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Novel formulated alumina-silica hybrid sol for the entire consolidation of waterlogged decayed ivory from Sanxingdui ruin site

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Abstract

Large amount of ivory was excavated from Sanxingdui site which was waterlogged, severely degraded and in urgent need for conservation. There has been much effort for the conservation of waterlogged ivory by scientists. However, due to a lack of appropriate conservation material and the need to use non-destructive methods, no satisfactory results have been achieved previously. In this work, a novel formulated water-based Al–Si hybrid sol of size about 20 nm was prepared and introduced through a quasi-dynamic equilibrium method to waterlogged ivory tusk for the purpose of conservation. Good conservation performance could be achieved, since Al–Si sol gradually permeates into the interior of the ivory, distributes homogeneously and connects the loose components of ivory. Samples treated with appropriate amount of Al–Si sol displayed satisfactory compressive strength and porous intact structure. It was found that the fluidity of Al–Si sol had a significant influence on the conservation effect. Moreover, Al–Si sol not only consolidated HAP but also worked well on the soil embedded in unearthed ivory, which was beneficial to conserve ivory intactly. Slightly negatively charged Al–Si hybrid gel could interact with ivory matrix through multiple interactions including van der Waals force, electrostatic interaction, chemical and hydrogen bonding.

Keywords Entire consolidation, Waterlogged ivory, Al–Si hybrid sol, Quasi-dynamic equilibrium method

Introduction

The Sanxingdui ruin site [1] is located in Guanghan County, 40 km northwest of Chengdu, China. This archaeological site, which was a political, economic, religious and cultural center in ancient Shu Kingdom, has vital significance to traditional Chinese culture. Massive ivory artifacts were discovered during excavation in Sanxingdui [2]. Being similar to the unearthed ivories from Jinsa site, they were waterlogged and severely deteriorated. The conservation of these unique cultural relics became very urgent for better understanding the ancient environment, historical climate, the origin of these ivories and local human culture, etc.

As the dentin part of tusk, ivory is a biological inorganic/organic nano-composite material, mainly composed of an organic collagen-based matrix and a hydroxyapatite (HAP) mineral phase [3]. In waterlogged environment, the collagen matrix is apt to be degraded by hydrolysis and microbial activities [4] over thousands of years. In Contrast, no obvious change occurs in the carbonated hydroxyapatite crystal structure, but degree of crystallinity slightly increases and HPO_4^{2-} content drops [5]. Ivory is highly susceptible to diagenetic

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alterations [6] in the sub-micrometer and nanometer levels. However, the diagenetic processes at these scales remain incompletely understood. Due to the degradation and loss of organic collagen, unearthed ivory generally has a porous carbonated hydroxyapatite framework. The internal structure was supported by water and invaded soil.Once unearthed waterlogged ivory is exposed to air, the rapid water volatilization would cause its collapse inevitably [7].

Traditional polymers [8], such as acrylate copolymers, PVAc water emulsions and polyethylene glycol, have been attempted to reinforce ivory due to their optical clarity, superior mechanical strength and adhesion capability. However, these polymers are susceptible to degradation by oxidation and chain scission reactions [9]. Besides, the penetration depth of these polymers was severely restricted when used on waterlogged ivories. Until now, only a few successful treatments have been achieved on small ivory samples. There are almost no success cases that have been reported for relatively large waterlogged ivory in bulk. In recent decades, with the development of nanomaterial in the conservation of cultural heritage [10, 11], it has been used in ivory conservation tentatively. For example, TiO_2 nanoparticles were applied to slow down photo-oxidative activity of acrylate copolymer [12]. Consolidation via plastination has also been proposed as an alternative. This treatment replaces water and lipids in biological tissues with curable silicone-type polymers. In terms of ivory conservation, it has produced positive outcomes [13]. However, this treatment contains considerable risks since unreacted residues remains in ivory [14]. As the main composition of ivory, hydroxyapatite was used to consolidate ancient ivory [15]. It is comparatively more compatible with ivory in comparison with other conservation materials. However, for the consolidation materials discussed above, they were all limited to the conservation of small ivory samples. When they were used for the conservation of waterlogged ivory, the encountered common problem, which was how to introduce these conservation materials successfully, had not been solved properly. It is difficult for conservation material to permeate into ivory in bulk since there is no adequate space for accommodation of conservation material in waterlogged unearthed ivory. It has been found that an appropriate amount of water plays an important role in keeping the structural stable for waterlogged decayed ivory. Once water content exceeds a certain range, it is risky to cause irreversible damage for ivory. Hence, taking the place of water with an appropriate conservation material in a safe way becomes very crucial for the conservation of ivory. Considering the large volume of unearthed ivory and the requirements of the exhibition, it is necessary to conserve ivory in bulk. To meet this purpose, aims of this research include: (1) preparing stable sol and adding it efficiently into waterlogged decayed ivory; (2) evaluating conservation effects; and (3) speculating conservation mechanisms.

Sol–gel method is highly perspective for cultural heritage conservation. Sol in liquid can be easily introduced into cultural heritage, where it solidifies via gelation and/or drying processes [16, 17]. It has been widely used to conserve stone [18, 19], paper [20] and paintings [21]. In this study, a hybrid sol with very nice compatibility between two components was prepared by mixing home-made alumina sol and silica sol and it was introduced by a Quasi-Dynamic Equilibrium Method for the conservation of ivory in relatively large size. Structural characteristics and chemical compositions of unearthed ivory were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD). The conservation performance was evaluated on compressive strength, microscopic structure of samples and distribution of conservation material.

