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Were the casing stones of Senefru's Bent Pyramid in Dahshour cast or carved? Multinuclear NMR evidence

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ABSTRACT

A comparison was made of the solid-state ^{29}Si, ^{27}Al and ^{43}Ca MAS NMR spectra of the outer casing stone from Snefru's Bent Pyramid in Dahshour, Egypt, with two quarry limestones from the area. The NMR results suggest that the casing stones consist of limestone grains from the Tura quarry, cemented with an amorphous calcium-silicate gel formed by human intervention, by the addition of extra silica, possibly diatomaceous earth, from the Fayium area.

1. Introduction

The methods by which the great Egyptian pyramids were built have long been a matter of interest and speculation. Conventional theories suggest that the constituent limestone blocks were cut from adjacent quarries, accurately dressed and lifted into position. An alternative, but still controversial theory first proposed by Davidovits [1,2], suggested that the blocks were a type of early concrete consisting of disaggregated limestone from the Giza plateau, held together by a sodium or potassium polysilico-oxo-aluminate (geopolymer) binder [1,2] and cast into blocks *in situ*. However, a more recent detailed scanning electron microscope study of pyramid samples of known provenance [3] has demonstrated the ubiquitous occurrence of silicon in conjunction with calcium, rather than with sodium, potassium or aluminium, as postulated by Davidovits.

Although silica occurs in all the limestones from the potential source quarries (in Giza and Tura) for the pyramid stones, the 60–100 nm spherical silica particles occurring in the pyramid stones are not found in the local natural sedimentary limestone [3], only Opal-CT silica being reported in Giza and Tura limestones [4]. This has led to a suggestion that the calcium-silicate binder phase in the pyramid stones was formed by rapid precipitation from an alkaline silica-rich solution possibly resulting from the dissolution of diatomaceous earth from the Fayium region in a lime solution [3]. XRD and our unpublished neutron diffraction results indicate that the crystalline phases in both the casing and natural quarry samples contain about 97–98 wt.% randomly oriented crystalline calcite, with traces of gypsum, $CaSO_4.2H_2O$ and quartz in some cases, but no crystalline calcium silicates (Table 1), suggesting that the most likely binding phase is amorphous Ca-silicate. It has recently been shown that a mixture of lime, diatomaceous earth and water will bind a fine-aggregate limestone by forming amorphous calcium-silicate-hydrate (C-S-H) [5,6].

In this communication we compare the chemical environments of the Si, Ca and Al cations occurring in the pyramid samples, the natural quarry rocks from the vicinity of the pyramids and the possible binder material. Since the Si-containing binder phases are X-ray amorphous, this information can conveniently be obtained by multinuclear solid-state MAS NMR spectroscopy.

2. Materials and methods

The pyramid stone studied here is from the outer casing blocks of Snefru's Bent Pyramid, BP, in Dahshour. For comparison, spectra were acquired from Tura and Khufu (Giza) quarry stones, synthetic calcite, and a calcium-silicate-hydrate (C-S-H) gel synthesised by the method of Chen et al. [7].

The ^{29}Si and ^{27}Al MAS NMR spectra were acquired at a magnetic field of 11.7 T using a Bruker Avance 500 spectrometer and Doty MAS probes spun at about 4 kHz for ^{29}Si and about 12 kHz for ^{27}Al. The ^{29}Si spectra were acquired at 99.926 MHz using a 6 μs (π/10) pulse and a 100 s delay, the spectra referenced to tetramethylsilane (TMS) at 0 ppm. The ^{27}Al

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Table 1
Mineralogical and minor element analyses (at.%) for Bent Pyramid stone and quarry limestones. All analyses except Na are by PIXE, Na values were obtained by PIGE.

Bent Pyramid		Tura quarry	Khufu quarry
Calcite, gypsum (tr)		Calcite, quartz (tr)	Calcite, gypsum (tr), quartz (tr)
Si	2.30%	4.79%	1.44%
Al	0.32%	0.48%	0.50%
Na	0.12%	0.23%	0.09%
K	0.33%	0.26%	0.55%
S	0.48%	0.14%	0.13%
Cl	0.20%	0.25%	0.16%

spectra were acquired at 130.224 MHz using a 1 μs (π/10 pulse for solution) and a 1 s delay, the spectra referenced to $Al(H_2O)_6^{3+}$. The natural-abundance ^{43}Ca MAS NMR spectra were acquired at a magnetic field of 14.1 T using Varian 620 and Bruker II^+ spectrometers operating at 40.388 MHz and a Varian 9.5 mm MAS probe spun at 4 kHz. A single excitation pulse with 3.5–4 μs (π/9 pulse for solution) and a delay of 0.5–5 s was used for the Ca spectroscopy. In some cases, RAPT signal enhancement pulses were implemented prior the excitation pulse and the spectra were referenced to a 1.0 mol L^{-1} $CaCl_2$ solution as 0 ppm [8]. Up to 80,000–250,000 scans were accumulated for each spectrum.

