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Ancient geopolymer in south-American monument. SEM and petrographic evidence

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A B S T R A C T

The make-up of the sandstone megalithic blocks, weighing between 130 and 180 tonnes each, from Pumapunku -Tiwanaku, Bolivia, was compared with three geological sandstone sites from the area. The SEM/EDS, XRD and thin section results suggest that the sandstone megalithic blocks consist of sandstone grains from the Kallamarka geological site, cemented with an amorphous ferro-sialate geopolymer matrix formed by human intervention, by the addition of extra alkaline salt (natron) from the Laguna Cachi in the Altiplano, Bolivia.

1. Introduction

Ancient megalithic structure building methods have long been a matter of interest and speculation. Conventional theories suggest that the constituent stone blocks were cut from quarries sometimes remotely located, accurately dressed and lifted into position. For the Egyptian pyramids, MacKenzie *et al.* [1] confirmed in this journal the alternative, but still controversial theory first proposed by Davidovits [2], who suggested that the blocks were a type of early geopolymer concrete. There is currently little research done by materials scientists on these controversial topics. However, from a geopolymer material science point of view, the knowledge that we expect to acquire through this type of archaeological study is manifold. In particular, it generates examples that are useful for the determination of the long-term properties of geopolymer concretes. It helps understanding of the chemical transformation which a geopolymer matrix can undergo over a long time range (hundreds if not thousands of years), and could provide data on the crystallization mechanism and mineralogical evolution.

In this communication we present our preliminary research results on monuments in the South American Andes. They were built 1400 years ago (ca. AD 600) by the Tiwanaku Empire, one of the civilizations of the pre-Columbian Americas (Fig. 1A). The platform on top of the 4 step pyramid of Pumapunku consists of 4 megalithic red sandstone slabs, weighing between 130 and 180 tonnes each (Fig. 1C, D), the largest among the New World monuments. Our study suggests that the slabs are a type of sandstone geopolymer concrete cast on the spot.

One early Spanish conquistador chronicler, Pedro de Cieza de Leon, who visited the Altiplano in 1549, marvelled over the ruins of Pumapunku, wondering what tools could have been used to achieve such perfection (English translation) "*... I asked the natives, whether these edifices were built in the time of the Incas, and they laughed at the question, affirming that they were made before the Incas ever reigned, but that they could not say who made them......*" According to modern archaeology, the monument was destroyed around AD 900, i.e. 500 years before the rise of the Inca Empire.

Travelers mostly agreed that the sandstone was mainly from the Kimsachata mountain range south of Tiwanaku. Yet, it remained unclear how these megaliths were quarried and transported on steep llama tracks as in Fig. 2(1). The first scientific studies conducted and published in the early 1970s by Bolivian archaeologists [3], set out to determine the source of the sandstone employed to construct the Pumapunku complex. They conducted geological studies in 6 drainage valleys, isolating several potential sandstone quarries, totalizing 47 samples. With comparative investigations including X-ray diffraction, XRF, geochemical analysis, and lithic petrography, they concluded that Pumapunku sandstone (20 samples) came from the Kausani *quebrada* (geological site K in Fig. 1B). However, our detailed study of their published chemical analysis contradicts this.

