

Analysis of thermal phases in calcareous Iron Age pottery using FT-IR and Raman spectroscopy

Shlomo Shoval · Ester Yadin · Gerard Panczer

Cultural Heritage Special Chapter
© Akadémiai Kiadó, Budapest, Hungary 2011

Abstract The work deals with the FT-IR and micro-Raman spectroscopy study of the pseudo-amorphous and crystalline thermal phases in the composition of calcareous Iron Age pottery from the Galilee. The application of second-derivative and curve-fitting techniques improves the identification of the thermal phases in the composition of the pottery and makes it possible to analyze the pseudo-amorphous phases which are formed during the firing of the clayey raw material to pottery. This technique makes it possible to distinguish between meta-smectite and meta-kaolinite and to estimate the firing temperature of the pottery. The Micro-Raman spectroscopy is sensitive to the structural degree of ordering of the thermal phases and enables point analysis of peculiar components in the composition of the pottery. Based on the spectroscopic study, it is concluded that the calcareous pottery contained large amounts of microcrystalline-recarbonated calcite mixed with the meta-clay. The large amount of recarbonated calcite in the pottery material and the relatively low firing temperature indicates that instead of sintering the clay, lime technology was used for the cementation of the calcareous vessels. This process took place after the firing

by recarbonation of the decomposed calcite which leads to cementation of the vessels with microcrystalline calcite.

Keywords Ceramic · Curve fitting · Firing temperature · Gehlenite · Iron Age · Meta-smectite · Meta-kaolinite · Recarbonated calcite · Recarbonation · Rehydroxylation · Second derivative · Spectra

Introduction

Iron Age pottery from an archeological site in the Galilee was analyzed [1]. The pottery was excavated at Tel-Hadar, on the eastern shore of the Sea of Galilee. The excavation was carried out in the framework of the Land of Geshur Archaeological Project of the Institute of Archaeology, Tel Aviv University [2]. The calcareous pottery was found in a storage room of a pillared building from the eleventh century B.C. Figure 1 shows some of the pottery studied. Calcareous pottery is recognized by its light color, thick walls, low-fired fabric, and large amount of calcite in its composition. These vessels were produced for daily use and comprise storage jars and tableware vessels, excluding cooking pots.

Spectroscopic study of ancient pottery

FT-IR spectroscopy is a useful method for mineralogical analysis of pottery and this method has been used by us for investigation of pottery since 1991 [3–8]. The FT-IR spectroscopy was applied mainly for the identification of crystalline phases in the composition of the pottery [9–11]. The identification of the thermal phases by IR spectroscopy is based on their indicative bands in the spectra [12]. Furthermore, this method is advantageous in identification of pseudo-amorphous and short-range ordered thermal

S. Shoval (✉)
Geology Group, Department of Natural Sciences, The Open
University of Israel, The Dorothy de Rothschild Campus,
1 University Road, POB 808, Raanana, Israel
e-mail: shovals@openu.ac.il

E. Yadin
Institute of Archaeology, Tel-Aviv University, Tel-Aviv, Israel

G. Panczer
LPCML, UMR 5620 CNRS, Claude Bernard University, Lyon 1,
43 boulevard du 11 Novembre 1918, 69622 Villeurbanne cedex,
France



Fig. 1 Some of the pottery studied. The pottery was excavated at Tel Hadar in the framework of the Land of Geshur Archaeological Project [2]

phases, which lack XRD (X-ray diffraction) peaks [7]. In the present study, FT-IR spectroscopy is used for identification of the pseudo-amorphous thermal phases as well as the crystalline minerals in the composition of the pottery. The IR spectra of the pottery exhibit broad maxima of mixtures of phases whose bands overlap partially and appear as asymmetric bands and as shoulders. The use of second derivatives of the IR spectra enables the separation of partly overlay bands and thus improvement in the identification of the individual phases in the composition of the pottery [8, 9]. Curve-fitting technique is also applied for spectral analysis [13, 14].

Micro-Raman spectroscopy enables point analysis of peculiar components in the composition of the pottery [15]. This technique was applied mainly for the identification of minerals such as quartz, hematite, anatase, and feldspar [16, 17], and for examination of binders and pigments in the decoration of the vessels [15]. Moreover, this method is advantageous in the sensitivity to the degree of ordering of the thermal phases [14].

Firing of calcareous raw material to pottery

Two main types of raw materials were used in manufacture of ancient pottery, calcareous, and non-calcareous clays [1, 6]. Each of them has different advantages for pottery production. The thermal phases formed during firing of clayey raw material to pottery have been the subject of many studies. In firing of non-calcareous kaolinitic raw material, the kaolinite dehydroxylates mostly at about 450 °C and a pseudo-amorphous phase of meta-kaolinite is formed [6, 7]. The reaction from meta-kaolinite to mullite is undergone through short-range thermal phases [14]. The intermediary phases in this process have been described as defect Al-spinel or γ -alumina phase and poorly crystallized

cubic mullite. Al-spinel phase is detected at about 900 °C [14]. The formation of well-crystallized phases of mullite is observed at about 1,200 °C. In firing smectitic (montmorillonitic) clay, the smectite dehydroxylates mostly at about 600 °C, and with increasing temperature meta-smectite is formed [6]. The major phases formed by the heating of smectite have been identified as meta-smectite, spinel, mullite, cordierite, and cristobalite [18]. Over time, some rehydroxylation of the meta-clay within the fired material takes place and rehydroxylated clay is reconstructed in the pottery material [3].