Materials and methods

Materials

Silicon powder (99.9% in metals basis, 1–3 μm), 1 N NaOH solution, Aluminum chloride hexahydrate (Reagent Plus, 99%) and phosphoric acid (GR, ≥ 85 wt % in H_2O) were purchased from Aladdin Co., Ltd. Hydroxyapatite powder (HAP, 12 μm, analytical grade) was received from Adamas-beta. All materials were used as it was received without further purification. Deionized water was obtained from a Millipore Milli-Q water purification system. Soil collected from Sanxingdui ruin site was naturally dried in ambient conditions for 1 week before sample fabrication. Ivory blocks were used with the permission from Sichuan provincial cultural relics and archaeology research institute.

Preparation and characterization of conservation material

Water-based Al–Si hybrid sol used as consolidant in this study was prepared by mixing home-made alumina sol and silica sol with the atomic ratio of Al/Si as 1:3. It was a patented (CN 202310057296X) product with high stability, low viscosity and could be arbitrarily diluted with water.

Silica sol was prepared by direct hydrolyzing silicon powder in NaOH solution. In a typical procedure, 200 ml NaOH solution with the pH value of 10 was obtained by diluting 1 N NaOH solution with deionized water and it was loaded in the round bottom flask with three necks. A 25 g silicon powder was added slowly under stirring. The hydrolysis reaction was conducted in an oil bath setting temperature at 80 ℃ for 10 h with refluxing and continuous stirring. Silica sol was obtained after separating residual silicon powder by a filter.

Alumina sol was prepared through acidolysis of freshly made $Al(OH)_3$ precipitation by phosphoric acid under ambient conditions. For the preparation of fresh $Al(OH)_3$ sediment, 100 g aluminum chloride hexahydrate was dissolved in 300 ml water and reacted with 250 g 20 wt% NaOH solution under stirring at room temperature. The precipitation was centrifuged and rinsed repeatedly until no chloride ion could be detected. The precipitation was transferred to 200 ml 0.03 M phosphoric acid solution and carried out acidolysis reaction for 24 h at room temperature.

The solid contents of silica sol and alumina sol based on SiO_2 and Al_2O_3 respectively were analyzed by igniting dried sols at 800 ℃ separately. The Tyndall effect signals were detected by a 532 nm green laser pointer pen (Deli Group Co., Ltd., China). The size and zeta potential of colloidal particles were measured using Zetasizer nano laser particle size analyzer (Malvern Instruments Co., Ltd., UK).

Characterization of unearthed ivory

The average water content of the unearthed ivory was estimated by measuring several small blocks after drying at 105 ℃ for 24 h in an electric oven. Some similar samples were dried in ambient conditions for one week for other characterization. The infrared absorption spectra of the samples were determined by a Fourier Transform Infrared spectrometer (FTIR, Nicolet IS50). The spectra were obtained from 128 scans with 4 cm^{-1} of optical resolution, in the 4000–600 cm^{-1} range. The crystal structures of the samples were investigated by X-ray diffractometry (XRD, D/MAX2200V PCX) using Cu K_α radiation (λ = 1.5406 Å), operated under 40 kV and 40 mA.

Consolidation and assessment of samples

Consolidation and assessment of mockups

Mockups were prepared by mixing HAP, soil or the combination of them in a total mass of 10 g and conservation materials including Al–Si hybrid sol and water. The information about components of mockups and conservation materials were summarized in Table 1. The mixture was homogenized in an electric agate mortar and then compressed in a die of 20 mm in diameter by a tablet presser (769YP-15A) at 2 MPa. Samples about 15 mm in height were obtained. These samples were cured for 14 days in an environment of 25 °C and 50% RH. Compressive strength was measured by a microcomputer-controlled electronic universal testing equipment (CTM8050, Xie Qiang Instrument Manufacturing (Shanghai) Co., ltd.) under the loading rate of 0.5 mm/min.

Consolidation and assessment of waterlogged decayed ivory

Al–Si hybrid sol with a solid content of 8 wt% was used in this study. Prior to the entire consolidation of the waterlogged decayed ivory tusk, several small unearthed ivory blocks were tested for the decision of method about introducing hybrid sol. Solid weight of each block and ivory tusk were estimated by considering the average water content of waterlogged ivory. Generally, the

Table 1 Composition of mockups and the application of conservation materials

Serial No.	Mockup components		Conservation material		Mechanical strength
	HAP (g)	Soil (g)	Al–Si sol (g)	Water (g)	Compressive strength (MPa)
A	10.00	0	0.50	0	2.72
			0.75		5.65
			1.00		6.10
			1.25		5.67
			1.50		6.63
B	10.00	0	0	1.00	4.18
			0.25	0.75	5.48
			0.50	0.50	6.11
			0.75	0.25	5.74
			1.00	0	6.05
C	10.00	0	1.00	0	5.97
	7.50	2.50			6.35
	5.00	5.00			8.92
	2.50	7.50			12.94
	0	10.00			21.60

introducing methods could be divided into two categories depending on whether the consolidant was introduced by once or by step by step. For instance, to introduce consolidant by once, 2.26 g Al–Si hybrid sol was introduced into a small unearthed ivory block with the weight of 8.34 g by once. For the case of introducing consolidant step by step, 6 g of Al–Si hybrid sol was introduced into another small unearthed ivory block with the weight of 6.96 g by 20 times. For each time, 0.3 g of sol was added after the evaporating of the same amount of water. After being air-dried to a constant weight, macroscopic features of these ivories were recorded.