Global elemental analysis for Si, Al and K was carried out on the BP and two quarry samples by Particle-Induced X-ray Emission (PIXE), and for Na by proton-induced gamma-ray emission (PIGE) using a 2.5 MeV proton beam. The results are listed in Table 1.

3. Results and discussion

XRD and neutron diffraction show that the present samples consist principally of calcite, but with Si in greater than trace amounts (Table 1). Microanalysis of the casing stone [3] shows that locally high concentrations of Si occur in conjunction with Ca (typically ~11.2 at.% Si, 6.6 at.% Ca), suggesting the presence of amorphous Ca silicates undetectable by XRD. The elevated level of sulfur in the BP sample is presumably from gypsum, consistent with the microstructural analysis [3].

Fig. 1 shows the BP casing stone ^{29}Si MAS NMR spectrum, together with limestones from the Tura and Khufu quarries. The BP spectrum (Fig. 1A) contains two major resonances, that at −111 ppm arising from silica; this occurs in the same position as that of diatomaceous earth (Fig. 1D), a suggested source of silica for the ancient Egyptians [3]. The second major ^{29}Si NMR feature in the BP outer casing sample occurs at −94 ppm; this and a shoulder at about −84 ppm is in the region of Ca–O–Si resonances, for example, as in wollastonite, $CaSiO_3$ [9], although crystalline calcium silicates are not detected by XRD. Both major ^{29}Si resonances appearing in the BP sample also occur in the spectrum of the Tura limestone quarry (Fig. 1B). However, the silica resonance at −111 ppm is absent from the Khufu quarry limestone spectrum (Fig. 1C), providing clear evidence that this material could not by itself have been the source of the BP casing stone.

A visual comparison of the relative intensities of the major ^{29}Si resonances of the Tura (Fig. 1B) and BP limestones (Fig 1A) shows the silica resonance in the latter is dominant, suggesting that if the Tura quarry provided the source material, additional silica would still have been required.

Of considerable interest is the shoulder at about −84 ppm in the BP sample (Fig. 1A). This is a characteristic resonance in the spectrum of C-S-H gel, and corresponds to the mid-chain Q^2 units [10], but importantly, is *not* present in the Tura limestone. However, the −84 ppm peak does not in itself unambiguously prove the presence of C-S-H gel, since the corresponding Q^1 end-chain C-S-H resonance at about −79 ppm is absent from this spectrum. Since these blocks have been aging under desert conditions for ~4500 y, the Q^1 end-fraction may have become negligible, but at present there is no explanation for this discrepancy.

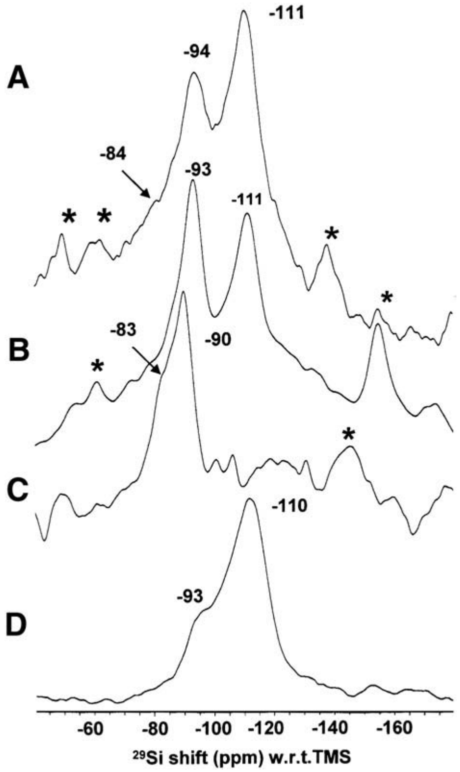

Fig. 1. 11.7 T ^{29}Si MAS NMR spectra of A. Bent pyramid casing stone, B. Tura quarry limestone, C. Khufu quarry limestone and D. Diatomaceous earth. * indicates spinning sidebands.

