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The effects of chemical composition and distribution on the preservation of phytolith morphology

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Abstract Different types of phytolith even when coming from the same plant react to high temperatures in different ways. To understand the behavior of phytoliths upon heating, we examined composition and distribution of some elements within different phytolith types using SEM-EDS and synchrotron radiation µ-X-ray fluorescence. By analyzing phytoliths from rice husk, rice leaf and *Than* tree leaf, we find that the compositions and distributions of metal oxides within different phytolith types are quite different. It is well known that metal oxides have been used as fluxing agent to reduce the melting temperature of SiO_2 in the production of glass, and different metal oxides can be used to produce a variety of glass with diverse features. Similarly, metal elements including potassium, magnesium and calcium in phytoliths should also act as a fluxing agent under high temperature, and the differential compositions and distributions of these metal elements within the phytoliths resulted in the variable reaction to heating. In sum, there is a negative relationship between the flux elements composition in phytoliths, and the temperatures at which phytoliths deform; furthermore, potassium and calcium in the rice leaf phytolith are almost evenly distributed in all parts, which may cause the phytolith's shape to deform evenly. In comparison, *Than* tree leaf phytolith is found to have a high percentage of potassium and calcium located exclusively on the outside, which may explain why the deformation of *Than* tree leaf phytolith occurs firstly at the outside.

1 Introduction

Phytoliths, or opal phytoliths, are microscopic biogenic mineral structures composed primarily of silica that, depending on the species of plant, are deposited between the plant cells, within cell walls, or completely infilling the cells. Since phytoliths can take on a considerable variety of forms, they can be used to provide significant taxonomic information for identifying a specific genus or species according to their shape, size, ornaments, cell orientation and other anatomical features [11, 12, 18]. During the last decade phytolith analysis has brought new insights into environmental and agricultural archaeology (e.g., [1, 6, 9–12, 14–16]). A few studies have focused on the chemical composition of the silica component of phytoliths to learn about past climatic conditions or taphonomy [2, 4, 17]. The organic molecules trapped within the silica have also been studied in order to learn about prehistoric plant biochemistry or for radiocarbon dating [7, 13].

In our previous work, we studied the phytolith extracted from Xuan Paper which is widely used in ancient painting to explore a new method for characterization and identification of ancient paper [5, 8]. It is well known that Xuan Paper was made from two types of material: (1) *Pteroceltis tatarinowii* Maxim., also called *Than* tree in Chinese, which is a unique tree in China. (2) *Oryza sativa* L. (Rice). In our

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study, we can find an abundance of rice phytolith in handmade Xuan paper. However, we can hardly find any phytolith which has obvious characteristics of *Than* tree [8]. To make clear the reason, we investigated the alteration of rice phytolith and *Than* tree phytolith in extreme environments. We designed a set of experiments that the rice phytolith and *Than* tree phytolith were heated at a series of temperatures. Based on the morphological analysis [8, 19], it was demonstrated that different types of phytolith lose their diagnostic morphological characteristics under significantly different high temperatures. The consistent loss of morphological characteristics is demonstrated by heating phytolith types at graduated intervals. Given the consistent results of the alteration of different type of phytoliths at specific temperatures it should eventually be possible to use phytolith alterations as a proximal measure of the original firing temperature of ancient objects and features [19]. In this work, we will continue to study the chemical composition and distribution of these phytoliths using SEM–EDS and synchrotron radiation μ-X-ray fluorescence to understand the reason for their different behaviors at high temperatures.

2 Materials and methods

We obtained rice husk phytolith, rice leaf phytolith and *Than* tree leaf phytolith from modern plant materials from four different places within China, including the provinces of Anhui, Henan, Jiangxi, Zhejiang [19]. We analyze one sample of rice husk, rice leaf and *Than* tree leaf from each location. For each type of phytolith, we choose one representative phytolith for analysis. For rice husk phytolith, we analyzed the double peaked glume cell from the epidermis of the rice husk. For rice leaf phytolith, we analyzed the bilobates short cell from the rice leaf bottom epidermis, which is parallel to each other along the long axes with thick multiple ridges. For *Than* tree leaf phytolith, we analyzed hair cell base. Following the resulting slides were scanned for diagnostic phytoliths under a light microscope, the phytoliths were examined for their chemical constituents using by SEM–EDS and synchrotron radiation μ-X-ray fluorescence.