As would be demonstrated later, introducing consolidant via a dynamic balance Al–Si sol replenishment method through a single small amount of water volatilization and the corresponding reinforcement liquid balance supplement was important for the fulfillment of successful consolidation for waterlogged decayed ivory. Here, the most important closely linked parameters included the amount of added consolidant in each step and the interval between two steps. Consolidant accommodation became possible by volatilization of water. For the safety consideration, in this study the added amount of consolidant for each step was set equal to the evaporated amount of water. The optimized procedure was charted in Fig. 1, named as quasi-dynamic equilibrium method, which was designed for safe introducing of consolidant to a relatively large ivory tusk with the weight of 326 g. The experiment of consolidation was conducted under ambient conditions in a room avoiding evident convection at 20 ℃. The ivory tusk was placed in a PE box lined with a sponge and the weight variation was monitored during natural volatilization of water using an electronic balance. Roughly 10 g of water could be evaporated for 10 h. After that 10 g of hybrid sol, which was the same quantity of evaporated water, was introduced from the ivory surface using a cotton swab followed with the rehydration equilibrium and static homogenization for 14 h keeping the PE box covered. Before the next cycle, the ivory tusk was flipped over by hand with the aim to introduce consolidant as uniformly as possible by double-side introducing. In the consolidation process, the previously mentioned cycles were carried out 16 times which meant that the total mass of added sol was 160 g. In the process of natural dehydration and drying, the ivory tusk was flipped over by hand every 12 h, letting water evaporation occurred from the upper and bottom surfaces alternatively. The quality of evaporated water was recorded every day until no discernible change could be observed.

The microstructure of entirely consolidated ivory tusk was observed on a high performance microfocus X-ray CT system (Shimadzu inspeXio SMX-225CT FPD HR Plus) operating at 115 kV and 120 μA with the slice width of 0.086 mm and the image resolution of 1024 × 1024 pixels. Several small ivory blocks were embedded into epoxy and cut by a thin sectioning system (PetroThin™, Buehler, USA) for observation under a digital optical microscope (RH-2000, HiRox Co., Ltd, Japan) and scanning electron microscope (SEM, Hitachi SU8020, Japan). SEM images were taken under the accelerating voltage of 3 kV, working distance of 8.4 mm and emission current of 9400 nA. The energy dispersive spectroscopy (EDS, Bruker, XFlash 6160, America) attachment equipped with SEM was used to characterize the distributions of elements.

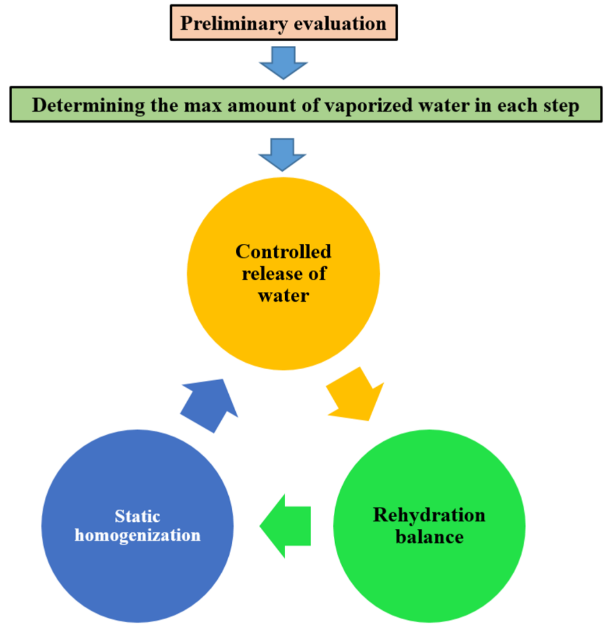

Fig. 1 Charting for the process of quasi-dynamic equilibrium method for conserving unearthed ivory

Results and discussion

Properties of unearthed ivory

The water content of measured small ivory blocks were not consistent, which ranged from 40 to 50%. Therefore, it was reasonable to take 45% as the average water content of ivory. And it was adopted as a gauge for evaluation of solid weight of ivory and further estimating the ratio between consolidant and solid weight of ivory. It was found that water content played a very important role in maintaining the structural integrality of waterlogged ivory tusk. Due to the surface tension force applied by water within the pore spaces, there are upper and lower critical water content limitations for waterlogged ivory. Immersing in water or adding further water in the ivory block would cause disintegration, while losing adequate water could also cause the same result.

As shown in Fig. 2a, the inset image was one of the selected small blocks of unearthed waterlogged ivory used for the measurement of water content. After being dried, ivory fragmented into pieces. It indicated that a moderate amount of water in waterlogged ivory supported the structure of ivory acting as binding agent. Once dehydrated, the structure of ivory collapsed.

The FTIR spectrum of unearthed ivory was presented in Fig. 2b. The band at 3353 cm^{-1} represented the O–H stretching vibration of absorbed water in ivory. The peak at 1637 cm^{-1} was associated with the deformation vibration mode of – OH bond from water molecules [22]. The 1416 cm^{-1} and 1447 cm^{-1} bands were attributed to the substitution of PO_4^{3-} by CO_3^{2-}, which indicated that inorganic phase of unearthed ivory was a carbonate-substituted hydroxyapatite [23]. The most characteristic features in the 1200–1800 cm^{-1} region that are bands produced by organic matter (e.g. C=O and the C–N bonds of amide) [24] disappeared almost completely. The peak around 1017 cm^{-1} was attributed to PO_4^{3-} [25]. The FTIR result indicated that the inorganic matter in unearthed ivory was a carbonate-hydroxyapatite while organic matter had been lost or decomposed.

