Research on the modification of two traditional building materials in ancient China

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Abstract
Silicate material is one of the most typical materials used in both traditional and modern buildings. This paper presents a comparative analysis of two silicate materials (ginger nut and Aga soil) used in ancient Chinese buildings. The research suggests that ginger nut and Aga soil have similar chemical compositions and physical properties. After they are burned at a temperature of 700°C ~ 1400°C, they will have a dual characteristic of hydraulicity and non-hydraulicity. As the temperature rises, the non-hydraulic constituent increases at first and then decreases, while the hydraulic constituent is increasing regularly. Their chemical composition and characteristics are similar to those of the "hydraulic lime" in Europe, and the modified ginger nut and Aga soil can be used for repairing and reinforcing the stone, earthen, brick and ceramic relics.

Keywords: Ancient buildings, Silicate, Material, Property

Introduction
In the late 1970s, a group of residential remains of the Yangshao Period were discovered at the Dadiwan site in Qin'an County, Gansu Province, China [1]. One of these discoveries is named as “original palace” (number F-901) in the archaeological world, and is the largest and top leveled residential site in prehistoric times. This site belongs to the middle Yangshao Period and was used for convocation, worshiping and religious ceremonies by tribes or tribe allies over 5000 years ago. When it was discovered, the site had a bright and clean house floor that was of exquisite workmanship. Preliminary research [2] indicates that the housing floor of the site was made by lightweight calcined Kunkur as aggregate and the powder of calcined ginger nut mixed with a small amount of laterite as bonding materials. After more than five thousand years, the compressive resistance of the floor is close to that of cement mortar No.100. Moreover, the remains of kilns for burning light weight concrete and ginger nut were discovered nearby the site. The research shows that the calcinated temperature of ginger nut could reach up to 900°C [3]. Ginger nut is a type of ginger stone (locally called as ginger nut) in quaternary loess and is composed of 60-80% calcium carbonate and 10-20% clay mineral. When ginger nut is calcinated at a temperature of 900°C, it will produce 25.8% $\beta$-CaSiO$_3$, 17.6% Ca$_2$Al$_2$SiO$_7$ and 33.9% CaO. $\beta$-CaSiO$_3$ and Ca$_2$Al$_2$SiO$_7$ are hydraulic binding materials, and CaO is a non-hydraulic binding material [4]. Therefore, the building materials of F-901 floor in which manmade hydraulic binding materials had been used can be called as the earliest “concrete” in the world, which is a miracle in the history of architecture [3].

Aga soil is another kind of silicate building material widely used in Tibet, and it is the siliceous limestone [5] that contains 70 ~ 93% CaCO$_3$ and 7 ~ 30% SiO$_2$. When Aga soil is used as building material for floor and house (roof), the unburned Aga soil with 40% in a diameter of 5.6 mm, 30% in a diameter of 2.6 mm and 30% 0.15 mm diameter will be made to pulp at the ratio of 0.32 water and then is rammed by a special stone pester. Until the grout completely becomes solid, it will be sanded first and then repeatedly polished with sheepskin and butter. This technique is called “ramming Aga” [6], and for centuries, this traditional material and building technology have been used to construct floors and roofs of temples in Tibet.

In Tibet, there are over one thousand temples that are very valuable cultural relics, such as the well-known Potala Palace, Norbulingka Summer Palace and Sakya Monastery. The Chinese government attaches great importance to the conservation of Tibetan cultural relics.
In the last two decades, two large projects for the conservation and restoration of key relics including the Potala Palace and Sakya Monastery have been carried out [5,7]. The restoration work focuses on ancient buildings and murals, and the main kinds of deterioration are associated with Aga soil used in the roofs. In Tibetan, traditional materials for the roofs of the temple are unburned Aga soil that was crushed into the powder of 0.15 mm in diameters as “gelation” and it was mixed with proper amount of natural gum [6] to make mortar. But unburned Aga soil has low strength and poor weathering resistance but the property of chemical gelatinization. Influenced by the freezing and thawing cycles and the fluctuating temperature and humidity, the natural gum will quickly deteriorate and break. When the rain infiltrated through the cracks, wooden components will decay, fall apart or become leaning, causing subsequent deterioration, such as detachment, large-area loss, disruption and flaking, and thus terribly damaging the murals [7].