In firing of calcareous raw material composed of a mixture of clay minerals and microcrystalline calcite, the calcite decomposes above 600 °C, carbon dioxide gas (CO₂) is released, and free-lime (CaO) is formed [4]. This earlier decarbonation temperature of the calcite is due to the microcrystalline structure of the calcite in the calcareous raw material, the presence of clay, and the extended firing duration. In parallel, dehydroxylation of the clay to form the pseudo-amorphous phase of meta-clay takes place [19]. In firing of calcareous kaolinitic raw material above 900 °C, the free-lime reacts with the meta-kaolinite and gehlenite is formed [19, 20]. At higher temperatures, plagioclase-anorthite is crystallized [19–21]. In progressive firing, calcareous smectitic clay larnite and β -wollastonite are formed. After the firing, recarbonation of the non-reacted free-lime takes place by the reaction with vapor and carbon dioxide from the air and recarbonated calcite is formed in the pottery material [4, 22].

In the present work, we applied FT-IR and Micro-Raman spectroscopy methods in analysis of the thermal phases in the composition of calcareous pottery. The use of FT-IR spectroscopy has advantages in identification of amorphous and short-range ordered thermal phases, which are unsuccessfully observed by XRD. Curve-fitting and second-derivative techniques are applied for improvement of the identification. The Raman response is sensitive to the degree of crystallinity of the thermal products. The firing temperature and the advantage of using calcareous raw materials in the manufacture of ancient pottery are discussed.

Materials and methods

Pottery

Iron Age pottery was excavated from Tel-Hadar [2]. A list of the pottery investigated is shown in Table 1. Ancient pottery usually contains temper particles within the ceramic material. The analysis was applied on the pottery material after separation of the temper particles under binocular microscope. The temper particles were examined separately.

Table 1 A list of the investigated Iron Age pottery excavated from Tel-Hadar

Type	Pottery number and excavation number			
Jars	TH-3 1734/2	TH-4 1809/1	TH-11 1823/1	TH-16 1873/1
Jars	TH-18 1810/1	TH-20 1757/1	TH-24 1562/1	TH-28 1783/2
Jars	TH-29 2290/1	TH-30 1783/1	TH-200 1834/1	TH-202 1277/1
Jars	TH-204 1867/2	TH-209 1865/1	TH-250 1267/1	TH-301 2225/1
Jars	TH-302 2060/1	TH-308 2148/1	TH-309 2139/1	
Jugs	TH-9 1790/1	TH-206 1565/1	TH-261 2105/1	
Kraters	TH-13 2108/1	TH-14 1740/1	TH-32 1828/2	
Pithoi	TH-15 1302/1	TH-264 2238/1		
Chalice	TH-36 2149/1			
Bowl	TH-40 1844/2			
Lamp	TH-44 1868/2			

The sample number used for the experiments (e.g., TH-3, TH = Tel Hadar) and the excavation symbol (e.g., 1734/2) are depicted

Reference thermal phases

Reference thermal phases of meta-kaolinite and meta-smectite were obtained by heating samples of local smectite and kaolinite in an electric kiln. The samples were heated to 600, 700, 800, and 900 °C for 6 h at each temperature. The measurements were obtained at room temperature.

Methods

The samples were investigated by the following methods:

X-ray diffractometry (XRD)

XRD was performed with a Philips PW-3710 diffractometer using Cu K α radiation 35 kV-40 mA, and a curved graphite monochromator. Diffractograms from powdered samples of the pottery material were obtained.

Infrared spectroscopy (FT-IR)

FT-IR was recorded using a Jasco-4100 FT-IR spectrometer and Spectra Manager software. Spectra of powdered samples of the pottery were obtained using KBr disks. The disks were prepared using 1 and 5 mg of the sample in 150 mg of KBr. The concentrated disks were designed for observation of relatively weak OH bands in the pottery material [3]. The disks were heated to 110 and 250 °C to remove absorbed water bands. Immediately after heating, the disks were repressed (without regrinding) to improve their transmission. Accumulations of 60 s were applied for the spectra collection.

Micro-Raman spectroscopy

Micro-Raman spectroscopy was recorded using a Horiba-Jobin Yvon ARAMIS Raman spectrometer with a UV laser

325 nm, 30 mW, 1.5 cm⁻¹/pixel at 360 nm, 2,400 Grating lines/mm Resolution spatial, 2 μ m avec objective 100 \times . Accumulations lasting 30 s were obtained. The advantage in the use of UV laser in this spectrometer is in the prevention of the interruption of luminescence on the Raman spectra of the pottery. Some Raman spectra were recorded using Renishaw RM 1000 Raman spectrometer with an excitation 532 nm sortie laser.