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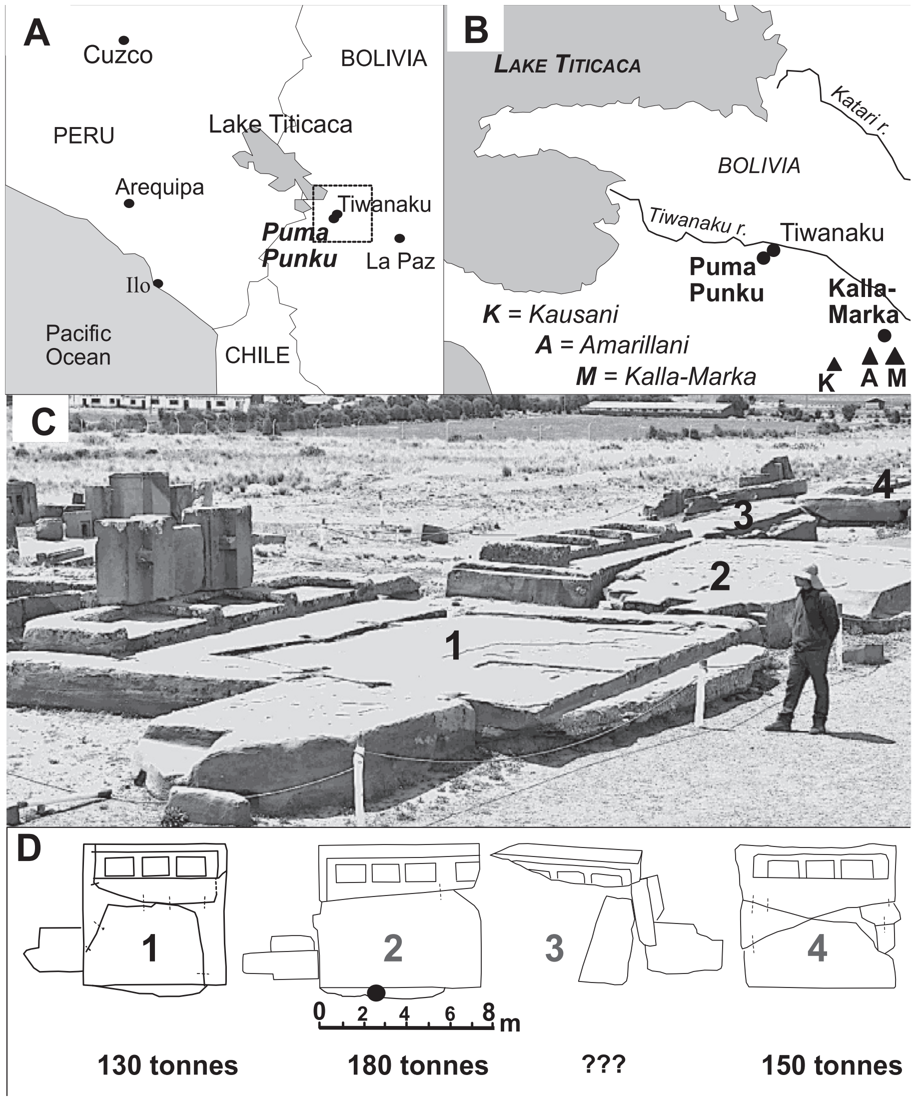

Fig. 1. (A) South American Andes with Pumapunku/Tiwanaku. (B) Location of the geological sites selected in this study. (C) The 4 megalithic red sandstone slabs of Pumapunku. (D) Drawing and dimensions of the 4 slabs.

2. Materials and methods

The Pumapunku red sandstone studied here is from slab No. 2. In Fig. 1D, the sampling place is marked by a black dot. It is near one of the pieces (No. 9) taken and studied in the 1970s. This sample was divided into several fragments for further analysis. For comparison, we selected three geological sites (Fig. 1B): K (Kausani) and A (Amarillani) already studied in the 1970s in which the samples were taken from solid quadratic sandstone blocks as in Fig. 2(2); we added site M located at Kallamarka, a village already known during the ancient time of Tiwanaku. The M sample was not taken from a solid quadratic sandstone block but from a flat weathered sandstone bed as in Fig. 2(4).

The thin 30 μm thick sections were studied under transmitted light (polarized or not) with a Leica 4500 DMP optical microscope. The results are shown in Fig. 2; the thin sections are marked KAU (Kausani), AMA (Amarillani), MAR (Kallamarka) and PP4 (Pumapunku fragment No. 4).

XRD spectra were acquired using a XD8 Advance "BRUKER" AXS (Siemens) spectrometer, calibrated and interpreted according to ICDD/COD international databases from 2013 and DIFFRAC.EVA v.4.1 software. The results are listed in Table 1, with file codes for some elements and semi-quantitative analysis.

XRF data were taken from reference [3], acquired with equipment dating back to 1960.

The SEM images and EDS analysis for Na, Mg, Al, Si, K, Ca and Fe were acquired using a JEOL JSM-6510LV scanning electron microscope. The results are listed in Table 1 and Fig. 3.

3. Results and discussion

In the thin sections of Fig. 2 (optical microscopy), the quartz and feldspar crystal size is: for KAU 100 μm, for AMA 200–400 μm, for MAR and PP4, 150–200 μm (with detrital sandstone fragment particles similar and larger). The mineralogical composition of all samples falls in the range of 40% for quartz, 40% for feldspar and 20% for stone fragments (volcanic and sandstone).