The X-ray diffraction patterns of unearthed ivory and soil samples collected from the same sacrificial pit of Sanxingdui were presented in Fig. 2c and d respectively. XRD patterns of soil samples collected from various locations in one sacrificial pit revealed that the mineral compositions for these samples were very similar. The predominant mineral was indexed as quartz and the associated minerals included albite, illite and microcline. Notably, the X-ray diffraction pattern of ivory contained a well-resolved reflection at 26.6°attributing to quartz (SiO_2) which was the main crystal component of soil collected from Sanxingdui ruin site. This was reasonable since soil intruded into porous ivory with water flow in damp underground environment for thousands of years. Three relatively intense peaks at approximately 25.9°, 31.8° and 32.2° were consistent with the standard pattern of hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2$ according to JCPDS 09-0432, indicating that the predominant inorganic phase of unearthed ivory was hydroxyapatite. The peak intensity in X-ray diffraction reflected that the hydroxyapatite had low crystallinity and ivory had been degraded severely.

Properties of conservation materials

Tyndall effect, a type of light scattering, takes place in a colloidal solution that contains particles of sizes less than the wavelength of visible light (from 380 to 780 nm). This

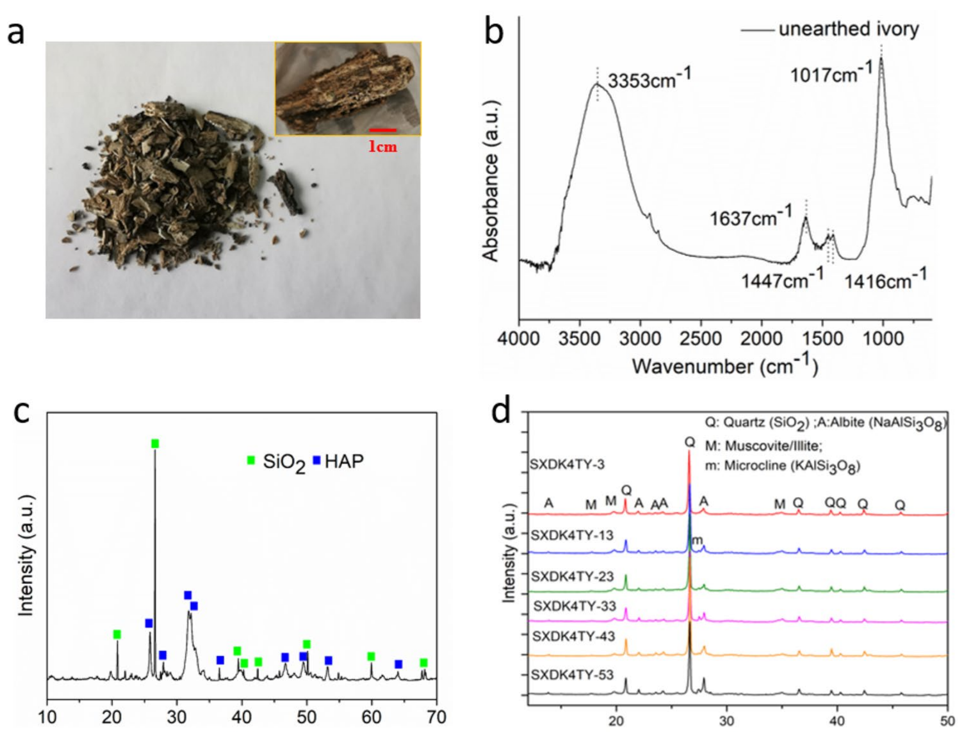

Fig. 2 Optical images of ivory before (inset) and after dehydration. **a** FT-IR spectrum; **b** XRD pattern of ivory (**c**) and soil (**d**) collected from the same sacrificial pit of Sanxingdui

effect depends on colloidal particle size and concentration. Here, Tyndall effect intensity of Al–Si sol in different concentrations was taken as the qualitative readout to measure whether dilution affected the formation of colloidal particles. Figure 3a–j depicted that as excepted, the green laser beam became invisible in deionized water, while a pathway of laser beam going through Al–Si sol could be clearly observed for sols varying with concentrations from 0.1 wt % to 10 wt %. In other words, all the samples of hybrid sol showed clear Tyndall effect. This indicated that the size of Al–Si sol was still in the range of colloidal dimension. Notably, enhanced Tyndall effect was shown in Al–Si sol owing higher concentration. The higher number of particles in a fixed volume results stronger light scattering and stronger Tyndall effect.

The colloidal size and zeta potential of Al–Si hybrid sol were further quantitatively characterized by a Zetasizer nano laser particle size analyzer. The zeta potential measurement indicated that the colloidal was slightly negatively charged with a potential value of − 2.29 mV. As was shown in Fig. 3k, colloidal particles were dimensionally stable and distributed within a narrow range of 22–27 nm for samples with sol concentration from 0.1 to 10 wt%. The results also indicated that the size of colloidal particle was almost concentration independent, which meant that our home-made hybrid sol could be diluted arbitrary. It was beneficial for application. From the point view of application, the small and stable particle size of sol is beneficial for the penetration of particles in cultural heritage. Beside this, our home-made hybrid sol showed high stability, which could be stored for years in closed container.

