

Archeology and Conservation

THERMAL BEHAVIOUR OF LIMESTONE AND MONOCRYSTALLINE CALCITE TEMPERS DURING FIRING AND THEIR USE IN ANCIENT VESSELS

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Limestone and monocrySTALLINE calcite tempers (grains) are abundant in ancient pottery. In pottery from the Canaan area the former is common in Iron Age storage and table-ware vessels and the latter is present in cooking pots. Limestone is much more widespread than monocrySTALLINE calcite and the potters used it often as tempers when manufacturing pottery vessels, but usually not for cooking pots. While defects appear frequently around limestone tempers, they do not appear around monocrySTALLINE calcite ones. This study examines the reason for using the latter tempers rather than the former ones.

Raw materials of carbonate tempers in a clay matrix were fired and the decarbonation process was followed by quantitative IR thermospectrometry. The results indicate that the monocrySTALLINE calcite tempers prevent formation of defects in the cooking pots during firing or during use. The reasons for this are higher thermostability at elevated temperatures, lower intensity of decarbonation, and retention of grain shape, as compared to limestone tempers.

Keywords: ancient vessels, limestone, monocrySTALLINE calcite

Introduction

The use of limestone and monocrySTALLINE calcite tempers in ancient and traditional pottery production is well known [1, 2]. Potters in Ticul, Yucatan, selected pure crystalline calcite as a temper for fired cooking vessels while rejecting limestone composed of crypto-crystalline calcite [2]. The latter materials were used

only as a temper for non-cooking vessels. Although potters may not be able to provide a scientific explanation for the superior quality of crystalline calcite for cooking pots, it is obvious that its behavioural characteristics have long been known [2].

This paper examines the reason for the advantage of using monocrystalline calcite rather than polycrystalline calcite limestone tempers for the manufacture of ancient pottery vessels. The thermal decarbonation process has been intensively studied in pure calcite [3] and in its mixtures with clay [4–8]. This investigation has concentrated on the thermal behaviour of carbonate tempers in pottery raw materials. Natural monocrystalline calcite, limestone and chalk were heated as tempers in a clay matrix to various temperatures for extended firing times.

Experimental

Samples

Carbonate tempers in Iron Age cooking pots, storage and tableware vessels were examined. Most of the pottery samples were taken from Tel-Haddar, excavated in the framework of 'Land of Gashur Archaeological Project' [9].

Different limestones, chalks and natural monocrystalline calcite, which could have been potential sources for pottery tempers in ancient times were collected and analysed. Samples of limestones and chalks were taken from carbonate rock formations. Samples of monocrystalline calcite were taken from secondary calcite druses and veins found in these rocks. Clays used for the matrices were local kaolinite and smectite.

Methods

Petrographic analyses of thin sections of the carbonate tempers in the pottery were made using a polarizing microscope.

The thermal decomposition of the carbonate tempers in the clay matrix during firing was examined by FT-IR thermospectrometry, using a Nicolet ZDX FT-IR spectrometer. Disks were prepared using 1 mg of the sample and 150 mg of KBr [10].

Pottery raw materials were prepared from mixtures containing 1:1 proportions of carbonate grains of temper sizing with local kaolinite or smectite clay. The raw mixes were heated in an electric kiln under oxidizing conditions at various temperatures and for different times to replicate actual firing conditions. After heating, the carbonate grains and clay matrix were homogenized by grinding and shaking, and then examined by IR spectroscopy. Ratios of CO₃ and SiO main

bands of carbonate tempers and fired clay matrix, respectively, were calculated from the IR spectra using integrated area measurements.

Results

Pottery

The Iron Age storage and table-ware vessels show, in many cases, defects concentrated around the limestone tempers. Those defects were not usually present around the monocrystalline calcite tempers of the cooking pots. Defects in the form of split craters that formed on the surface above the limestone tempers of a storage jar sherd are shown in Fig. 1.

