series II SEM – Robinson BS Detector – 20Kv*

**Figure 21**: SE and BSE images of Tura limestone showing a bunch of silica-rich lepispheres with an analysis of one such sphere marked as “A”. All spheres are similar in compositions, with Si>>>Ca>Na>Al>Mg, identical to those detected in the Lauer sample and EA-491, and represent impure lepispheres. Area “B” is probably a dolomite phase (also detected in XRD study).



**TURA LIMESTONE – SILICA-RICH MICROCONSTITUENTS**

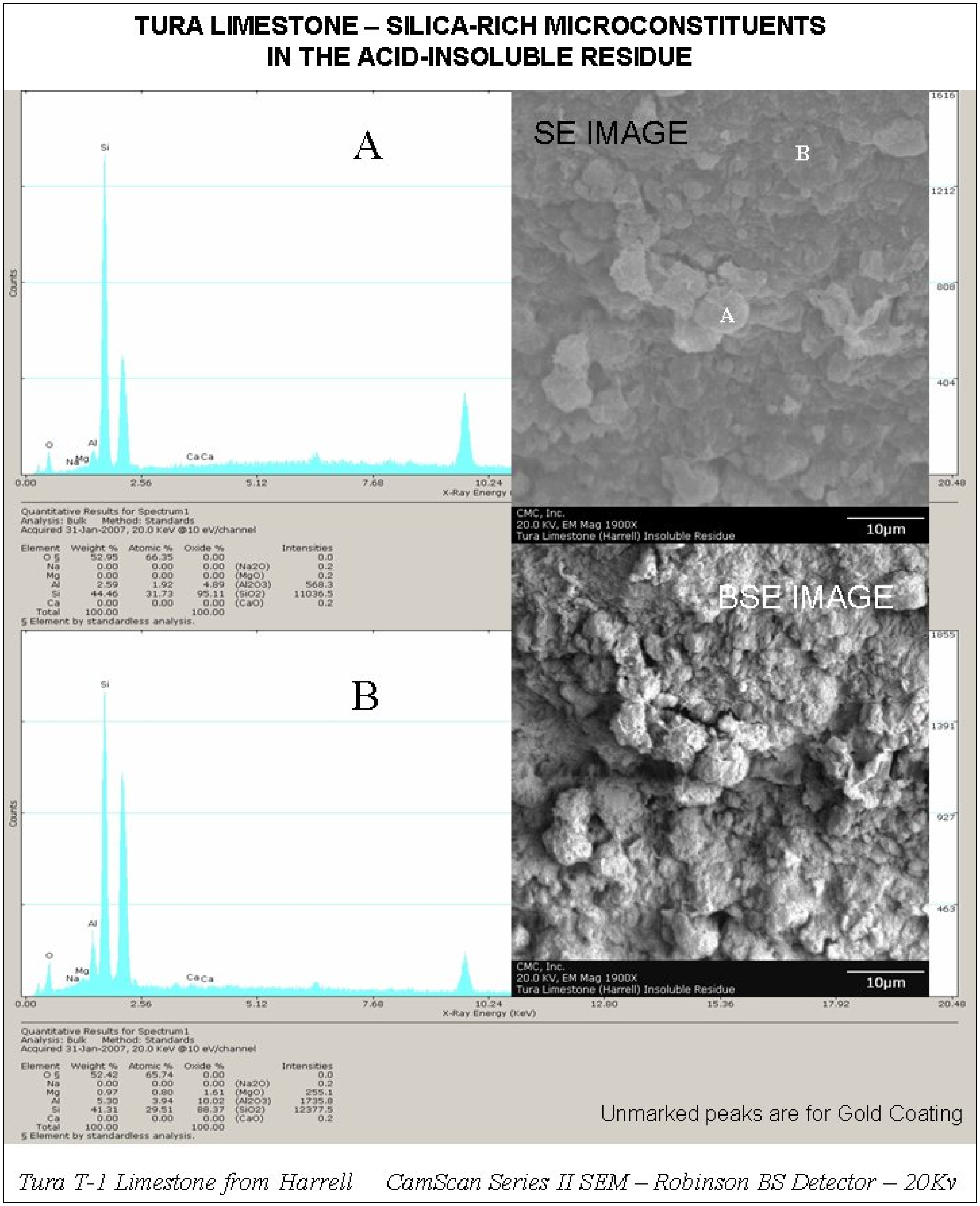
```
Quantitative Results for Spectrum1
Analysis: Bulk     Method: Standards
Acquired 01-Feb-2007, 20.0 KeV @10 eV/channel

Element  Weight %  Atomic %  Oxide %            Intensities
   O §      47.22     62.41     0.00                    0.0
   Na        3.51      3.23     4.74  (Na2O)          435.9
   Mg        0.77      0.67     1.27  (MgO)           160.7
   Al        1.41      1.11     2.67  (Al2O3)         406.1
   Si       34.36     25.87    73.52  (SiO2)        10955.9
   Ca       12.73      6.71    17.80  (CaO)          3033.9
 Total     100.00             100.00
§ Element by standardless analysis.
```

```
Quantitative Results for Spectrum1
Analysis: Bulk     Method: Standards
Acquired 01-Feb-2007, 20.0 KeV @10 eV/channel

Element  Weight %  Atomic %  Oxide %            Intensities
   O §      32.80     53.76     0.00                    0.0
   Na        0.01      0.01     0.01  (Na2O)            0.2
   Mg        0.00      0.00     0.01  (MgO)             0.2
   Al        0.00      0.00     0.01  (Al2O3)           0.2
   Si        8.06      7.53    17.25  (SiO2)          755.6
   Ca       59.13     38.69    82.73  (CaO)          5039.7
 Total     100.00             100.00
§ Element by standardless analysis.
```