In Table 1, XRD analysis gives the semi-quantitative mineral composition of the sandstone samples. It confirms that the crystalline minerals are mainly quartz and feldspars. Interestingly, we find additional minerals in MAR: calcite $CaCO_3$, kaolinite and illite clays.

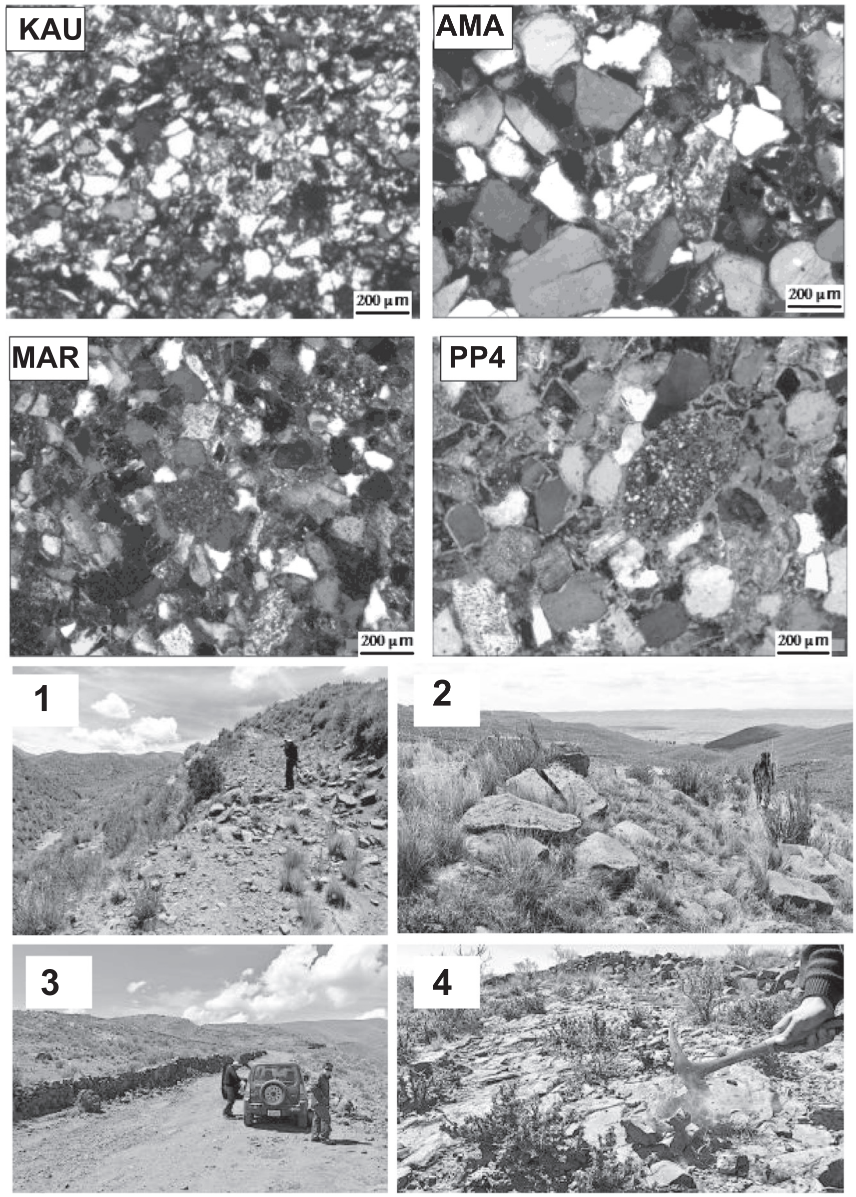

Fig. 2. Thin sections of sample KAU (Kausani), AMA (Amarillani), MAR (Kallamarka), PP4 (Pumapunku monument stone, fragment nr. 4). Geological sites: (1) steep llama track to KAU Kausani; (2) Kausani quadratic sandstone blocks resulting from natural weathering, geological processes of fracturing; (3) road to MAR Kallamarka; (4) MAR sampling site of easily disaggregated kaolinitized sandstone.

Table 1
Element (at%) and mineralogical analyses for Pumapunku red sandstone and geological sandstone. X-ray fluorescence data for boron (B) are from reference [3].