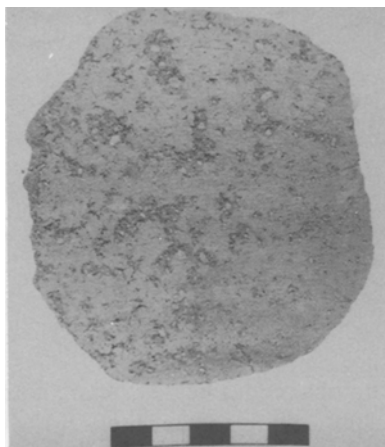


Fig. 1 Defects in the form of splitting crater on the surface above the limestone tempers of storage jar sherd, Tel-Haddar

Representative thin-section micrographs of a cooking pot sherd containing calcite tempers and a storage jar sherd containing limestone tempers are shown in Fig. 2. Petrographic analysis showed that calcite tempers often occurred as transparent single crystals or several large crystals. Many of the limestone tempers had microcrystalline (micrite) textures.

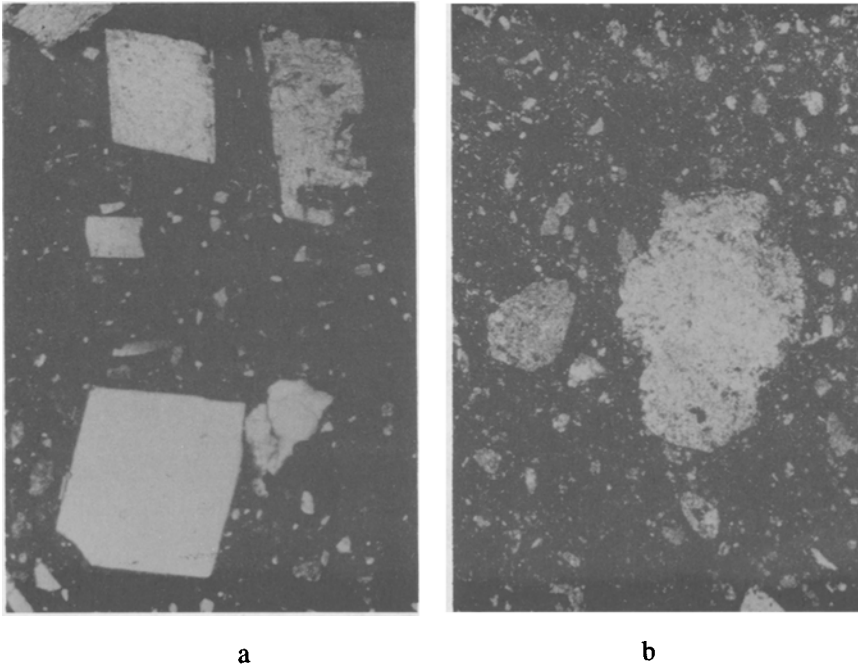


Fig. 2 Thin-section micrographs of (a) cooking pot containing calcite tempers, (b) storage jar containing limestone tempers, Tel-Haddar

Thermal analysis

Representative IR spectra of samples heated for six hours at various temperatures and after heating at 700°C for different times are shown in Figs 3 and 4, respectively.

The main CO_3 band of the partly decarbonated samples is located at about 1425 cm^{-1} . The main CaO band of the decarbonated product occurs below 400 cm^{-1} . An OH-stretching band of $\text{Ca}(\text{OH})_2$, formed by the reaction of CaO with atmospheric water vapour during disk preparation, appears at 3645 cm^{-1} . The main SiO band of the fired clay is located in the $1035\text{--}1095\text{ cm}^{-1}$ region. The sequence of spectra show that the main CO_3 bands decrease relative to the main SiO band with increasing temperatures and heating time.

After heating the carbonate tempers in the clay matrices for six hours the following processes were observed (Fig. 3).

- At 600°C a weak decarbonation starts in the limestone and monocrystalline calcite. The decarbonation of chalk is almost complete.
- At 650°C the decarbonation of limestone is almost complete.