Consolidation effect of Al–Si sol on mockups

As was shown in Fig. 4a, the compressive strength of samples increased significantly with the increasing amount of Al–Si sol until it reached 1 g. The highest strength was approximately 6 MPa even higher amount of Al–Si sol was added. It indicated that the amount of conservation material was vital for the consolidation effect. Appropriate amount of conservation material was the guarantee for consolidation effect. Further

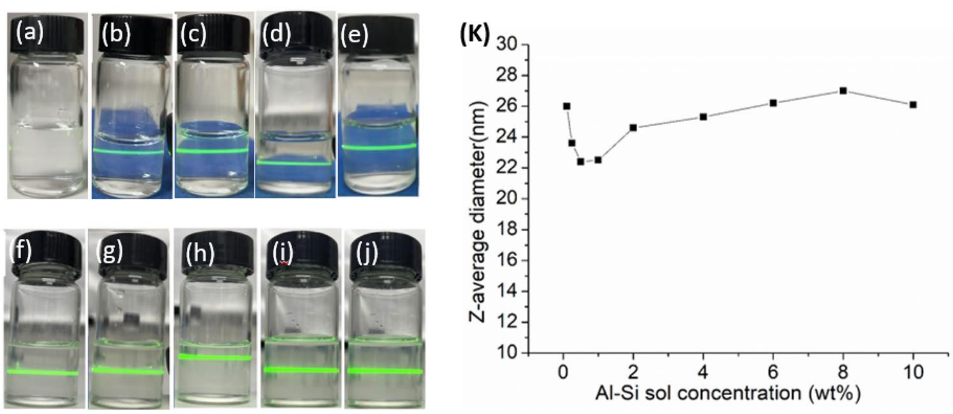

Fig. 3 photos showing Tyndall effect of Al–Si hybrid sol in concentration of **a** 0, **b** 0.1 wt%, **c** 0.25 wt%, **d** 0.5 wt%, **e** 1 wt%, **f** 2 wt%, **g** 4 wt%, **h** 6 wt%, **i** 8 wt% and **j** 10 wt%; effects of the Al–Si sol concentration (wt%) on the size of colloidal particles (**k**)

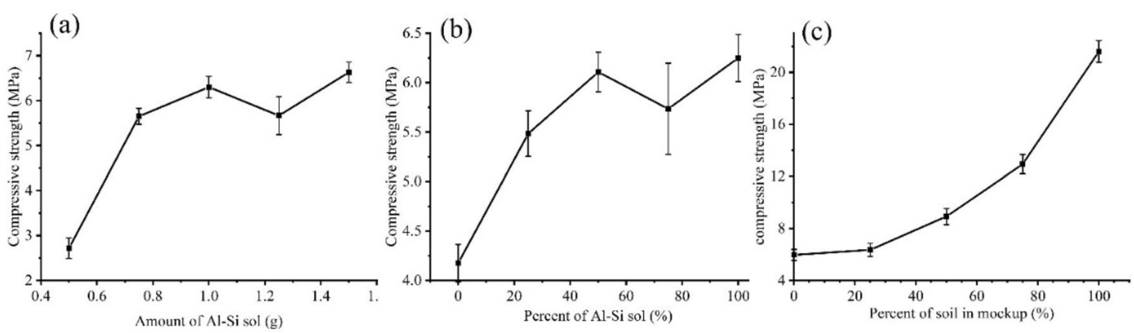

Fig. 4 Compressive strength of mockups. **a** conserved by different amount of Al–Si sol; **b** conserved by 1 g of conservation material containing different percentage of Al–Si sol; **c** containing different percentage of soil. The weight of all mockups was 10 g. Other information could be found from Table 1

addition of Al–Si sol could not further strengthen the mechanical strength. It could be deduced from this result combining experimental conditions that the main contribution for compressive strength gaining was binding contacted HAP powder by home-made hybrid sol. When these spots were welded by consolidant, further addition of consolidant would fill the void through covering the HAP surface. Under a low loading ratio of consolidant, it could not form a framework to strengthen the compressive strength further.

Based on the above results, 1 g conservation material consisted of Al–Si sol and water was applied to the samples. As was shown in Fig. 4b, the mockup conserved only by 1 g of water also showed a certain degree of strength. The compressive strength of mockup increased significantly and reached a plateau (6 MPa) at a certain percent (50%) of Al–Si sol and then changed slightly at higher percent of Al–Si sol. Al–Si sol and water synergistically contributed to the reinforcement effect. Water was able to promote the fluidity of Al–Si sol facilitating its homogeneous distribution inside sample. Notably, water also acted as consolidation agent. The mechanical strength of sample conserved by 1 g water was even stronger than that conserved by 0.5 g Al–Si sol. This was probably attributed to hydrogen bonding of structural -OH groups on the surface of HAP crystals with the strongly adsorbed water monolayer present on HAP [26]. The results also supported our previous prediction that water played an important role for keeping structural integration of waterlogged ivory. In addition, the amount of conservation material, 1 g, was adequate for uniform distribution within a specimen of this magnitude.

Samples with different ratios of soil and HAP were prepared and 1 g of Al–Si sol was applied on these samples. As was shown in Fig. 4c, the compressive strength of samples increased significantly with the increasing percentages of soil. For samples completely made of soil, the corresponding compressive strength even could reach more than threefold increment than that of sample containing 100% of HAP. This indicated that Al–Si sol could not only interact with HAP but also interact more intensely with soil. These multiple interactions were beneficial to the holistic conservation of unearthed ivories containing soil.