Spectral analysis

The Raman and IR spectra were analyzed using the GRAMS/AI 32 software package of Thermo Electron Corporation. The second derivatives of the spectra were obtained with the derivative “Gap” function of the software. The curve fitting of the spectra were done with the Peak fitting function of the software. Lorentzian and Gaussian shapes were chosen in order to obtain best fit.

Results

X-ray diffraction

The XRD diffractograms of the pottery showed peaks of calcite settled on a wide rise of the baseline between 15° and 35° 2 θ . This appearance indicates that, in addition to the calcite, a pseudo-amorphous phase of meta-clay is found. Peaks of gehlenite were not observed in the examined pottery.

IR spectra and spectral analysis

IR spectra of reference thermal phases

The thermal phases in the pottery were identified by comparing their IR spectra to that of fired smectite and kaolinite.

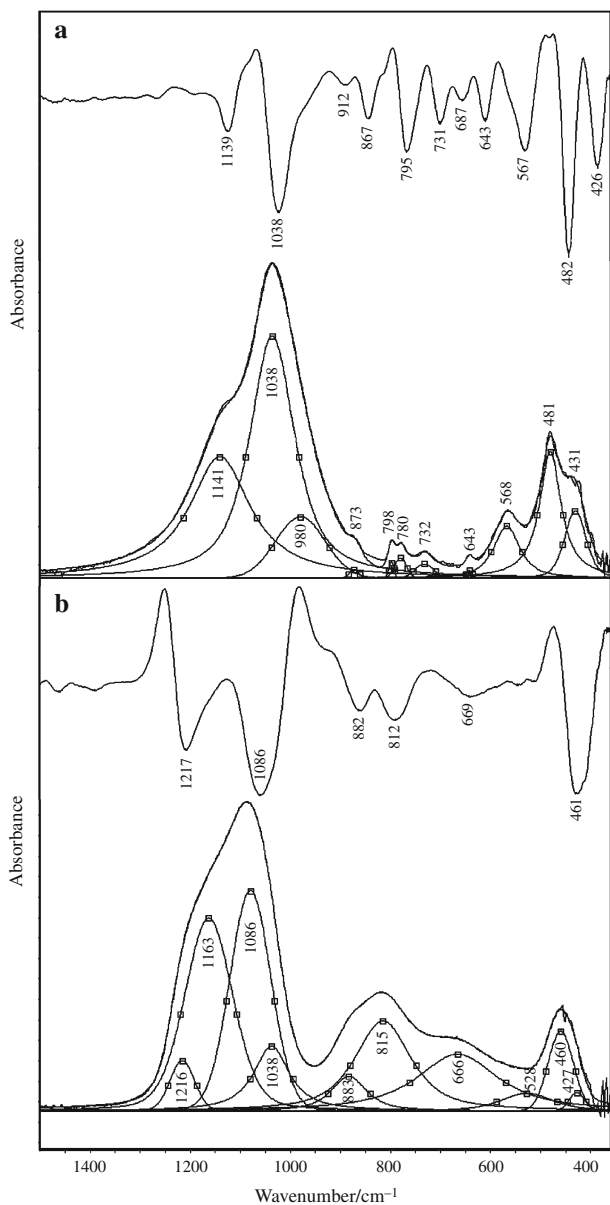


Fig. 2 Curve-fitted FT-IR spectra and second derivatives of: **a** meta-smectite and **b** meta-kaolinite after heating to 700 °C. The spectra were used as references for the identification of these phases in the composition of the pottery

Figure 2 shows curve-fitted FT-IR spectra and second derivatives of reference samples of meta-smectite and meta-kaolinite after heating to 700 °C. Figure 3 gives the location of the SiO-stretching band in the IR spectra of heated kaolinite and heated smectite as a function of the firing temperature. The main Si–O-stretching band of fired clay is progressively shifted to higher frequencies as the temperature increases. Figure 3 was used for estimation of the firing temperature of the pottery. The meta-smectite is distinguished from the meta-kaolinite by the location of the main Si–O-stretching band (Fig. 3). In the reference samples of

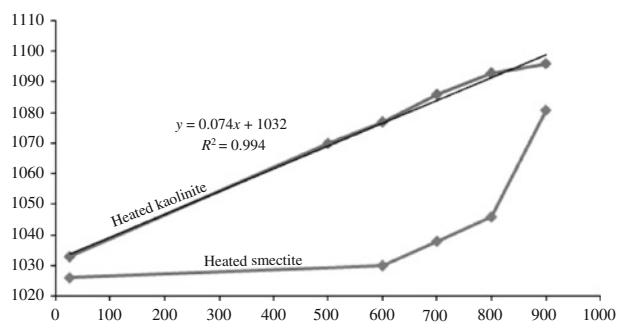


Fig. 3 The location of the SiO-stretching band in the IR spectra of heated kaolinite and heated smectite as a function of the firing temperature. The graph was used for estimation of the firing temperature of the pottery

meta-smectite and meta-kaolinite, this band is located at 1,038 and 1,086 cm^{-1} , respectively, after heating to 700 °C (Fig. 2). Weak bands at 780, 798 (795) cm^{-1} are of accessory quartz (Fig. 2a).