Therefore, the research and scientific modification of the two silicate materials in ancient Chinese buildings is very important for the restoration of stone, brick and pottery relics as well as the conservation of ancient Tibetan buildings and murals.

**The characteristic of ginger nut and aga soil**

Physical and mechanical properties of ginger nut and aga soil

The density and saturated water absorptivity of natural ginger nut and Aga soil were tested, and the samples in the size of 5 cm × 5 cm × 5 cm were made for the test of compressive strength (Table 1).

| Sample   | Density/g · cm⁻³ | Coefficient of water saturation/% | Compressive strength/MPa |
|----------|-------------------|----------------------------------|--------------------------|
| Ginger nut | 2.52              | 5.58                             | 55.78                    |
| Aga soil  | 2.61              | 4.60                             | 66.02                    |

**The chemical composition of ginger nut and Aga soil**

X-fluorescence was used to analyze the chemical compositions of ginger nut and Aga soil (Table 2).

| Sample       | Na₂O  | MgO   | Al₂O₃  | SiO₂  | P₂O₅ | K₂O   |
|--------------|-------|-------|--------|-------|------|-------|
| Ginger nut   | 0.90  | 1.49  | 6.44   | 22.06 | 0.11 | 0.98  |
| Aga soil     | 0.32  | 1.10  | 4.23   | 16.37 | 0.08 | 0.85  |

| Sample       | CaO   | Fe₂O₃ | TiO₂   | MnO   | CO₂  | Total |
|--------------|-------|-------|--------|-------|------|-------|
| Ginger nut   | 36.82 | 2.07  | 0.35   | 0.08  | 28.60| 99.90 |
| Aga soil     | 41.87 | 0.87  | 0.21   | 0.02  | 34.07| 99.99 |

**The properties of calcined ginger nut and aga soil**

The influence of calcination temperature to products

When ginger nut and Aga soil are calcined at a high temperature, both the hydraulic material CaO and nonhydraulic material β-CaSiO₃ and Ca₂Al₂SiO₇ will be produced. And the calcination temperature directly affects the ratio of two kinds of the binding materials (Figures 1 and 2).

A semi-quantitative analysis had been done to the main products CaO, β-CaSiO₃ and Ca₂Al₂SiO₇ in Ginger nut and Aga soil at different temperatures, and the curve lines showing how the products varied with temperature were made by comparing the analysis results (Figures 3 and 4).

Figures 1-4 indicate that at 700°C ginger nut produces 7.3% β-CaSiO₃ and 5.2% Ca₂Al₂SiO₇ with no CaO produced, and it produces 17.2% CaO, 24.7% β-CaSiO₃ and 16.3% Ca₂Al₂SiO₇ at 800°C. When the temperature rises from 800°C to 1100°C, the generating speed of CaO is obviously fast and it reaches up to the maximum 42.1%, and this is the best temperature to produce CaO. But the generating speed of β-CaSiO₃ increases less obviously from 24.7% to 28.4% and the speed of Ca₂Al₂SiO₇ from 16.3% to 19.15% is much less obviously. Thus this temperature range is not helpful for the generation of β-CaSiO₃ and Ca₂Al₂SiO₇. When the temperature rises from 1100°C to 1400°C, the amount of CaO quickly drops from 42.1% to 16.7% because CaO takes part in the reaction to produce β-CaSiO₃ and Ca₂Al₂SiO₇. While β-CaSiO₃ and Ca₂Al₂SiO₇ are generated more quickly: β-CaSiO₃ increases from 28.4% to 47.7% and Ca₂Al₂SiO₇ increases from 19.1% to 35.5%.