- At 700°C the chalk and limestone are totally decarbonated and most of the material has crumbled. In contrast, the calcite grains are only partly decarbonated and still retain their original shape.

- At 750°C the decarbonation process of the calcite grains is complete or almost complete but their shape is still retained.

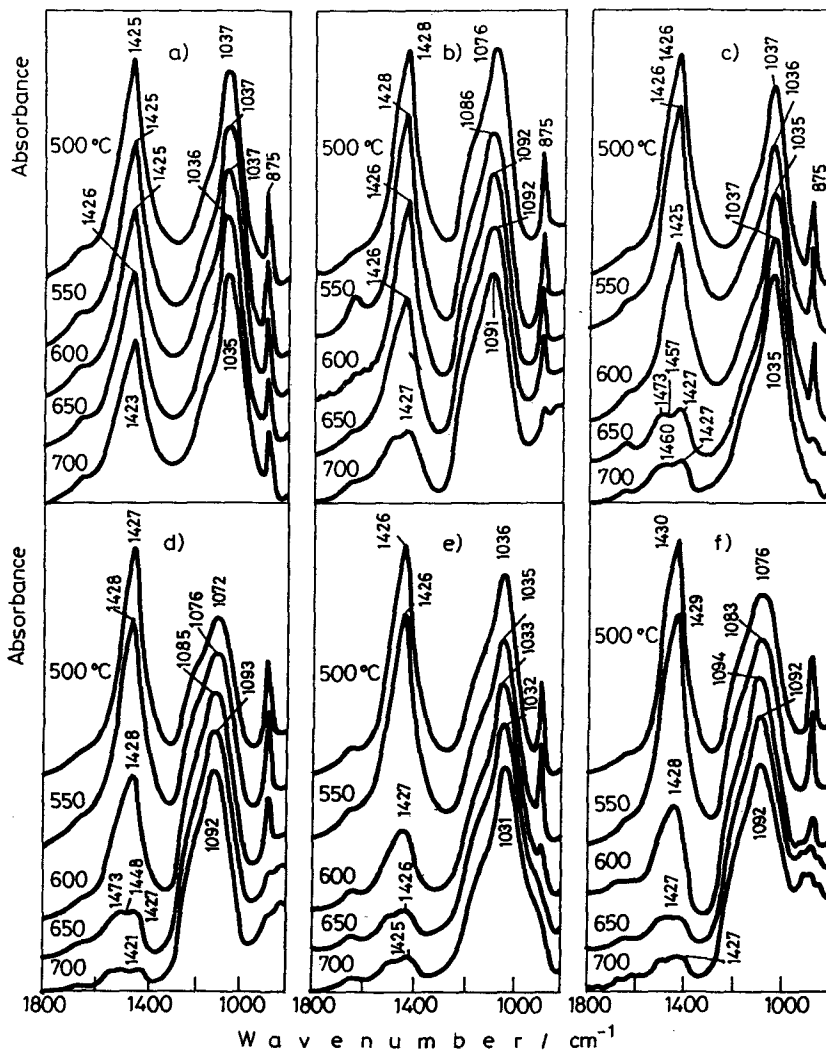


Fig. 3 Representative IR spectra of carbonate tempers in fired clay matrix after heating for six hours at various temperatures: (a) monocrystalline calcite in smectite matrix; (b) monocrystalline calcite in kaolinite matrix; (c) limestone in smectite matrix; (d) limestone in kaolinite matrix; (e) chalk in smectite matrix; (f) chalk in kaolinite matrix