Scanning electron microscopy (SEM) coupled with an energy dispersive X-ray analyzer (EDS) was used to study the morphology and elemental composition of material surfaces. In order to understand the source of variation in the melting temperature of phytoliths from different parts of plants, we use SEM–EDS to obtain elemental composition of rice husk phytoliths, rice leaf phytoliths and *Than* tree leaf phytoliths. All SEM–EDS values given were taken from a JSM-6610 LA scanning electron microscope with EDS. The characteristic X-rays were detected 1.0 nA and the measuring time was 30–70 seconds.

The X-ray microfocus beamline (BL15U1) at the Shanghai Synchrotron Radiation Facility, which is a hard X-ray microprobe designed for microanalysis of heterogeneous materials with sensitivity and high spatial resolution, can analyze distribution of elements and microstructure of samples. In order to explore the distribution of elements from phytoliths, synchrotron radiation μ-XRF mapping was performed in this beamline station. The X-ray energy was tuned to 11.96 keV by means of the undulator gap and a Si (111) double crystal monochromator (DCM). The beam spot size was set as $5.1 \times 4.4\ \mu\text{m}^2$. A few phytoliths of rice and *Than* tree were measured by μ-XRF mapping. We measured the types of phytolith four times, and found the elemental distribution of the same phytolith is similar. Representative pictures were selected to show the potassium and calcium's distribution in rice leaf phytolith and *Than* tree leaf phytolith.

3 Results and discussion

3.1 SEM–EDS

Our previous experiments showed that the morphology of the tested phytoliths altered differently at the designed temperatures [19]. Based on the morphological analysis (Table 1), it was found that the morphological characteristics of rice husk phytoliths can resist significant change even under temperature exceeding 1000 °C (Table 1). The physical characteristics of rice leaf phytoliths are significantly altered when the temperatures exceed 900 °C (Table 1). The morphology of phytoliths from *Than* tree leaf begins to lose their characteristic form at 700 °C (Table 1). To understand the behavior of rice husk phytolith, rice leaf phytolith and *Than* tree leaf phytolith under high temperature, we use SEM–EDS to obtain elemental composition of these phytoliths. We analyze one sample from each of four locations for three types of phytolith. As shown in Table 2, these phytoliths are composed of varying amounts of silicon, oxygen, calcium,

Table 1 Change degree of phytolith morphology in different temperatures

Type	400 °C	500 °C	600 °C	700 °C	800 °C	900 °C	1000 °C	1100 °C
rice husk phytolith	N	N	N	N	N	N	N	N
rice leaf phytolith	N	N	N	N	M	D	D	D
Than tree leaf phytolih	N	N	M	L	D	D	D	D

N: no change, S: slightly changed, M: partly changed, L: largely changed, D: destroyed

Table 2 SEM–EDX of phytoliths, showing elemental composition (wt%)

Samples	C	O	Mg	Na	Si	P	S	K	Ca
rice husk phytolith 1	1.72	19.21			76.61			2.46	
rice husk phytolith 2	2.14	15.30			79.91			2.74	
rice husk phytolith 3		18.41			78.5			3.09	
rice husk phytolith 4		26.19			71.64			2.17	
rice leaf phytolith 1		8.69	7.50		51.67	1.14		20.21	4.26
rice leaf phytolith 2		36.83			55.07			8.10	
rice leaf phytolith 3	10.08	31.46			41.68			13.06	3.71
rice leaf phytolith 4		40.61	3.61	0.67	39.43			8.69	6.98
Than tree leaf phytolith 1	6.67	6.98	7.43		41.8	1.2		15.6	12.21
Than tree leaf phytolith 2	2.33	14.96	6.14		57.97			16.16	2.44
Than tree leaf phytolith 3	3.09	12.41	22.93		7.34	8.39	0.79	11.21	33.84
Than tree leaf phytolith 4	4.09	13.08	7.34		41.84	0.87		10.14	22.63

potassium and magnesium, similar to glass. It is well known that K_2O, Na_2O, CaO, MgO, PbO, Ba_2O_3 are the typical metal oxides used as fluxing agent to reduce the melting temperature of SiO_2 in the production of glass, and different metal oxides can be used to produce a variety of glass with diverse features. Therefore, the reaction of phytoliths to heat is also similar to that of glass, namely: the higher the concentration of flux elements is, the easier the glass will soften under high temperature.