**Table 1 Physical-mechanical properties of natural ginger nut and aga soil**

| Sample   | Density/g · cm⁻³ | Coefficient of water saturation/% | Compressive strength/MPa |
|----------|-------------------|----------------------------------|--------------------------|
| Ginger nut | 2.52              | 5.58                             | 55.78                    |
| Aga soil  | 2.61              | 4.60                             | 66.02                    |

**Table 2 Chemical compositions of ginger nut and aga soil**

| Sample       | Na₂O  | MgO   | Al₂O₃  | SiO₂  | P₂O₅ | K₂O   |
|--------------|-------|-------|--------|-------|------|-------|
| Ginger nut   | 0.90  | 1.49  | 6.44   | 22.06 | 0.11 | 0.98  |
| Aga soil     | 0.32  | 1.10  | 4.23   | 16.37 | 0.08 | 0.85  |

| Sample       | CaO   | Fe₂O₃ | TiO₂   | MnO   | CO₂  | Total |
|--------------|-------|-------|--------|-------|------|-------|
| Ginger nut   | 36.82 | 2.07  | 0.35   | 0.08  | 28.60| 99.90 |
| Aga soil     | 41.87 | 0.87  | 0.21   | 0.02  | 34.07| 99.99 |

**Table 3 XRD analysis results of ginger nut and aga soil**

| Results | Analysis result of half quantitative/% |
|---------|---------------------------------------|
| Quartz  | 12.6                                  |
| Calcite | 61.8                                  |
| Feldspar| 10.9                                  |
| Clay    | 14.7                                  |
| Ginger nut | 10.5                                  |
| Aga soil  | 75.1                                  |
|          | 11.2                                  |
|          | 3.0                                   |
The condition of calcined Aga soil is similar to calcined ginger nut. At 700°C ginger nut produces 13.3% $\beta$-CaSiO$_3$ and 10.6% Ca$_2$Al$_2$SiO$_7$ with no CaO produced. At 800°C, it produces 32.1% CaO, two times of that produced by ginger nut at the same temperature. The main reason is that Aga soil has a larger amount of CaCO$_3$ than ginger nut and has half amount of SiO$_2$ compared with ginger nut, which is useful for producing CaO. At the temperature ranges from 800°C to 1100°C and from

![Figure 1 XRD spectra of ginger nut calcined at 700°C ~1400°C and comparison of products (1-CaCO$_3$; 2-SiO$_2$; 3-CaO; 4-$\beta$-CaSiO$_3$; 5-Ca$_2$Al$_2$SiO$_7$).](image1)

![Figure 2 XRD spectra of Aga soil calcined at 700°C ~1400°C and comparison of products (1-CaCO$_3$; 2-SiO$_2$; 3-CaO; 4-$\beta$-CaSiO$_3$; 5-Ca$_2$Al$_2$SiO$_7$).](image2)
1100°C to 1400°C, CaO decreases in amount from 44.6% to 33.9%, but not so obviously as ginger nut. The speed of producing $\beta$-CaSiO$_3$ and Ca$_2$Al$_2$SiO$_7$ increases, but it is not so quickly as ginger nut. $\beta$-CaSiO$_3$ increases from 30.1% to 40.6% and Ca$_2$Al$_2$SiO$_7$ increases from 19.2% to 25.4%. The reason is the same as stated above that Aga soil has less amount of SiO$_2$ and larger amount of CaCO$_3$ than ginger nut.

The chemical properties of calcined ginger nut and Aga soil

XRD and SEM were used to analyze ginger nut and Aga soil calcined for three hours at 1000°C and then analyze and study the process of their hydration and carbonization.

**XRD analysis**

Figures 5 and 6 are XRD spectra of calcined ginger nut and Aga soil at 1000°C together with their products of hydration and carbonization.