IR spectra of the pottery

Curve-fitted FT-IR spectra and second derivatives of representative calcareous pottery in the range 1,800–400 cm^{-1} are demonstrated in Fig. 4. The dominant bands in the IR spectra of the pottery are the SiO and CO_3 vibrations. These vibrations are related to meta-clay and recarbonated calcite, respectively. The locations of the SiO-stretching band of the meta-clay (meta-smectite and meta-kaolinite) and the main CO_3 band of recarbonated calcite in the IR spectra and in the second derivative are shown in Table 2.

The SiO bands

The IR spectra of the pottery have a broad SiO-stretching band located at 1,030–1,060 cm^{-1} (Table 2, Fig. 4a). In many spectra, an additional band is observed at about 1,076–1,082 cm^{-1} (Table 2, Fig. 4b). These bands are related to the composition of meta-clay (meta-smectite and meta-kaolinite) in the pottery. The use of the second derivative of the IR spectra of the pottery enables the identification of meta-smectite and meta-kaolinite in the pottery material (Fig. 4), according to the location of the main Si–O-stretching band (Figs. 2–3). The meta-smectite is identified in the second derivative by the location of the main SiO-stretching band at about 1,027–1,036 and the meta-kaolinite by the location at 1,082–1,090 cm^{-1} (Table 2). In some spectra, meta-smectite is the dominant phase (Fig. 4a), while in others mixtures of meta-smectite and meta-kaolinite are dominant (Fig. 4b). The pottery may contain some rehydrated clay and quartz. The main Si–O-stretching bands of these minerals are located at about 1,030 and at 1,084 cm^{-1} , similar to the location of the meta-smectite and the

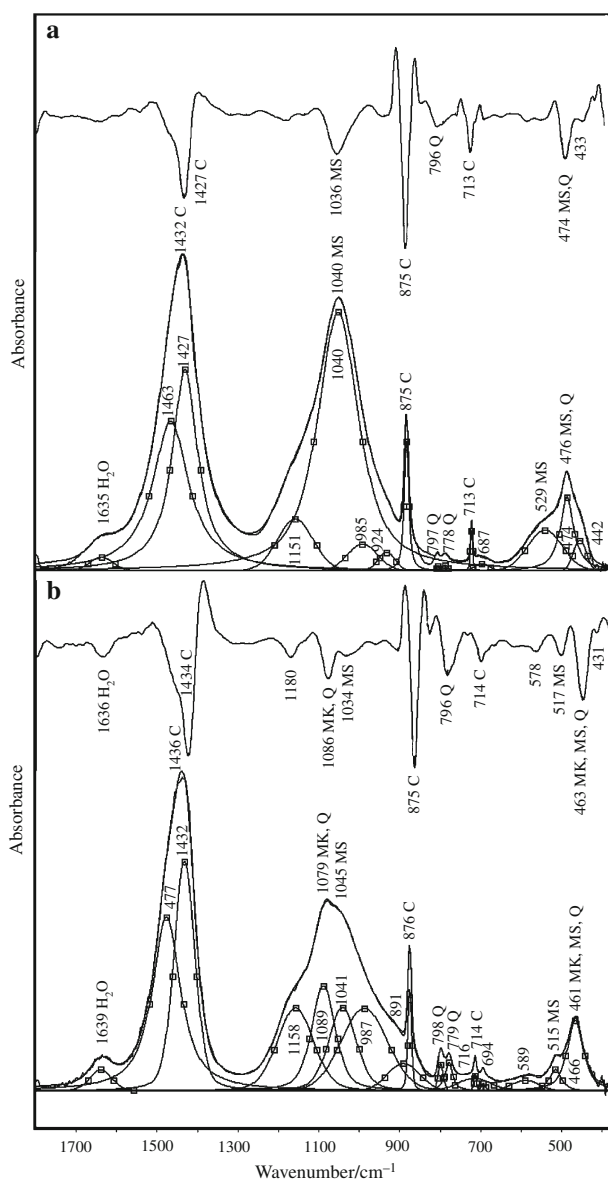


Fig. 4 Curve-fitted FT-IR spectra and second derivatives of calcareous Iron Age pottery in the range 1,800–400 cm^{-1} : **a** pottery rich in meta-smectite, recarbonated calcite and some quartz (TH-30); **b** pottery containing meta-smectite, meta-kaolinite, recarbonated calcite, and some quartz (TH-264). *MS* Meta-smectite, *MK* Meta-kaolinite, *C* Calcite, *Q* Quartz

meta-kaolinite, respectively (Table 2). The band-doublet at about 778 and 798 cm^{-1} demonstrates the presence of some quartz (Fig. 3).