Experimental results show the stability of phytoliths samples increases with the percentage of silica present for rice husk phytoliths, rice leaf phytoliths and *Than* tree leaf phytoliths. The predominant element in rice husk phytoliths is silica. Since silica has a melting point above 1700 °C due to the strong Si–O–Si bonds in the lattice, it is not surprising that rice husk phytoliths can withstand 1100 °C without deforming.

However, the percentage of silica in rice husk phytoliths is higher than that in rice leaf phytoliths. This difference in the percentage of silica matches the findings that the silica content in ignited samples of rice plants increased between rice leaves and husks [3]. Also the elemental composition of the ash residues from rice leaf phytolith is rich in potassium. The existence of potassium will act as a flux lowering the melting temperature of the silica in the rice leaf phytolith. So it is understandable why rice leaf phytoliths deform when they reach a temperature of 900 °C [19]. In comparison, the percentage of silica in *Than* tree leaf phytolith is much lower than that of rice husk phytolith. Besides, calcium and magnesium are rich in *Than* tree leaf phytolith. When the temperature is sufficiently high, calcium and magnesium will act as fluxing agents. Especially, the concentration ratio of the flux elements including K, Ca and Mg to Si in *Than* tree leaf phytolith is higher than that in rice husk phytolith and rice leaf phytolith. So it is understandable why *Than* tree leaf phytolith melted to indistinguishable masses when the experimental temperature reached 700 °C (Table 1).

3.2 Spatial distribution of flux elements in phytoliths

In our experiments, we also found that rice leaf phytolith's shape deforms evenly at the temperature of 900 °C (Fig. 1d). In comparison, the outside part of *Than* tree leaf phytolith is heavily deformed at 700 °C (Fig. 2d). To further understand the different behavior of rice leaf phytolith and *Than* tree leaf phytolith at high temperature, we analyzed the distribution of potassium and calcium using the synchrotron radiation μ-XRF mapping since potassium and calcium compromises a high percentage in both phytoliths. The μ-XRF mapping results of potassium and calcium are shown in Figs. 1a, 1b and 2a, 2b using jet color pattern, in which red corresponds to a higher density and blue corresponds to a lower density. As shown in Figs. 1a and 1b, potassium and calcium in the rice leaf phytolith is almost evenly distributed in all parts which might cause the phytolith's shape to deform evenly in a temperature of 900 °C. In comparison, *Than* tree leaf phytolith is found to have a high percentage of potassium and calcium located exclusively on the outside (Figs. 2a and 2b), which might be a reason that the surrounding part of Than tree leaf phytolith partly begins to deform in 700 °C. Therefore, the differential distribution of these elements within the phytoliths would result in the different reaction of the different phytolith types at high temperature.

4 Conclusion

Using SEM–EDS experimental evidence indicates that the structural stability of phytoliths from rice husks and rice leaves are related to the elemental composition of the phytoliths of different parts of the plant. Based on synchrotron radiation μ-XRF mapping analysis, the distribution of potassium and calcium in phytoliths from rice leaf and *Than* tree leaf resulted in variability in melting behavior of the two