The results of XRD analysis shows the ginger nut calcined for three hours at 1000°C includes 39.20% CaO, 26.70% $\beta$-CaSiO$_3$ and 18.90% Ca$_2$Al$_2$SiO$_7$ before hydration (Figure 5A). When hydrated in a relative humidity of 80%, it will produce 32.6% CaCO$_3$, 22.7% Ca(OH)$_2$ and 21.6% Ca$_2$Al$_2$SiO$_7$·nH$_2$O (Figure 5B) after five days. After 300 days, it will produce 86.2% CaCO$_3$ and 3.2% Ca$_2$Al$_2$SiO$_7$·nH$_2$O on the surface of samples, and at the depth of 2-3 mm of the samples it produces 54.6% CaCO$_3$, 2.1% Ca(OH)$_2$, 22.6% CaSiO$_3$·nH$_2$O and 13.2% Ca$_2$Al$_2$SiO$_7$·nH$_2$O.

When Aga soil is burned for three hours at 1000°C, it will produce 42.50% CaO, 29.40% $\beta$-CaSiO$_3$ and 18.00% Ca$_2$Al$_2$SiO$_7$ (Figure 6A). Hydrated in 80% relative humidity, it will produce 47.6% CaCO$_3$, 13.1% Ca(OH)$_2$ and 16.7% Ca$_2$Al$_2$SiO$_7$·nH$_2$O (Figure 6B) after five days. Three hundred days later, on the surface of the samples it produces 74.2% CaCO$_3$, 24.6% Ca(OH)$_2$, 5.3% $\beta$-CaSiO$_3$·nH$_2$O.

When Aga soil is burned for three hours at 1000°C, it will produce 42.50% CaO, 29.40% $\beta$-CaSiO$_3$ and 18.00% Ca$_2$Al$_2$SiO$_7$ (Figure 6A). Hydrated in 80% relative humidity, it will produce 47.6% CaCO$_3$, 13.1% Ca(OH)$_2$ and 16.7% Ca$_2$Al$_2$SiO$_7$·nH$_2$O (Figure 6B) after five days. Three hundred days later, on the surface of the samples it produces 74.2% CaCO$_3$, and at the depth of 2-3 mm produced 48.4% CaCO$_3$, 24.6% Ca(OH)$_2$, 5.3% $\beta$-CaSiO$_3$·nH$_2$O.

XRD semi-quantitative analysis verifies that after being calcined for three hours at 1000°C, ginger nut and Aga soil at 80% relative humidity have large speeds of hydration and carbonization. Five days
later, they respectively produce 32.6% and 47.6% CaCO₃, 22.7% and 21.6% Ca(OH)₂ and 16.7% Ca₂Al₂SiO₇·nH₂O. Three hundred days later, calcined ginger nut and Aga soil samples have a 3 mm depth of carbonized layer and produce 86.2% and 74.2% CaCO₃ respectively. At 3 mm depth, it generates 54.6% and 48.4% CaCO₃. Calcined ginger nut is carbonized more quickly than Aga soil.

**SEM-EDS analysis**

Figures 7 to 11 are SEM photos and EDS spectra of burned ginger nut and Aga soil and their products of hydration and carbonization.

SEM photos show that ginger nut and Aga soil calcined for three hours at 1000°C produce fine crystal aggregates of CaO, β-CaSiO₃ and Ca₂Al₂SiO₇ (Figure 7a and b). Five days later after hydration, the sample of calcined ginger nut produces little re-crystals CaCO₃ and crystal aggregates β-CaSiO₃ and Ca₂Al₂SiO₇. On the surface of calcined Aga soil, re-crystals CaCO₃ is produced (Figures 8a and 10a), and at the deep layer, the calcined ginger nut produces little crystals β-CaSiO₃·nH₂O and Ca₂Al₂SiO₇·nH₂O encircled by large quartz particles. The deep layer of Aga sample produces little re-crystals CaCO₃, crystals β-CaSiO₃·nH₂O and Ca₂Al₂SiO₇·nH₂O (Figures 8b and 10b). Three hundred days later after hydration, both of calcined ginger nut and Aga soil on the surface form a lot of compact re-crystals CaCO₃ (Figures 9a and 11a), and at their deep level it forms little re-crystals CaCO₃ and a lot of crystals β-CaSiO₃·nH₂O and Ca₂Al₂SiO₇·nH₂O (Figures 9b and 11b). Moreover, in the process of hydration Ca(OH)₂ will be produced, and it will gradually adsorb CO₂ generate CaCO₃.
Discussion