Consolidation effect of Al–Si sol on unearthed ivory

The primary experiments carried out on small ivory blocks revealed that introducing consolidant step by step could keep the small ivory block intact, while adding consolidant by once would cause liquefaction and disintegration of small ivory block. As shown in Fig. 5a_1, b_1, the structure of ivory collapsed after air-drying for a small 8.34 g ivory block conserved by introducing 2.26 g (~ 27% of the gross weight of the ivory block) Al–Si hybrid sol by once. As mentioned, water content for measured small ivory blocks ranged from 40 to 50%. It was reasonable to consider that controlling the weight variation of ivory less than 5 wt% might be safe in our conservation process for waterlogged ivory. Figure 5a_2, b_2 depicted the result for another small 6.96 g ivory block conserved by

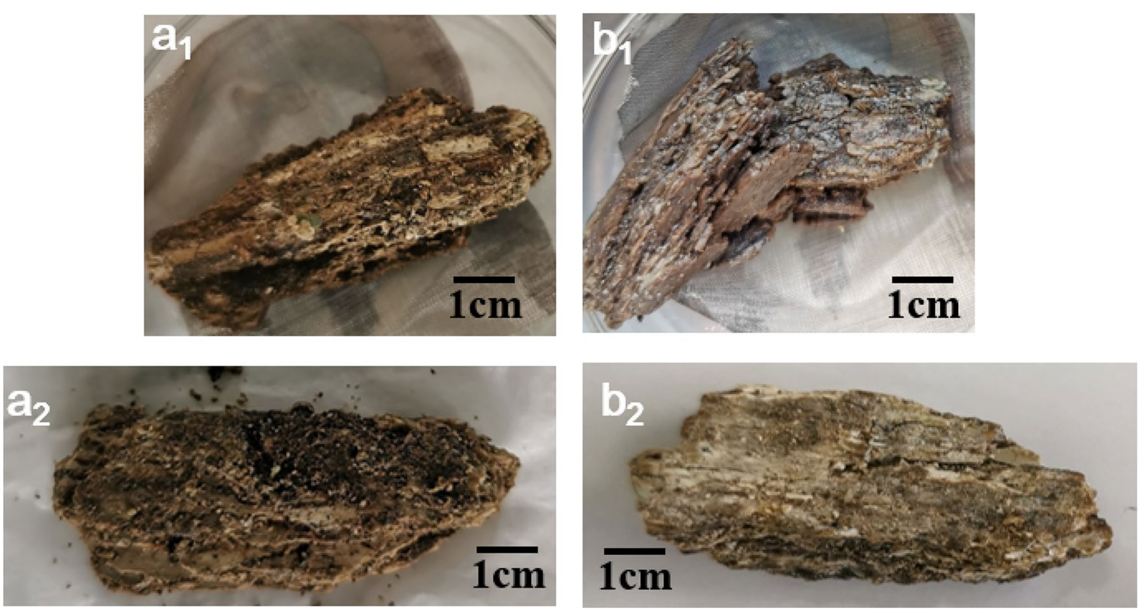

Fig. 5 **a1** image of original waterlogged ivory conserved by introducing consolidant by once, **b1** air-dried conserved ivory in **a1**; **a2** image of original waterlogged ivory conserved by adding consolidant step by step, **b2** air-dried conserved ivory in **a2**

adding hybrid sol step by step. In each step, about 0.3 g of hybrid sol (~4.31%) was added after the volatilization of the same amount of water. After the step was repeated 20 times, it was air-dried. The ivory block maintained its original appearance intact.

For the conservation of a large ivory sample, 10 g of hybrid sol (~3 wt% of the gross weight of ivory tusk) was added each time. After being conserved, ivory was exposed to air allowing water evaporation and promoting the gelation of Al–Si sol. Based on the dehydration rate (Fig. 6a), the entire dehydration process could be divided into three distinct stages. In the initial 5 days, ivory dehydrated rapidly. This could be attributed to the compensatory addition of Al–Si sol in low concentration (8 wt%) resulting a substantial amount of free water still remaining in the ivory. In the subsequent 5 days, dehydration rate progressively decelerated. This was probably due to the gelation of Al–Si sol, increasing of the viscosity of Al–Si sol containing solution and enhanced hydrogen bonds between water, Al–Si sol and ivory. During the last 10 days, the water loss mass reached a constant value, 140 g, achieving water equilibrium between ivory and external environment. Water content of the ivory task could be calculated as 47%, which corresponded with the estimated value. As mentioned, the mass of excavated ivory was 326 g with water content ranging from 40 to 50%. In other words, the water mass in ivory ranged from ~130 g to ~163 g. The water loss mass was within this range confirming that water equilibrium between ivory and external environment was achieved and the consolidation was completed.

Figure 6b and c demonstrated the macroscopic images of original waterlogged ivory and conserved ivory which was dried in the air to the constant weight respectively. It could be seen that conservation did not bring significant dimensional change to ivory indicating that conservation material intruded successfully into ivory and supported its internal structure. Dimensional stability is a critical factor for the assessment of conservation effect. The original ivory demonstrated dark color, while, the conserved ivory showed relatively lighter color. The dark color is due to water-filled structure of ivory which could suppress light scattering [27]. After being air-dried, ivory might become porous even though conservation material intruded into ivory. Pores in ivory could shorten optical length of incident light enhancing light scattering and resulting in shallow color [28].

As was shown in Fig. 7, ivory was scanned from three mutually perpendicular directions. Different degrees of x-ray attenuation occur depending on the properties of components in unearthed ivory. The CT images exhibited regions of ivory components (grey), radiolucent voids (black) and Al–Si gel (white, some was marked by red arrows) suggesting that the conserved ivory still possesses intact and porous internal structure. Al–Si gel was embedded in ivory and distributed evenly. It corresponded well to the stable dimension of conserved ivory.