The CO_3 bands

Curve-fitted FT-IR spectra and second derivatives of recarbonated calcite in pottery, in comparison with that of unheated calcite are demonstrated in Fig. 5. The spectra of the calcareous pottery have strong CO_3 bands, which are related to composition of calcite in the material. The

characteristics of the main CO_3 band in the pottery indicate that the calcite is recarbonated [4, 22]. The main CO_3 band in the spectra of the pottery is located at about 1,430–1,445 cm^{-1} and has a broad and asymmetric shape (Table 2, Fig. 5a). In contrast, in unheated calcite the main CO_3 band is located at 1,424 cm^{-1} and has a sharp top (Fig. 5b). In addition, the stronger intensity of the component at 1,473 cm^{-1} in the second derivative of the spectra of the pottery (Fig. 5a) relative to that in unheated calcite at 1,464 cm^{-1} (Fig. 5b) is also characteristic of recarbonated calcite.

The percentages of the recarbonated calcite in the pottery material (Table 2) were calculated from the IR spectra according to the relative intensities of the main CO_3 band of calcite at 1,430–1,445 cm^{-1} relative to the SiO-stretching band of the meta-clay at about 1,030–1,082 cm^{-1} . The relative intensities in calibration curves containing measured amounts of calcite were used for this determination. The results demonstrate that the amounts of the recarbonated calcite in the calcareous pottery range between 40 and 58%.

The H_2O and OH bands

Figure 6 demonstrates the curve-fitted FT-IR spectra and second derivatives of representative pottery in the range 4,000–2,600 cm^{-1} . The spectra show strong H_2O -stretching bands at about 3,410 cm^{-1} , which exist after drying the KBr disks at 110 $^\circ\text{C}$. It seems that the water is absorbed within the pseudo-amorphous phase of the pottery material [3]. Some interlayer water may appear within reconstructed clay minerals in the pottery material. The H_2O -stretching bands appear with components at about 3,435 and 3,232 cm^{-1} as observed by the curve fitting.

In addition to the water bands, the spectra of the pottery show the presence of weak OH-stretching bands at about 3,630 cm^{-1} , which are related to some reconstructed clay minerals in the pottery material. In the spectra recorded after drying the KBr disks at 110 $^\circ\text{C}$, the OH-stretching bands are distorted by the band of the absorbed water and observed as a shoulder (Fig. 6a). The second derivative enables the separation of this band from the broad H_2O -stretching band of the absorbed water (Fig. 6a). The OH-stretching bands are clearly observed after drying the KBr disk at 250 $^\circ\text{C}$ (Fig. 6b). These bands appear with components at about 3668, 3635, and 3583 cm^{-1} as observed by the curve fitting. The result demonstrates that over time, some clay is rehydroxylated and reconstructed from the meta-clay in the pottery material [4, 23].

Raman spectroscopy

Figure 7 gives curve-fitted Micro-Raman spectra of representative calcareous pottery. The broad bands in the

Table 2 The location of the SiO-stretching band of the meta-clay (meta-smectite and meta-kaolinite) and the main CO₃ band of recarbonated calcite in the IR spectra and in the second derivatives of the pottery

Pottery number	IR spectra			Second-derivative		Recarb. calcite/%	Firing temp./ Meta-smectite	Firing temp./ Meta-kaolinite
	Meta-clay, rehyd. clay	Meta-clay, quartz	Recarb. calcite	Meta-smectite, rehyd. clay	Meta-kaolinite, quartz			
TH-3	1,047	1,078	1,437	1,033m	1,088m	47	640	750
TH-4	1,038	1,082sh	1,432	1,036m	1,088w	52	675	750
TH-9	1,044	1,081	1,436	1,030m	1,088m	55	600	750
TH-11	1,037		1,432	1,030m	1,088w	54	600	750
TH-13	1,033		1,430	1,030m	1,088m	40	600	750
TH-14	1,039	1,078sh	1,436	1,030m	1,090m	45	600	780
TH-15	1,037		1,432	1,036m	–	45	675	
TH-16	1,041	1,077sh	1,441	1,033m	1,090w	39	640	780
TH-18	1,037	1,079sh	1,432	1,035m	1,090w	53	660	780
TH-20	1,035	1,078sh	1,434	1,033m	1,088w	38	640	750
TH-24	1,042	1,080	1,441	1,036w	1,086m	43	675	725
TH-28	1,037	1,076	1,435	1,030m	1,090m	56	600	780
TH-29	1,038	1,073sh	1,432	1,034m	1,086w	52	650	725
TH-30	1,045	1,079	1,436	1,034w	1,086m	47	650	725
TH-32	1,038	1,079sh	1,445	1,036m	1,087m	54	675	740
TH-36	1,037		1,430	1,035m	1,086vw	55	660	725
TH-40	1,037	1,078sh	1,432	1,030vw	1,086m	58	600	725
TH-44	1,044	1,078	1,432	1,034m	1,088m	45	650	750
TH-200	1,040	1,080	1,430	1,035m	1,090m	39	660	780
TH-202	1,037		1,436	1,036m	1,086w	40	675	725
TH-204	1,059	1,081	1,432	1,036w	1,088m	40	675	750
TH-206	1,036		1,432	1,032w	1,088m	45	625	750
TH-209	1,038	1,078sh	1,435	1,035m	1,090m	48	660	780
TH-250	1,043	1,078sh	1,430	1,036m	1,086w	50	675	725
TH-261	1,036		1,430	1,035m	1,082w	50	650	670
TH-264	1,040		1,432	1,036m	–	50	675	
TH-301	1,034		1,436	1,034w	–	52	650	
TH-302	1,043	1,076	1,430	1,030w	–	58	600	
TH-308	1,038	1,071sh	1,432	1,035w	1,086w	57	660	725
TH-309	1,036		1,434	1,031m	–	48	615	