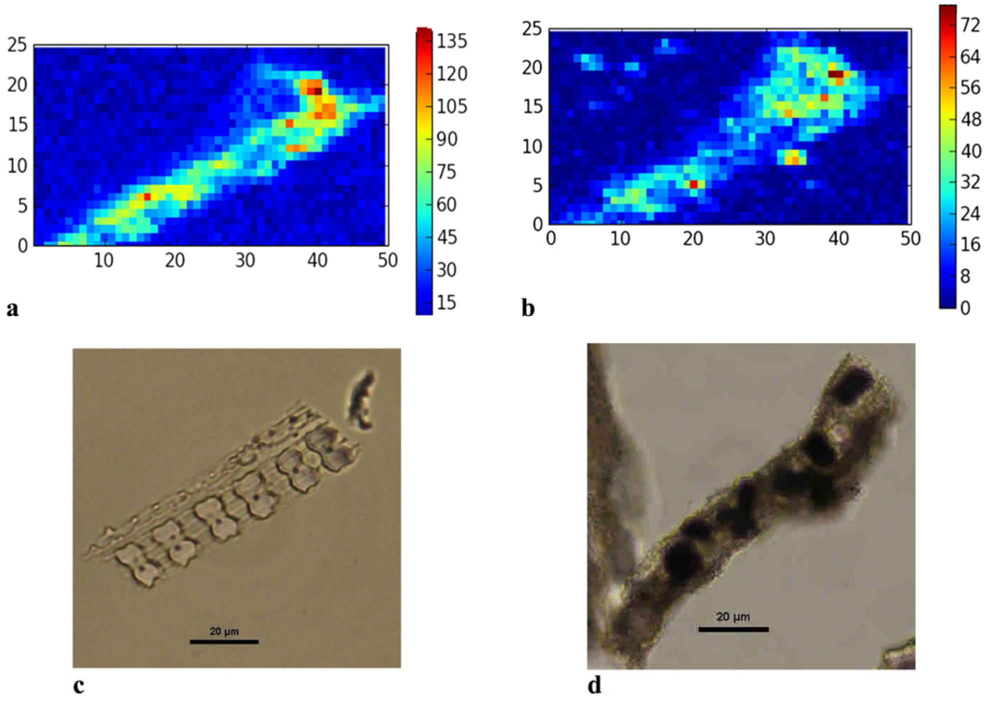

Fig. 1 Rice leaf phytolith's elemental distribution of potassium (**a**), calcium (**b**), and morphology at 600 °C (**c**) and 900 °C (**d**) (scale bar, 20 µm)

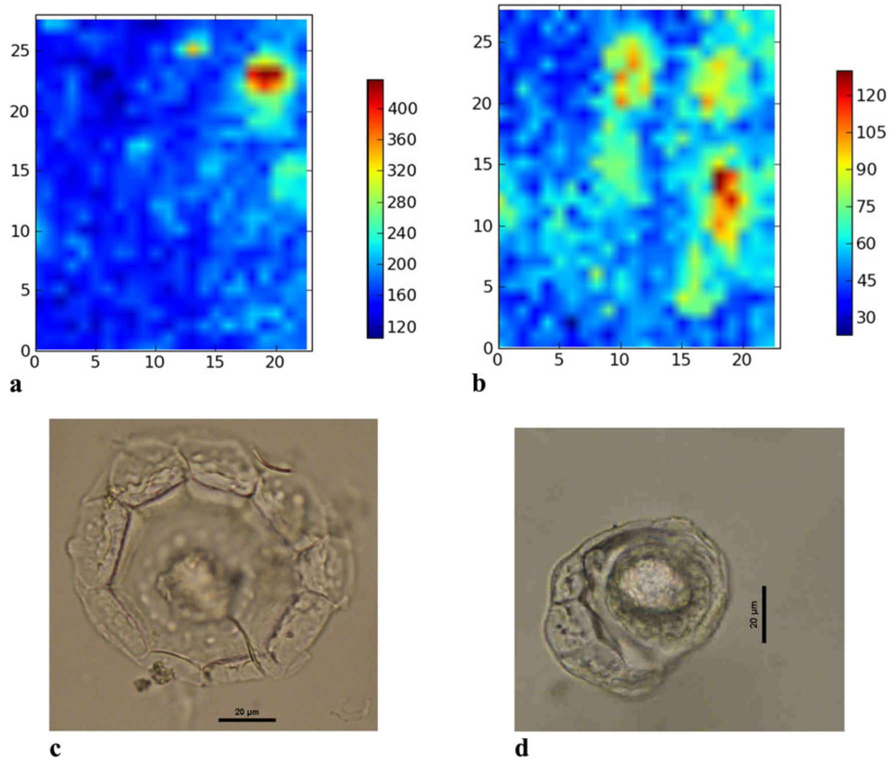

Fig. 2 *Than* tree leaf phytolith's elemental distribution of potassium (**a**), calcium (**b**), and morphology at 600 °C (**c**) and 700 °C (**d**) (scale bar, 20 µm)

different types of phytolith. Therefore, we cannot simply assign all phytoliths in a single melting temperature threshold. Rather we need to analyze the actual composition of each phytolith type to understand how the different elements that act as fluxing agents within the silica of the phytolith are distributed in the cells. Without additional analysis of the composition of phytoliths and conduct experiments that replicate the effects that different ancient pyrotechnologies had on phytoliths we cannot estimate the temperatures that ancient fires, pottery kilns or smelting operations reached based simply on the presence of altered phytoliths alone.

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