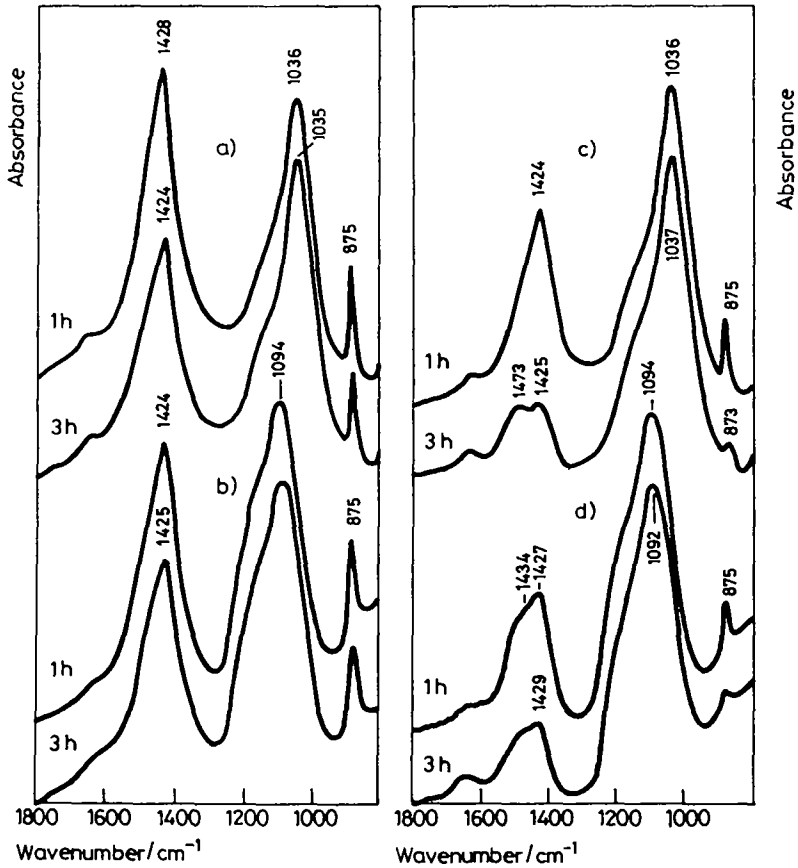


Fig. 4 Representative IR spectra of carbonate tempers in fired clay matrix after heating at 700°C for one and three hours: (a) monocrystalline calcite in smectite matrix; (b) monocrystalline calcite in kaolinite matrix; (c) limestone in smectite matrix; (d) limestone in kaolinite matrix. The chalk was totally decarbonated under these conditions and is not shown

At elevated temperatures the decarbonation process in the kaolinite matrix was more intensive than in the smectite matrix. Decarbonation of chalk was accompanied by the formation of small amounts of high-temperature Ca-silicates. Before heating, the chalk contained an insignificant amount of clay and siliceous impurities.

Discussion

Limestone and monocrystalline calcite tempers

Monocrystalline calcite tempers are very common in Iron Age cooking pots from the Canaan area [11]. Petrographic examination shows that these tempers are angular fragments, poorly sorted, broken along their cleavage planes, and often rhomb-shaped (Fig. 2a). These features indicate that they were crushed and added as tempers to the raw clay material during production [1]. Crystalline calcite is not commonly found and potters went to great lengths to find and collect this. On the other hand, limestone is much more widespread and potters often used it as tempers for pottery vessels, but not usually for cooking pots. In vessels containing limestone tempers many defects occur around the tempers (Fig. 1), but such defects do not appear around crystalline calcite tempers.

It has been assumed [2] that calcite tempers prevent fracturing and formation of defects due to thermal shock during rapid heating or cooling of the vessels because the thermal expansion coefficient of calcite is similar to that of the surrounding clay. However, many limestones are composed mainly of polycrystalline calcite and both tempers would be expected to have similar thermal expansion coefficients. Therefore, there could be another reason for the advantage of monocrystalline calcite tempers over limestone ones for manufacture of pottery vessels.