The percentages of recarbonated calcite and the estimated firing temperatures are depicted

TH Tel-haddar, *sh* band shoulder, *s* strong band, *m* medium band, *w* weak band, *vw* very weak band, *recarb.* recarbonated, *rehyd.* rehydroxylated

Raman spectra are related to the presence of disordered phases. The sharp bands demonstrate crystalline phases of calcite, quartz and anatase (Fig. 7).

Discussion

Thermal phases in the composition of the pottery

The IR spectra reveal that the principal thermal phases in the composition of the calcareous pottery are pseudo-amorphous meta-clays and microcrystalline-recarbonated

calcite. Both phases are mixed in the pottery material. The Raman spectroscopy confirms the presence of disordered phases in the pottery material.

The meta-clay

Meta-clay is the principal phase in firing of clayey raw material to pottery below 900 °C. The broad SiO-stretching band in the spectra of the pottery is related to composition of the meta-clay (Fig. 4). The broadening of this band is in accordance with the pseudo-amorphous structure of the meta-clay. The type of the meta-clay in the composition of

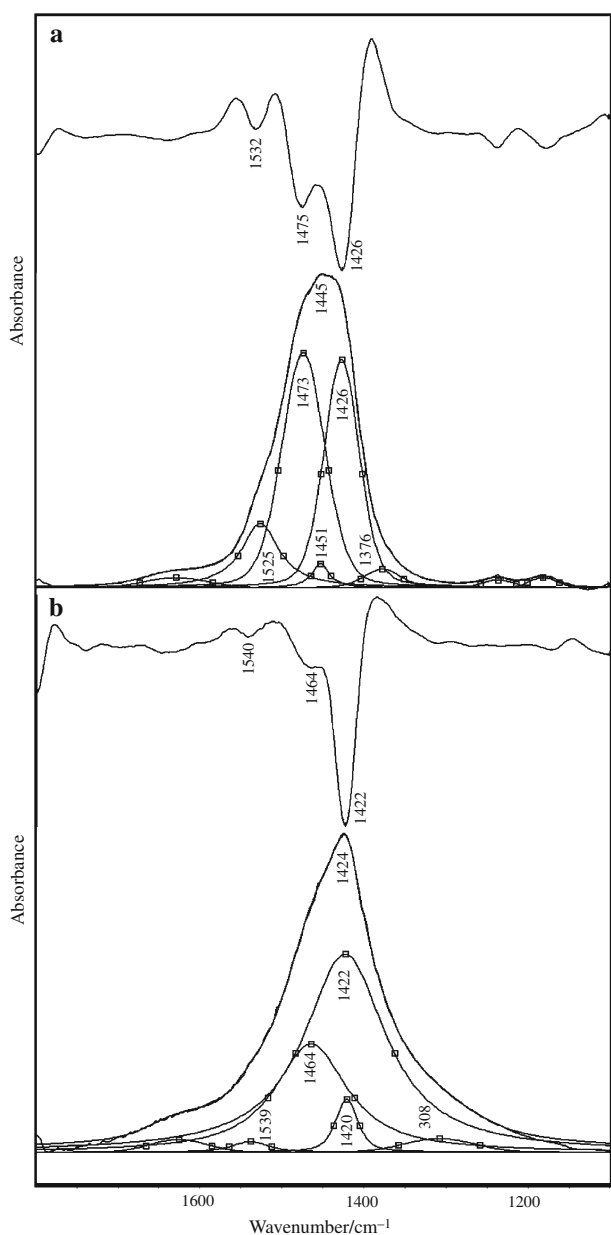


Fig. 5 Curve-fitted FT-IR spectra and second derivatives of: **a** re-carbonated calcite in pottery (TH-32), in comparison with **b** unheated calcite

the pottery is identified using curve-fitting and second-derivative techniques. The meta-smectite is identified in the second derivative by the location of the main SiO-stretching band at about 1,027–1,036 and the meta-kaolinite by the location at 1,082–1,090 cm^{-1} (Table 2). Meta-smectite is more abundant in the composition of pottery investigated (Table 2). Indeed, calcareous raw material containing interstratified smectite is more available in the region. The appearance of both phases in many spectra