In this study, Al–Si sol was applied to porous ivory in liquid form. It could permeate into the interior of ivory due to fluidity, gravitational effect and capillary action. Hydrogen bonds could form between Al–Si gel and HAP [29]. In addition, the main compositions of soil, silica and silicate, tend to form hydrogen bonds with Al–Si gel [30]. The chemical bonding and electrostatic effect could also contribute to the consolidation of ivory. In the gelation process, the –OH group in Si and Al sols could reacted

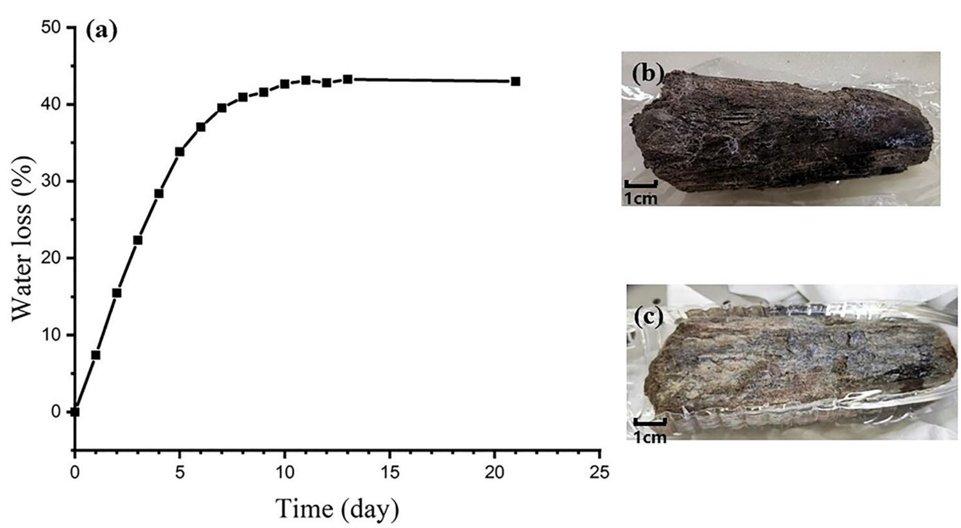

Fig. 6 **a** Water loss of conserved ivory during air-drying process, **b** images of original waterlogged ivory and c air-dried conserved ivory

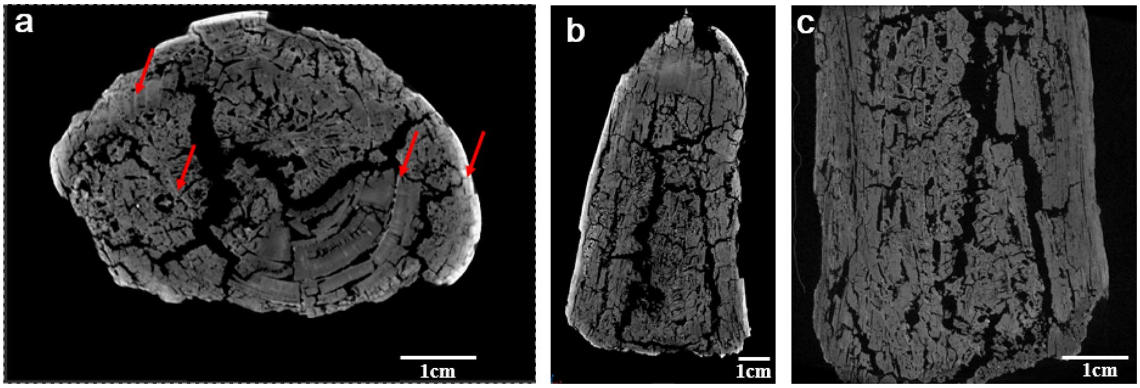

Fig. 7 CT images of conserved ivory scanned from different directions, **a** perpendicular to the length direction, **b** and **c** length direction with orthogonal relationship

with the matrix by dehydration, while most of them participated in the formation of hybrid gel via linking the polyhedrons of [SiO_4] and [AlO_x] (x: 4,5,6) through -O-bridge. In the gel, polyhedron of [SiO_4] is neutral, while the polyhedron of [AlO_x] is negatively charged [31] considering the chemical valance of Si and Al as + 4 and + 3 respectively. It could undergo electrostatic attraction with the positively charged calcium ions in HAP and other cations in ivory matrix. These multiple interactions, including van der Waals force, electrostatic interaction, chemical and hydrogen bonding, collectively contributed to the reinforcement effects.

After being conserved, typical microscopic structures of dentine and cementum were demonstrated in Fig. 8. Through the observation by optical microscopy, evident cracks could be found in ivory. When ivory was further observed by SEM, it seemed rough and cracks could still be observed at low magnification. Relatively smooth area was selected for further observation. Images at a higher magnification showed that ivory remains porous structure. It seemed that there was conservation material adhering to the walls of pores without apparent aggregation. To further characterize conserved ivory, elemental distributions in the ivory were mapped. Elements, Ca and P were selected as the characteristic elements of HAP. As was shown in Fig. 9, these two elements were homogeneously distributed in ivory except for the cracks, while the Al and Si elements uniformly distributed in the selected region. By comparing the distribution of elements (Ca, P, Al, Si), it could be concluded that the spatial distribution