Unmarked peaks are for Gold Coating

*Tura T-1 Limestone from Harrell*   *CamScan Series II SEM – Robinson BS Detector – 20Kv*

**Figure 22**: Another excellent example of a silica-rich microsphere in Tura limestone (marked as “A”) having significant amount of $SiO_2$, followed by $CaO>>Na_2O>Al_2O_3>MgO$. All these lepispheres in Figures 21 and 22 are silica-rich, detected in the casing stone samples as well as in natural limestone, and contain variable amounts of Ca, Mg, Al, and Na as impurities.



TURA LIMESTONE – SILICA-RICH MICROCONSTITUENTS IN THE ACID-INSOLUBLE RESIDUE

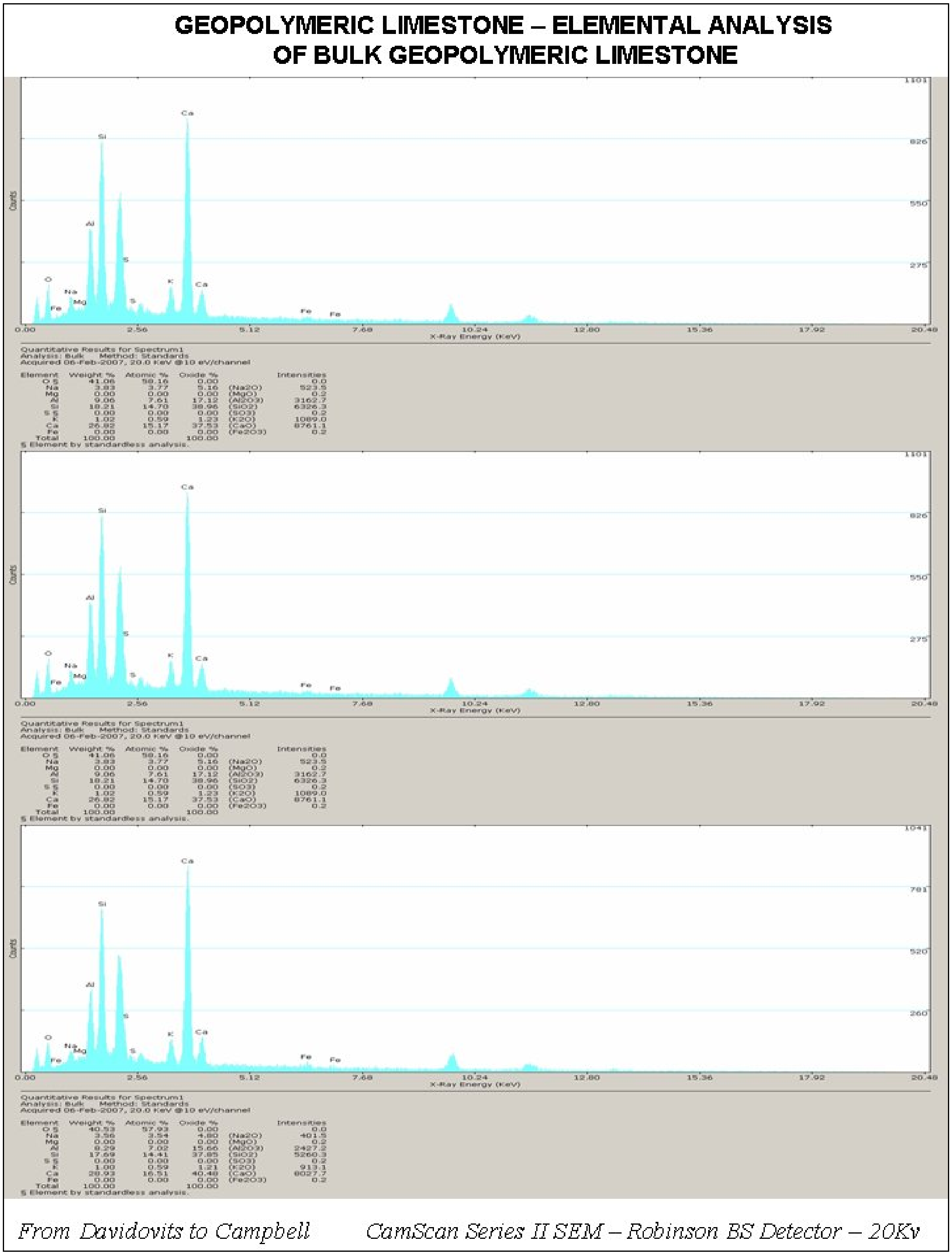
```
Quantitative Results for Spectrum1
Analysis: Bulk     Method: Standards
Acquired 31-Jan-2007, 20.0 KeV @10 eV/channel

Element  Weight %  Atomic %  Oxide %             Intensities
    O §     52.95     66.35     0.00                     0.0
     Na      0.00      0.00     0.00  (Na2O)             0.2
     Mg      0.00      0.00     0.00  (MgO)              0.2
     Al      2.59      1.92     4.89  (Al2O3)          568.3
     Si     44.46     31.73    95.11  (SiO2)         11036.5
     Ca      0.00      0.00     0.00  (CaO)              0.2
  Total    100.00            100.00
§ Element by standardless analysis.
```

```
Quantitative Results for Spectrum1
Analysis: Bulk     Method: Standards
Acquired 31-Jan-2007, 20.0 KeV @10 eV/channel

Element  Weight %  Atomic %  Oxide %             Intensities
    O §     52.42     65.74     0.00                     0.0
     Na      0.00      0.00     0.00  (Na2O)             0.2
     Mg      0.97      0.80     1.61  (MgO)            255.1
     Al      5.30      3.94    10.02  (Al2O3)         1735.8
     Si     41.31     29.51    88.37  (SiO2)         12377.5
     Ca      0.00      0.00     0.00  (CaO)              0.2
  Total    100.00            100.00
§ Element by standardless analysis.
```

Unmarked peaks are for Gold Coating

*Tura T-1 Limestone from Harrell     CamScan Series II SEM – Robinson BS Detector – 20Kv*

**Figure 23**: Acid-insoluble residue of Tura limestone showing the silica-rich composition and somewhat distorted microspheres with rougher surfaces (probably due to acid etching) than those detected in the previous photos in the bulk sample All these silica-rich microspheres in a natural limestone also contain noticeable amounts of alumina as impurity and certainly do not indicate an aluminosilicate precipitate from a geopolymeric matrix (Davidovits 2005).