	Kausani KAU	Amarillani AMA	Kallamarka MAR	Pumapunku PP4-global	Pumapunku PP4 matrix, see Fig. 3C-D
X-ray fluorescence B boron (ppm)	0 (6 samples)	100 (1 sample)	not available-	100 (20 samples)	not available
SEM/EDS analysis at. %					
Na	6.67	1.56	5.10	9.95	7.63
Mg	2.70	2.08	1.43	1.93	1.87
Al	17.18	13.38	18.48	16.21	15.43
Si	66.05	70.09	58.33	63.66	59.12
K	2,67	3.78	3.51	2.11	3.70
Ca	0	2.22	8.82	1.70	0.60
Fe	4.73	6.89	4.32	4.44	11.65
XRD minerals % semi-quantitative analysis					
Quartz	34.80	64.10	35.70	22.20	–
Feldspar	65.20	35.90	49.30	77.80	–
Calcite COD 9,016,706	0	0	7.40	0	–
Clays COD 1,011,045 Kaolinite	0	0	7.60 kaolinite + illite	0	–

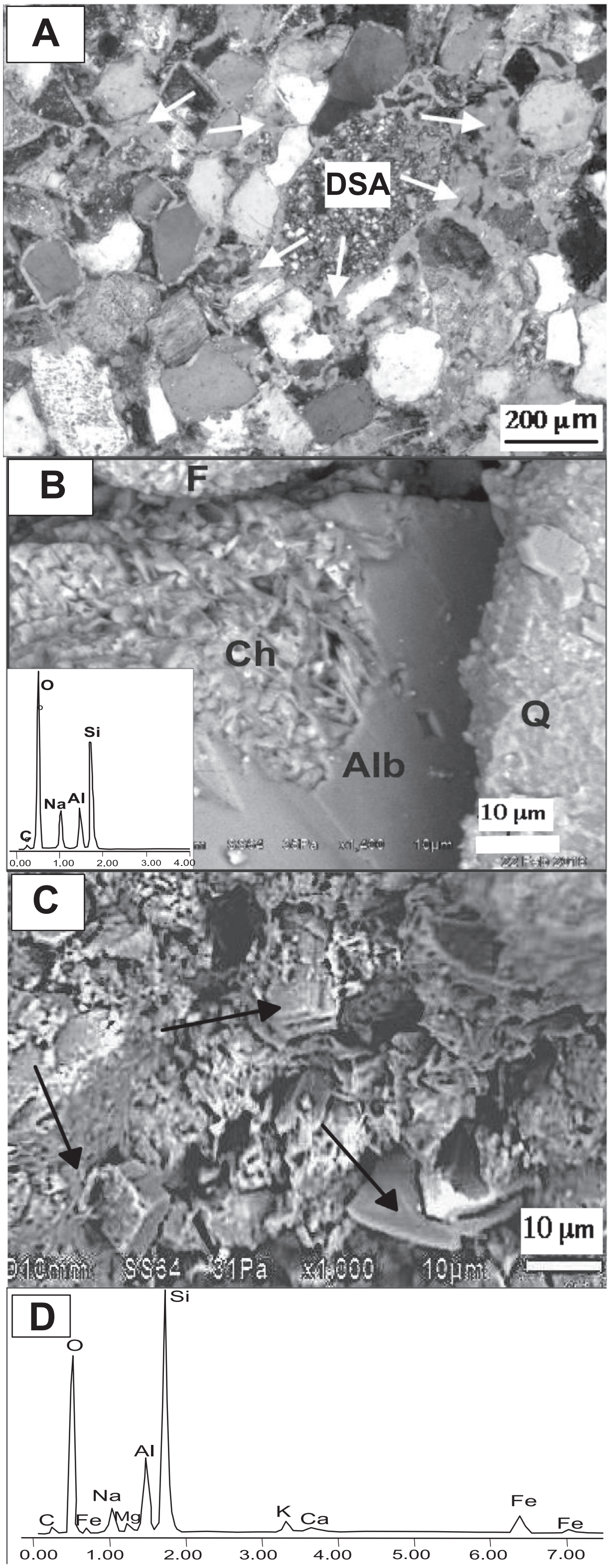

Fig. 3. (A) thin section of PP4, the white arrows pointing on red fluidal "ferro-sialate" matrix around a detrital sandstone aggregate (DSA) and other stone fragments. (B) SEM with authigenic albite sheet (2–3 μm thickness) overgrowth on chlorite blast, with EDS spectrum of pure albite. F = feldspar-plagioclase, Q = quartz, Alb = albite, Ch = chlorite. (C) Ferro-sialate matrix between quartz and feldspar grains, with regular geometrical structures (black arrows). (D) EDS spectrum of the structures shown in (C).