More than five thousand years ago in China, calcined ginger nut had been used as building material for building floors during the Yangshao Period. In Tibet, Aga soil had been used as a building material of temple floors and roofs for over one thousand years. Ginger nut can be also called clay limestone and Aga soil called silicious limestone. The contents of clay and SiO$_2$ in ginger nut and Aga soil differ from those from different regions. But whatever the contents of clay and SiO$_2$ in them, the raw ginger nut and Aga soil will not produce the binding materials and are not suitable for being used as building materials without being calcined. The percentages of silicon and clay in ginger nut and Aga soil decide the contents of non-hydraulicity and hydraulicity in the binding materials produced by high temperature calcination and also influence the properties of ginger nut and Aga soil calcined at different temperatures.

The above research proves that ginger nut from Qin’an Dadiwan of Gansu and Aga soil from Shan’nan in Tibet are calcined for three hours at eight temperatures from 700°C to 1400°C, and their products non-hydraulic material CaO and hydraulic materials $\beta$-CaSiO$_3$ and Ca$_2$Al$_2$SiO$_7$ change regularly in ratio. Their properties differ slightly because of their different ratios. For example, if there are much larger hydraulic components, the strength of materials grows faster at early stage and it will combine with the body of cultural relics repaired. But the main defect is the low porosity of cementitious materials formed, thus the material show bad air and water permeabilities. Influenced by temperature and humidity, the repairing materials will detach from the body of the restored relics in a short period (generally 3 to 5 years). So this material has bad durability. If the non-hydraulic components increase a little more, the strength of materials will grow slowly, and the repairing
material can’t combine with the relics in a short time and thus affect the results of restoration.

Calcined ginger nut and Aga soil have a key characteristic in repairing stone relics, namely CaO will combine with water to generate gel Ca(OH)$_2$, which then reacts with CO$_2$ and H$_2$O in the air to gradually produce large porosity gel CaCO$_3$. This process is called self-repairing effect of hydraulic limestone [8-14] by European scholars. Although the carbonization of non-hydraulic constitute is slow, the whole process of carbonization begins from the surface and extends in depth. When relative humidity in the environment is 80%, the hydration and carbonization will be fast on the surface and then become slowly in the depth because CO$_2$ is much less. Just because of this, CaCO$_3$, the gel with big porosity and good water permeability, will be produced during the slow carbonization process. The CaCO$_3$ produced from fast carbonization on the surface is complementary to the strength of the $\beta$-CaSiO$_3$·nH$_2$O and Ca$_2$Al$_2$SiO$_7$·nH$_2$O produced from fast hydration of hydraulic constituent sand therefore can meet the requirements for relics restoration. Then the gradual carbonization of this gel will make it tightly combined with the relics, creating good weathering resistance. Conservators in Europe had found the advantages of the binding material (hydraulic lime) calcined by clay limestone and siliceous limestone in the restoration of stone relics. In 1970s, they had used binding materials similar to Chinese ancient calcined ginger nut in the restoration of stone relics and obtained good conservation results [15-23]. They pointed out that hydraulic lime stone “has specific usefulness that can’t be replaced by concrete and non-hydraulic lime particularly in the restoration of ancient or old buildings” [24].