GEOPOLYMERIC LIMESTONE – ELEMENTAL ANALYSIS
OF BULK GEOPOLYMERIC LIMESTONE

Quantitative Results for Spectrum1
Analysis: Bulk Method: Standards
Acquired 06-Feb-2007, 20.0 KeV @10 eV/channel

| Element | Weight % | Atomic % | Oxide % | | Intensities |
|---|---|---|---|---|---|
| O § | 41.06 | 58.16 | 0.00 | | 0.0 |
| Na | 3.83 | 3.77 | 5.16 | (Na2O) | 523.5 |
| Mg | 0.00 | 0.00 | 0.00 | (MgO) | 0.2 |
| Al | 9.06 | 7.61 | 17.12 | (Al2O3) | 3162.7 |
| Si | 18.21 | 14.70 | 38.96 | (SiO2) | 6326.3 |
| S § | 0.00 | 0.00 | 0.00 | (SO3) | 0.2 |
| K | 1.02 | 0.59 | 1.23 | (K2O) | 1089.0 |
| Ca | 26.82 | 15.17 | 37.53 | (CaO) | 8761.1 |
| Fe | 0.00 | 0.00 | 0.00 | (Fe2O3) | 0.2 |
| Total | 100.00 | | 100.00 | | |

§ Element by standardless analysis.

Quantitative Results for Spectrum1
Analysis: Bulk Method: Standards
Acquired 06-Feb-2007, 20.0 KeV @10 eV/channel

| Element | Weight % | Atomic % | Oxide % | | Intensities |
|---|---|---|---|---|---|
| O § | 41.06 | 58.16 | 0.00 | | 0.0 |
| Na | 3.83 | 3.77 | 5.16 | (Na2O) | 523.5 |
| Mg | 0.00 | 0.00 | 0.00 | (MgO) | 0.2 |
| Al | 9.06 | 7.61 | 17.12 | (Al2O3) | 3162.7 |
| Si | 18.21 | 14.70 | 38.96 | (SiO2) | 6326.3 |
| S § | 0.00 | 0.00 | 0.00 | (SO3) | 0.2 |
| K | 1.02 | 0.59 | 1.23 | (K2O) | 1089.0 |
| Ca | 26.82 | 15.17 | 37.53 | (CaO) | 8761.1 |
| Fe | 0.00 | 0.00 | 0.00 | (Fe2O3) | 0.2 |
| Total | 100.00 | | 100.00 | | |

§ Element by standardless analysis.