Limestone and monocrystalline calcite thermal behaviour

Carbonate tempers create problems for potters due to their thermal decomposition, which causes formation of defects and porosity in the vessels. According to the present results (Table 1, Fig. 3), after six hours heating in clay matrices a weak decarbonation process starts at about 600°C in both limestone and monocrystalline calcite, and increases above this temperature. This process was completed at about 650°C in the limestone tempers, with most of them crumbling, while decarbonation was prolonged to about 750°C in the calcite tempers and their original shape was retained. Under the same conditions the chalk showed earlier decarbonation, which was completed by at 600°C. Traces of CO₃ bands in the spectra at elevated temperature appear to be due to recarbonation after heating.

In all carbonate temper types, decarbonation was complete at relatively low temperatures due to the long heating times, presence of impurities, and influence of the clay matrix.

The carbonate tempers examined are represented by three degrees of crystallinity: monocrystalline calcite, sparry calcite (sparite) of the limestone and microcrystalline calcite (micrite) of the chalk. Chalk and limestone composed of

polycrystalline calcite decomposed earlier. The latter have larger specific areas and, frequently, more crystalline defects and impurities than monocrystalline calcite, which lead to earlier intensive thermal decarbonation.

The presence of clay reduces the decarbonation temperature in mixtures of calcite and clays [4–8], and in marl rocks composed of those components [12]. Internal clay impurities within the carbonate temper may stimulate earlier decarbonation depending on the amount of clay. It appears that both the crystal size and the presence of clay and siliceous matter impurities in the chalk are responsible for its earlier decarbonation, which is accompanied by the formation of small amounts of high-temperature silicates. On the other hand, the external clay matrix surrounding the carbonate tempers in the ceramics appears to have less influence on decarbonation, since the contact between them is only at grain surfaces. The present results show that at elevated temperatures a kaolinite matrix influences this process more than a smectite matrix.

Table 1 Relative ratios of CO₃ and SiO main bands of carbonate tempers and fired clay matrix, respectively, after heating for six hours at various temperatures

Temper samples	Relative ratios of CO ₃ and SiO main bands						
	500°	550°	600°	650°	700°	750°	800°
Calcite* tempers in smectite matrix	0.70	0.67	0.58	0.55	0.48	0.18	TR
Calcite* tempers in kaolinite matrix	0.67	0.67	0.57	0.49	0.22	0.10	TR
Limestone tempers in smectite matrix	0.93	0.90	0.79	0.19	0.12	TR	
Limestone tempers in kaolinite matrix	1.02	0.87	0.85	0.18	0.09	TR	
Chalk tempers in smectite matrix	0.74	0.70	0.19	0.09	0.07	TR	
Chalk tempers in kaolinite matrix	0.85	0.81	0.33	0.13	0.10	TR	

*Monocrystalline ; TR= Traces

The decarbonation temperature is also affected by the amount of carbon dioxide present during firing. However, ancient firing techniques allowed little control of the firing atmosphere.

Defect formation in vessels due to thermal decomposition

It appears that the defects formed in the vessels by the thermal decomposition of the carbonate tempers resulted from mechanical damage that took place during or after firing.

This damage could occur during firing as a result of CO₂ pressure. Large amounts of CO₂ are released rapidly, which leads to grain splitting, removal of crystalline boundaries, and crumbling of crystals. As a result, blowing and frac-

tures can occur, generating defects in the vessels, which is characteristic of limestone tempers.

On the other hand, monocrystalline calcite is stable to higher temperatures, the intensity of decarbonation is weaker and the grain shape is retained, which prevents formation of defects in the cooking pots.

Additional damage could occur after firing as result of stress due to the crystallization process in the decarbonated tempers followed by their expansion. The specific volume of the CaO decarbonation product is less than that of calcite [13]. But, after firing, CaO may react with water or with atmospheric water vapour resulting in Ca(OH)₂ formation. The latter occupies a considerably greater volume in the pottery than the original calcite. The result is spalling at best, or severe cracking and crumbling at worst [2]. At identical firing temperatures, larger amounts of CaO followed by Ca(OH)₂ are formed in limestone tempers than in calcite tempers. Therefore, this kind of damage could be more intensive with limestone tempers. With time Ca(OH)₂ reacts with CO₂ from the air and recarbonated calcite is formed.