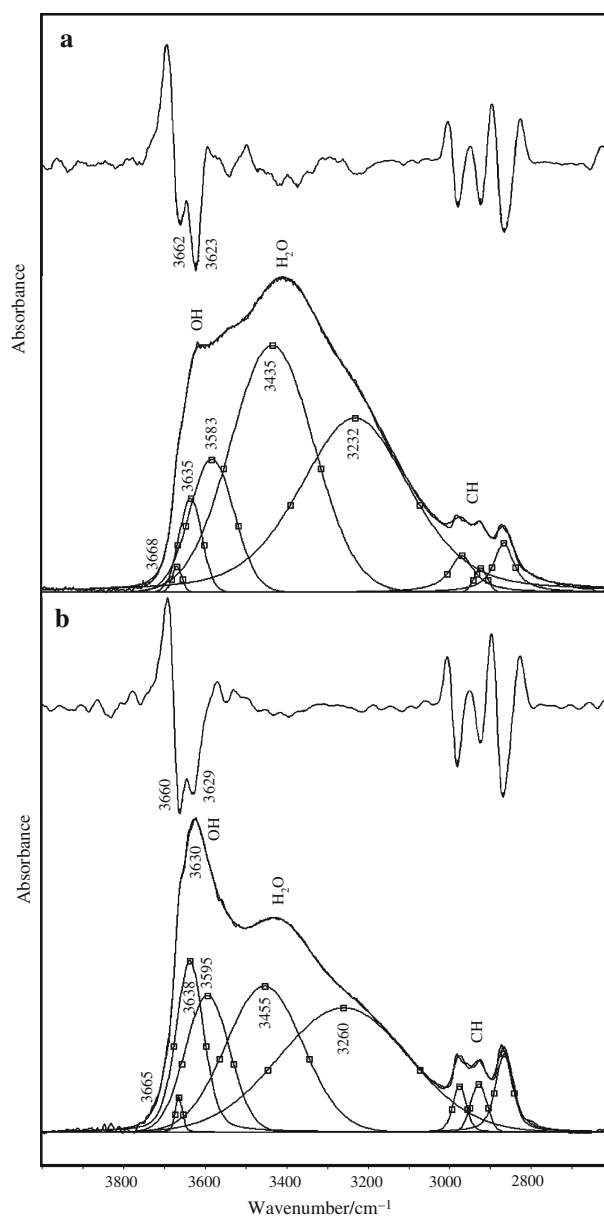


Fig. 6 Curve-fitted FT-IR spectra and second derivatives of calcareous Iron Age pottery (TH-30) in the range 4,000–2,600 cm^{-1} : **a** spectra and second derivative recorded after drying the KBr disks at 110 °C, **b** spectra and second derivative after drying the KBr disks at 250 °C. H_2O absorbed water, OH OH-stretching band of rehydroxylated clay, CH CH groups of organic matter

indicates that calcareous raw materials containing smectite and kaolinite were used for their manufacture.

The re-carbonated calcite

The calcareous pottery contained large amounts of microcrystalline-re-carbonated calcite mixed with the meta-clay (Table 2). This composition demonstrates that, during the firing, the primary calcite of the raw

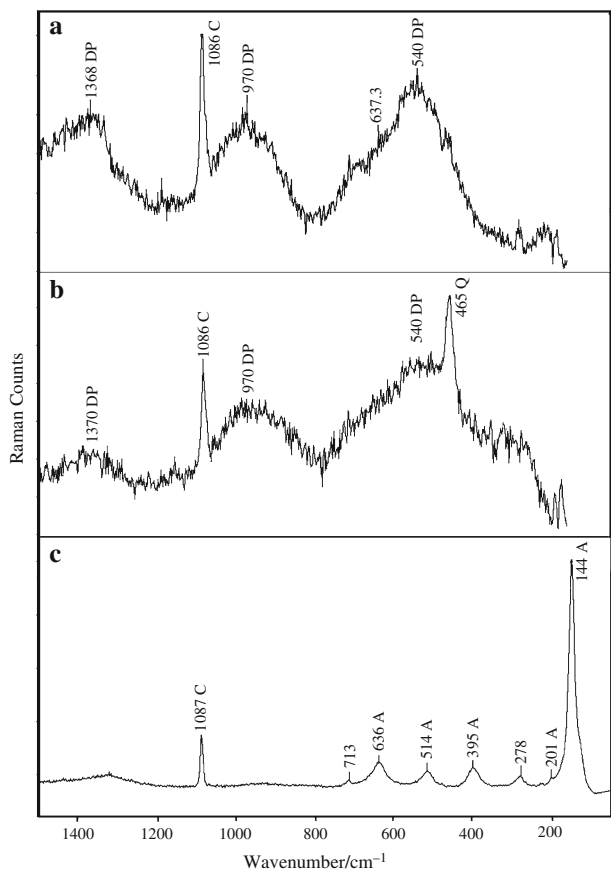


Fig. 7 Micro-Raman spectra of calcareous Iron Age pottery: **a** pottery containing disordered phase and calcite (TH-30), **b** pottery containing disordered phase, calcite, and quartz (TH-33), **c** pottery containing anatase and calcite (TH-4). *DP* disordered phase, *C* calcite, *Q* quartz, *A* anatase