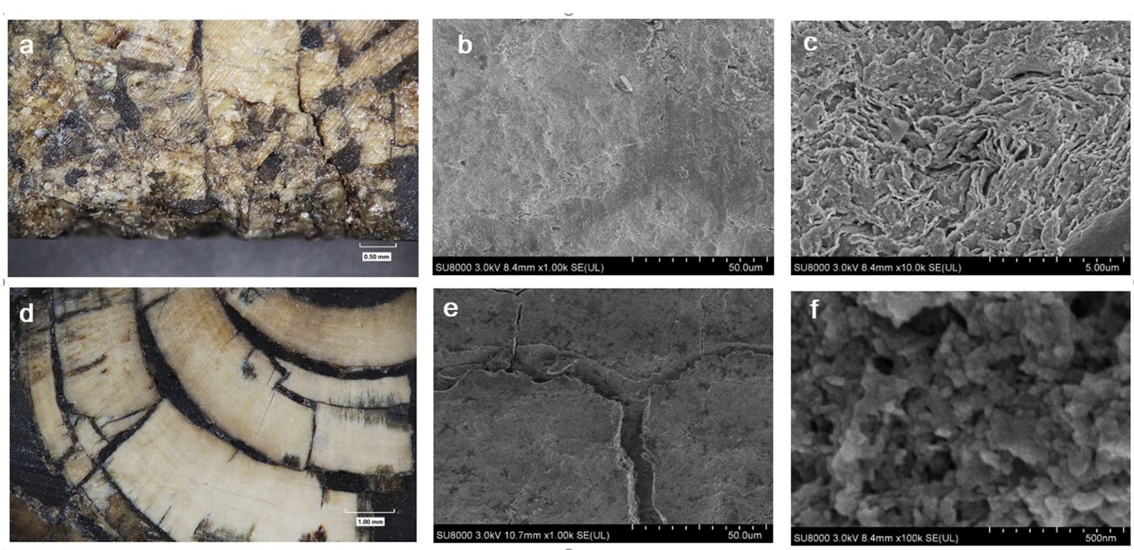

Fig. 8 **a** optical image and **b**, **c** SEM micrographs of conserved dentine. **d** Optical image and **e**, **f** SEM micrographs of conserved cementum

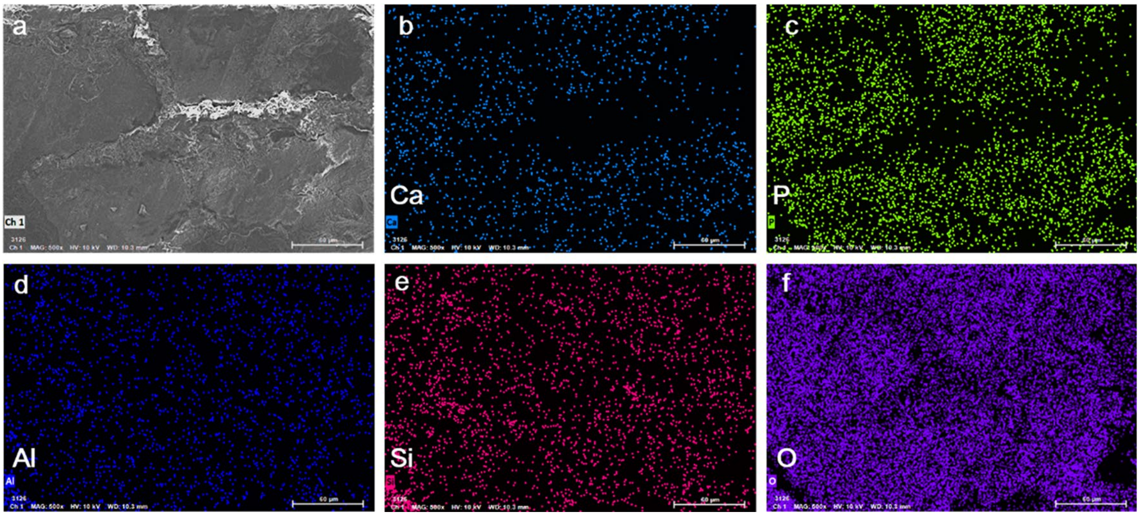

Fig. 9 SEM micrograph of **a** a partial conserved ivory and the corresponding EDS mapping images of element **b** Ca, **c** P, **d** Al, **e** Si and **f** O

of Al–Si gel was highly uniform in ivory. The homogeneous distribution of Al–Si gel was attributed to the porous structure of ivory and fluidity of hybrid sol. As a result, Al–Si gel formed a solid network and connected the components of ivory acting as binding agents.

Conclusion

In this work, Al–Si hybrid sol with high stability was prepared by mixing the home-made silica and alumina sols. The results indicated that colloidal particles in Al–Si sol were negatively charged with a weak potential. The hybrid sol could be arbitrarily diluted with water with stable particle size between the range of 22–27 nm which were beneficial for permeating into porous ivory.

Unearthed ivory from Sanxingdui site had degraded severely. The remaining compositions of unearthed ivory were mainly HAP and some invaded soil. Al–Si sol was evaluated for potential ivory conservation for the first time. Conservation evaluation results showed that mockups treated with a certain amount of Al–Si sol demonstrated enhanced compressive strength. Al–Si sol was gradually added into ivory by quasi-dynamic equilibrium method. An adequate amount of Al–Si sol and its sufficient fluidity were two important factors for achieving reinforcement effects. Apparently, fluidity and slightly negatively charged characteristics of Al–Si sol could promote its permeation into ivory and homogeneous distribution. Al–Si sol interacted well not only with HAP but also with soil by van der Waals force, electrostatic interaction, hydrogen and chemical bonding. Our results showed that Al–Si sol reported in this work was highly potential for unearthed waterlogged decayed ivory conservation.

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Author contributions

Conceptualization; Shidong JI. Methodology and Investigation; Yusong Liu, Qingmeng Xu, Sifan Li, Zhenbin Xie, Qiang Li. Writing—original draft preparation; Yusong Liu, Qingmeng Xu. Writing—review and editing; Yusong Liu, Qingmeng Xu, Sifan Li, Zhenbin Xie, Qiang Li, Hongjie Luo, Shidong Ji. All authors read and approved the final manuscript. Yusong Liu & Qingmeng Xu contributed equally to this work and should be considered co-first authors.

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Availability of data and materials

All data generated or analyzed during this study are included in this manuscript.

Declarations

Ethical approval and consent to participate

Not applicable.

Competing interests

The authors declare no competing interests.

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