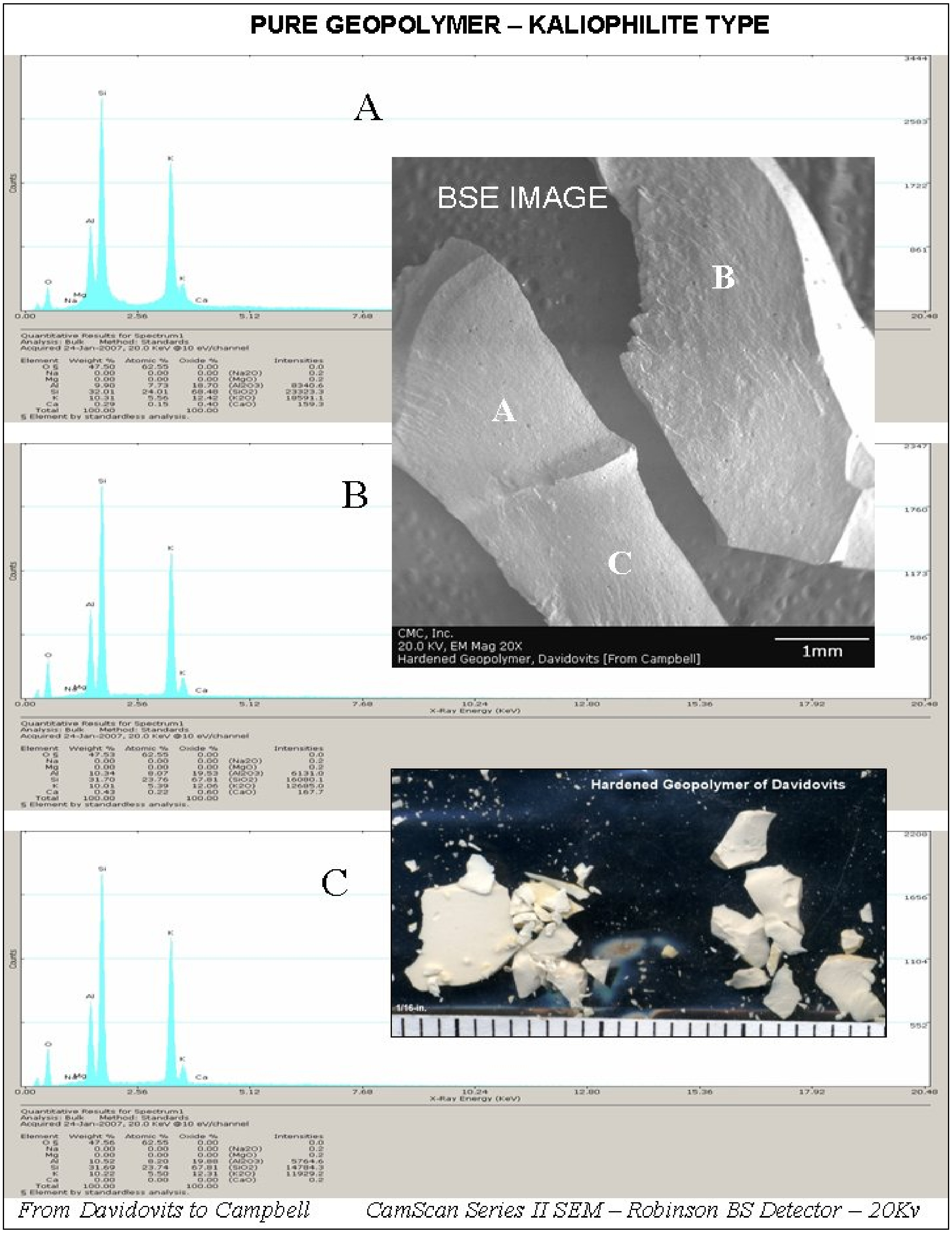
Quantitative Results for Spectrum1
Analysis: Bulk Method: Standards
Acquired 06-Feb-2007, 20.0 KeV @10 eV/channel

| Element | Weight % | Atomic % | Oxide % | | Intensities |
|---|---|---|---|---|---|
| O § | 40.53 | 57.93 | 0.00 | | 0.0 |
| Na | 3.56 | 3.54 | 4.80 | (Na2O) | 401.5 |
| Mg | 0.00 | 0.00 | 0.00 | (MgO) | 0.2 |
| Al | 8.29 | 7.02 | 15.66 | (Al2O3) | 2427.2 |
| Si | 17.69 | 14.41 | 37.85 | (SiO2) | 5260.3 |
| S § | 0.00 | 0.00 | 0.00 | (SO3) | 0.2 |
| K | 1.00 | 0.59 | 1.21 | (K2O) | 913.1 |
| Ca | 28.93 | 16.51 | 40.48 | (CaO) | 8027.7 |
| Fe | 0.00 | 0.00 | 0.00 | (Fe2O3) | 0.2 |
| Total | 100.00 | | 100.00 | | |

§ Element by standardless analysis.