Recarbonated calcite usually recrystallizes with a low degree of crystallinity [14] and has a microcrystalline texture (micrite). Nevertheless, petrographic analyses of many thin sections of cooking pots showed that the calcite temper was transparent and exhibited behaviour of a single crystal or of several large crystals. These features may indicate that the monocrystalline calcite temper was not totally decomposed at the firing temperature and that the partly decomposed calcite was reconstructed almost to the original form of a single crystal. This indicates that, in such cases, the firing temperatures of the vessels were below that of total decomposition of the calcite. Another possibility is that the monocrystalline calcite temper was totally decomposed at the firing temperature, but that its original shape was retained and the decomposition product remained undisturbed inside the clay matrix, allowing the decomposed calcite to be recarbonated and reconstructed almost to its original form without causing damage to the vessels.

Importance of monocrystalline calcite tempers for manufacture of cooking pots

Two main types of raw materials were used for the clay component of Iron Age pottery from Canaan area: calcareous and non-calcareous clays. Non-calcareous clays were preferred for cooking pots and calcareous ones for storage and tableware vessels [15, 16]. Each of these raw materials has certain advantages. The calcareous clay contains lime as a flux, and vessels prepared from such a clay sinter at lower temperatures. Therefore, this raw material was preferred for storage and tableware vessels. For cooking pots, on the other hand, a clay material that is not permeable and is stable under repeated heating and cooling and in direct contact with fire is needed. For these properties, non-calcareous clays were used. The use of non-calcareous clays led to the need for a flux, and it

appears that carbonate tempers were used for this purpose. Since the use of limestone tempers is accompanied by the formation of defects, it is inappropriate for cooking pots, and a special carbonate temper was needed. This seems to explain why the potters went to great efforts to obtain the rarely found calcite material which they used for a temper.

Conclusions

Quantitative investigation of the thermal decomposition processes of natural monocrystalline calcite, limestone and chalk, heated in clay matrices for long times revealed differences in decarbonation temperatures and intensity.

The results demonstrate that the advantages of crystalline calcite over limestone and chalk tempers are their stability at higher temperatures, lower intensity of decarbonation process and retention of grain shape, which prevent formation of defects in the vessels. These properties are especially important for cooking vessels.

Knowledge of the tempers needed for different raw materials and their use according to their specific advantages for the preparation of different types of domestic vessels is an indication of the sophistication of the ancient potters.

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Zusammenfassung — In alten Töpferwaren werden reichlich Kalkstein und monokristalline Kalzitmischungen gefunden. Bei Töpferwaren aus dem Gebiet Canaan ist ersteres bei Vorrats- und Tischgeschirrgefäßen, letzteres bei Kochtöpfen üblich. Kalkstein ist weitverbreiteter als monokristallines Kalzit und es wurde von den Töpfern bei der Fertigung von Töpfereigefäßen oft als Mischung eingesetzt, jedoch nicht für Kochgeschirr. Während Defekte oft an Kalksteinmischungen auftreten, kommen sie an monokristallinen Kalzitmischungen nicht vor. In dieser Arbeit wird der Grund dafür gesucht, daß die letzteren Mischungen den ersteren vorgezogen wurden.

Rohmaterialien aus Karbonatmischungen wurden in einer Tonmatrix gebrannt und der Dekarbonierungsprozeß mittels IR Thermospektrometrie verfolgt. Die Resultate zeigen, daß monokristalline Kalzitmischungen beim Brennen oder bei der Benutzung die Bildung von Defekten bei Kochgeschirr verhindern. Die Gründe dafür liegen – verglichen mit Kalksteinmischungen – in der höheren Thermostabilität bei erhöhten Temperaturen, in der weniger intensiven Dekarbonierung und in der Beibehaltung der Gefügestruktur.