But, the X-ray fluorescence and EDS analysis show that the KAU sample has neither B (boron) nor Ca (Table 1). In the chemical analysis of the 1970s [3], for the 6 KAU samples, CaO = 0%, whereas for 20 monument samples, CaO = 1.45 (medium value). In Table 1, for PP4-global, Ca = 1.70.

Chemical analysis and thin sections suggest that KAU and AMA are dissimilar to PP4, i.e. that the stone material PP4 of the monument does not originate from KAU (Kausani), nor AMA (Amarillani).

In Table 1, in the EDS analysis for PP4-global, Na at% = 9.95; this is substantially higher than for KAU (6.67), AMA (1.56) and MAR (5.10). If MAR is the source for PP4, an alkaline hardener is needed in the stone geopolymer slurry, for example the salt natron, Na_2CO_3, extracted from Laguna Cachi, a small lake (*salar*) in the Altiplano desert, (Bolivia). This high amount of Na relates to the SEM image of Fig. 3B, showing authigenic albite $NaSi_3AlO_8$ formed after consolidation of the sandstone. In natural sandstone, authigenic albite results from the permeation of weak alkaline waters and dissolution of the feldspar. But this requires high pressures (between 3600 and 5000 m depth) and temperatures (100–150 °C) [4]. In a geopolymer sandstone, the alkaline concentration is high and albite formation might occur very rapidly. Yet, to our present knowledge, we cannot differentiate between authigenic and "artificial" albite.

In Table 1, for PP4 matrix, Fe at% = 11.65, which is very high and related to the spectrum in Fig. 3D. Its SEM image in Fig. 3C shows regular geometrical structures (black arrows). From the Si, Al, Fe and Na content we can classify the matrix as a "ferro-sialate" geopolymer [5].

In Fig. 3A, the thin section for PP4 shows the thick fluidal red ferro-sialate matrix (white arrows). To our knowledge, this feature is very unusual in sandstone formed geologically or, at least, it has not been reported in petrographic studies on the red sandstone of the area [3,6]. It represents a *unicum* and supports the idea of an artificial sandstone geopolymer concrete.

In Table 1, the XRD analysis for MAR shows one of the major minerals commonly found in geopolymer synthesis, kaolinite clay. MAR sandstone is subject to weathering actions transforming the feldspar into kaolinite. It is readily disintegrated manually as in Fig. 2(4). But MAR also contains calcite $CaCO_3$, not found in PP4. However, the weathering action may vary from place to place. The Kallamarka plateau covers a large area and subsequent work on samples from this site may produce XRD spectra more similar to the present PP4 spectrum. Actually, the petrographic analyses of the 1970s list calcite in 15 samples from the monument, from a total of 20. Our specimen PP4 was taken very close to their sample M9, which like the other 5 does not contain calcite.

4. Conclusion

The thin section of a sample taken from the Pumapunku red sandstone monument shows grain boundaries made of a thick fluidal red ferro-sialate matrix. To our knowledge, this feature is very unusual in sandstone formed geologically. It represents a *unicum* and supports the idea of artificial sandstone geopolymer concrete. Complementary SEM/EDS analysis for Na, Mg, Al, Si, K, Ca, Fe suggests that the Kallamarka site is the source for Pumapunku megalithic blocks. To make their geopolymer sandstone concrete, the builders may have transported finely weathered, kaolinitized sandstone from the Kallamarka site and added foreign elements such as natron (Na_2CO_3) extracted from Laguna Cachi, a small lake (*salar*) in the Altiplano, (Bolivia). In the absence of contrary evidence, the present conclusions are sound and the Pumapunku megalithic slabs are made of ancient geopolymer. This kind of study could provide data on the long-term crystallization mechanisms and mineralogical evolution of geopolymer molecules.

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