*From Davidovits to Campbell*  *CamScan Series II SEM – Robinson BS Detector – 20Kv*

**Figure 24**: X-ray elemental analysis of different areas of geopolymeric limestone sample of Davidovits showing its distinct characteristic composition of calcium (from limestone) and enriched alkali (Na+K)-aluminosilicate composition, as expected for a geopolymeric binder. Notice the total alkali ($Na_2O$+$K_2O$) and alumina ($Al_2O_3$) content in this limestone is significantly higher than those detected in all silica-rich microconstituents. These results are consistent with uniform enrichment of Si-Na-K-Al found in the elemental maps of this limestone. Neither the casing stone nor the natural limestone showed this characteristic composition.



```
Quantitative Results for Spectrum1
Analysis: Bulk    Method: Standards
Acquired 24-Jan-2007, 20.0 KeV @10 eV/channel

Element  Weight %  Atomic %  Oxide %            Intensities
    O §     47.50     62.55     0.00                    0.0
     Na      0.00      0.00     0.00  (Na2O)            0.2
     Mg      0.00      0.00     0.00  (MgO)             0.2
     Al      9.90      7.73    18.70  (Al2O3)        8340.6
     Si     32.01     24.01    68.48  (SiO2)        23323.3
      K     10.31      5.56    12.42  (K2O)         18591.1
     Ca      0.29      0.15     0.40  (CaO)           159.3
  Total    100.00             100.00
§ Element by standardless analysis.
```

```
Quantitative Results for Spectrum1
Analysis: Bulk    Method: Standards
Acquired 24-Jan-2007, 20.0 KeV @10 eV/channel

Element  Weight %  Atomic %  Oxide %            Intensities
    O §     47.53     62.55     0.00                    0.0
     Na      0.00      0.00     0.00  (Na2O)            0.2
     Mg      0.00      0.00     0.00  (MgO)             0.2
     Al     10.34      8.07    19.53  (Al2O3)        6131.0
     Si     31.70     23.76    67.81  (SiO2)        16080.1
      K     10.01      5.39    12.06  (K2O)         12685.0
     Ca      0.43      0.22     0.60  (CaO)           167.7
  Total    100.00             100.00
§ Element by standardless analysis.
```

```
Quantitative Results for Spectrum1
Analysis: Bulk    Method: Standards
Acquired 24-Jan-2007, 20.0 KeV @10 eV/channel

Element  Weight %  Atomic %  Oxide %            Intensities
    O §     47.56     62.55     0.00                    0.0
     Na      0.00      0.00     0.00  (Na2O)            0.2
     Mg      0.00      0.00     0.00  (MgO)             0.2
     Al     10.52      8.20    19.88  (Al2O3)        5764.6
     Si     31.69     23.74    67.81  (SiO2)        14784.3
      K     10.22      5.50    12.31  (K2O)         11929.2
     Ca      0.00      0.00     0.00  (CaO)             0.2
  Total    100.00             100.00
§ Element by standardless analysis.
```

**Figure 25**: Backscatter electron image (the top right photo), actual fragments as received (the bottom right photo), and x-ray elemental analyses of three areas (marked as A, B, and C) of Davidovits' pure geopolymer sample (Kaliophilite base - type K-PSS) showing its characteristic potassium aluminosilicate composition. A geopolymeric limestone, made using a similar sodium or potassium activated aluminosilicate binder should detect similar composition (i.e., analcime or kaliophilite-type zeolitic composition) in the "binder" phases of limestone, which is well detected in the geopolymeric limestone of this study but not found in any of the casing stone samples. The lime-natron-clay-based recipe in the geopolymer hypothesis of construction of pyramid stones is apparently yet to be detected in a pyramid sample.