Calcined ginger nut had been used as the binding materials in the building floors of the Dadiwan site in Gansu Qin’an during the Yangshao Period. No matter what

Figure 8 SEM photos and EDS spectra of ginger calcined in 1000°C after hydration and carbonization for five days. a. The forming of minor calcium carbonate re-crystalline on the surface, and the aggregate with calcium silicate and aluminum calcium silicate crystal. b. The forming of minor hydrated calcium silicate in the deep layer, and the crystal of hydrated aluminum calcium silicate covering big quartz particles.
percentage of CaO, $\beta$-CaSiO$_3$ and Ca$_2$Al$_2$SiO$_7$ was in calcined ginger nut, for thousands of years, the site of housing was buried under loess of farm land of hillside. Non-hydraulic and hydraulic materials mainly changed into porous CaCO$_3$ through their interaction with CO$_2$ and H$_2$O. So after more than five thousand years, F-901 floor material at Dadiwan is similar to modern No. 100 cement mortar floor in compressive strength. However for centuries, the Aga soil used in Tibetan building floors and roofs was never burned at high temperature. This material didn’t include non-hydraulic binding material and hydraulic material, thus this building material had low strength and poor weathering resistance. The roofs of temples have to be restored once in three to five years, not only involving a lot of work and time, and but also increasing cost and damages. Preliminary tests demonstrate the floor and roof material added with powder of 30% calcined Aga soil as binding material can obviously improve the strength and weathering resistance of materials.

**Conclusion**

The following conclusions can be reached through the above tests and discussion:

(1) By controlling the calcining temperature and selecting ginger nut and Aga soil with proper amounts of clay and SiO$_2$, binding materials which contain non-hydraulic material CaO and hydraulic materials $\beta$-CaSiO$_3$ and Ca$_2$Al$_2$SiO$_7$ in various ratios can be made.

(2) The ginger nut from Qin’an in Gansu will produce about 39.2% CaO, 45.6% $\beta$-CaSiO$_3$ and Ca$_2$Al$_2$SiO$_7$ if calcined for three hours at 1000°C, while the Aga soil in Tibetan Shan’nan will produce about 42.5% CaO, 47.4% $\beta$-CaSiO$_3$ and Ca$_2$Al$_2$SiO$_7$ after being calcined for three hours at 1000°C.
(3) As calcining temperature rises (700°C~1400°C), non-hydraulic constitutes will reach the peak point at 1100°C and then drop to the bottom point at 1400°C, and hydraulic constitutes will keep rising to the peak point at 1400°C.

(4) Calcined ginger nut and Aga soil in the environment of 80% relative humidity have a faster speed of hydration and carbonization. After five days hydration, calcined ginger nut will produce 32.6% CaCO$_3$ and 21.6% Ca$_2$Al$_2$SiO$_7$·nH$_2$O; while calcined Aga soil will produces 47.6% CaCO$_3$ and 16.7% Ca$_2$Al$_2$SiO$_7$·nH$_2$O. Three hundred days later after hydration and carbonization, the thickness of carbonization on sample surface reaches 3 mm with 80% CaCO$_3$ produced. Even under the depth of 3 mm, it also produces 50% CaCO$_3$, 34% β-CaSiO$_3$·nH$_2$O and Ca$_2$Al$_2$SiO$_7$·nH$_2$O.

(5) Controlling the ratio of non-hydraulic constitutes CaO, hydraulic constitutes β-CaSiO$_3$ and Ca$_2$Al$_2$SiO$_7$ in binding materials can not only adjust its early strength but also form the calculus of large porosity, good weathering resistance and high strength in the process of slow ‘carbonization’ that will firmly integrate with the stone relics and meet the requirements of conservation and consolidation of cultural relics.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
The work presented here was carried out in collaboration between all authors. LZ and ZL defined the research theme. LZ, ZL, LL and WJ designed methods and experiments, carried out the laboratory experiments, analyzed the data, interpreted the results and wrote the paper. All authors have contributed to, seen and approved the manuscript.

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Figure 11 SEM photos and EDS spectra of Aga soil calcined in 1000°C after hydration and carbonization for 300 days. a. The forming of a large number of calcium carbonate re-crystalline on the surface. b. The forming of minor calcium carbonate re-crystalline, and a large number of hydrated calcium silicate and hydrated aluminum calcium silicate crystal in the deep layer.
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