The ^{27}Al MAS NMR spectra of diatomaceous earth, the BP and quarry samples are shown in Fig. 2. The BP spectrum (Fig. 2A), like the

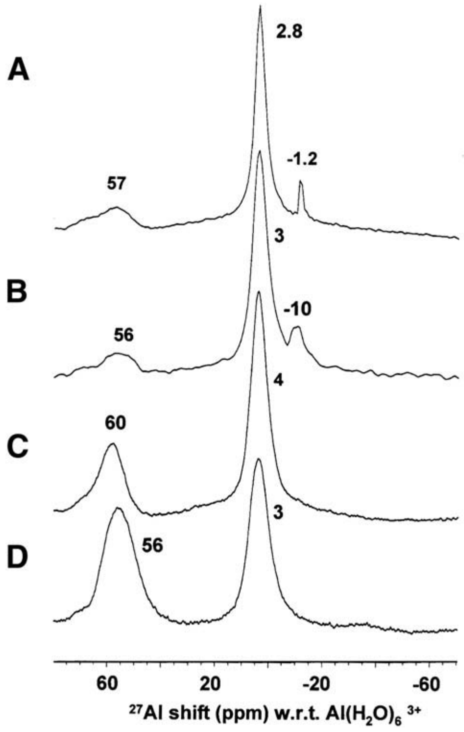

Fig. 2. 11.7 T ^{27} Al MAS NMR spectra of A. Bent pyramid casing stone, B. Tura quarry limestone, C. Khufu quarry limestone and D. diatomaceous earth.

Tura limestone spectrum (Fig. 2B), shows two sharp features, at 3 and −11.8 ppm, corresponding to AlO_6 octahedra and a small, broad resonance at about 56 ppm arising from tetrahedral AlO_4 [9,11]. The Khufu limestone (Fig. 2C), only exhibits one broad AlO_6 resonance at 3 ppm and a more intense AlO_4 peak than the BP stone, confirming Tura as the source of the limestone for the BP casing. The ^{27}Al spectrum of diatomaceous earth (Fig. 2D) contains both octahedral and tetrahedral Al, probably arising from a smectite clay impurity in the Fayium diatomite deposit [12]. The Tura and BP samples thus contain less clay than the other two samples.

The ^{43}Ca MAS NMR spectra of the pyramid and quarry samples (Fig. 3) contain a single resonance at 22 ppm, in the position of the major constituent, calcite (Fig. 3E). The BP casing and quarry stone spectra also show signs of poorly-resolved quadrupolar lineshapes [9,13], with estimated nuclear quadrupolar coupling constants (C_q) of 1.4–1.5 MHz, similar to the value of 1.4 MHz of pure calcite [14]. The center of gravity position of these calcite resonances is similar to the single, much broader resonance of the C-S-H gel (Fig. 3D) [15]. The BP spectrum is therefore consistent with that of calcite, with a possible slight broadening due to a small amount of C-S-H gel binder. The presence in the BP stone of a smaller range of Ca environments than in fresh C-S-H gel may again reflect the much longer period over which the pyramid samples have been aging.

4. Conclusions

Complementary multinuclear (^{29}Si, ^{27}Al, ^{43}Ca) NMR spectra suggest that the BP casing stone was formed from Tura, rather than Khufu limestone from Giza. Furthermore, the differing ratio of the ^{29}Si resonances in the BP and Tura limestones suggests that a silica source such as Fayium diatomaceous earth was probably added to the latter. In view of the fineness and uniformity of the calcite grains [3] the builders may have transported finely weathered limestone from Tura on the East side of the Nile to the West side to make their synthetic blocks.

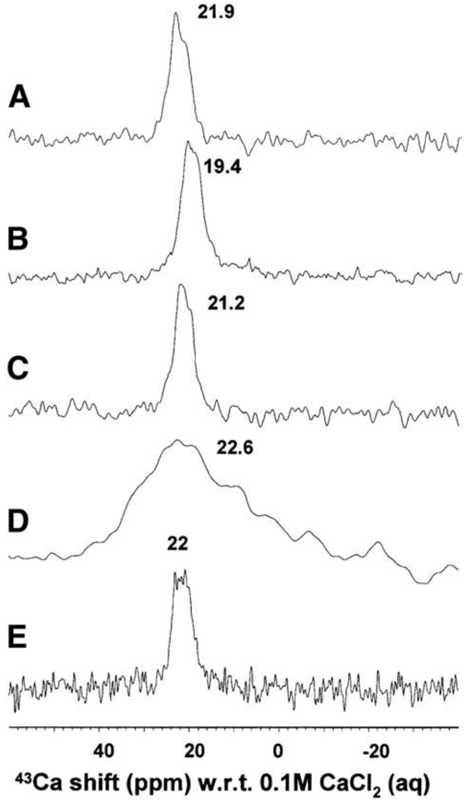

Fig. 3. 14.1 T natural-abundance ^{43}Ca MAS NMR spectra of A. Bent pyramid casing stone, B. Tura quarry limestone, C. Khufu quarry limestone, D. C-S-H gel and E. synthetic $CaCO_3$.

Since both the Giza plateau and Tura quarries cover a large area, subsequent work on samples from these quarries may produce NMR spectra more similar to that of the present BP spectra, but in the absence of contrary evidence, the present conclusions are sound.

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