material was decarbonated and free-lime was formed. The recarbonated calcite was crystallized after the firing by the reaction of the free-lime with water vapor and carbon dioxide from the air [4]. In the IR spectra, the recarbonated calcite is distinguished from the unheated calcite by the shift of the main CO_3 band to higher frequencies and by the broad and asymmetric shape (Fig. 5). The stronger intensity of the component at $1,473\text{ cm}^{-1}$ in the second derivative of the spectra of the pottery (Fig. 5a) relative to that in unheated calcite at $1,464\text{ cm}^{-1}$ (Fig. 5b) is also characteristic of recarbonated calcite. The shift of the main CO_3 band from $1,424\text{ cm}^{-1}$ in the spectrum of unheated calcite to $1,430\text{--}1,445\text{ cm}^{-1}$ in that of the recarbonated calcite might be associated with the incorporation of Mg ions. The fired smectite contains Mg ions in the composition and as exchangeable cation and it seems that during the recarbonation of the microcrystalline calcite some incorporation of Mg took place and magnesium-rich calcite was formed.

The Raman response is sensitive to the degree of ordering in the structure of the thermal phases. The broad bands in the Raman spectra are related to the presence of disordered crystalline phases (Fig. 7). The Micro-Raman spectroscopy enables point analysis of peculiar components of the pottery such as calcite, quartz, and anatase. Quartz usually appears in the pottery material as grains or silt fragments [1]. Anatase is commonly accessory mineral in kaolinites [24] and the detection of anatase in some of the vessels (Fig. 7c) demonstrates the content of kaolinite in the raw material.

Reconstruction of clay minerals

The presence of weak OH-stretching bands in the IR spectra of the pottery (Fig. 6a) demonstrate that some clay is reconstructed within the pottery material [3]. The OH band is clearly observed in the second derivative or after drying the KBr disks at $250\text{ }^\circ\text{C}$ (Fig. 6b). The location and shape of the OH-stretching band resembles that in trimorphic clay minerals. OH-stretching bands characteristic of kaolinite are not observed in the IR spectra. The result demonstrates that, over time, some clay is rehydroxylated and reconstructed from the meta-clay in the pottery material [3]. The rehydroxylation of the clay after the firing takes place slowly. Therefore, rehydroxylation dating was suggested as a method for dating of ancient pottery [23].

The firing temperature

Several methods were previously applied for the determination of the firing temperature of ancient pottery [25–29]. In many studies XRD is used for such determination, based on the crystalline phases which are formed during the firing. However, much ancient pottery was fired at temperature intervals in which the principal thermal phases are meta-clays, and these thermal phases are amorphous for XRD detection. Thus, determination by XRD is limited to pottery fired at a relatively high temperature in which the crystalline phases are formed. Such determination is limited to highly fired calcareous pottery in which crystalline thermal phases of gehlenite, plagioclase-anorthite, and pyroxene diopside-wollastonite are formed [20, 21]. It should be noted that some phases which seem to be formed by the firing can be derived from the raw material. For example, the detection of plagioclase-anorthite, pyroxene, and amphibole in pottery manufacture from basaltic soil may originate from the basalt residue and not thermal phases of the firing.

FT-IR spectroscopy was also used for estimating the firing temperature [6, 8, 25–27]. The use of FT-IR spectroscopy enables the estimation of the firing

temperature of low fired pottery according to the following criteria:

The meta-clay

The composition of meta-clay in the calcareous pottery examined demonstrates that the pottery was fired above the dehydroxylation temperature of the clay minerals. Kaolinite dehydroxylates to form meta-kaolinite mainly at about 450 °C and smectite (montmorillonite) dehydroxylates to form meta-smectite mainly at about 600 °C [19].

The recarbonated calcite

The composition of recarbonated calcite in the calcareous pottery examined demonstrates that the pottery was fired above the decarbonation temperature of the initial calcite, above 600 °C. Some studies relate the presence of calcite in the pottery material to the initial calcite of the raw material and concluded that the pottery was fired below the decarbonation temperature of this mineral. Nevertheless, the calcite in the pottery material is usually formed by recarbonation of the decomposed calcite, and is not the initial calcite [4]. The recarbonated calcite is formed above the decomposition temperature of the initial calcite and thus the presence of calcite in the pottery material cannot be used as higher limit of the firing temperature.

Moreover, some publications reported that the calcite in the pottery is decomposed at about 800–900 °C. This is true in DTA experiments in which monocrystalline calcite is treated under fast rate of heating. Nevertheless, in firing of calcareous raw material, an early decarbonation takes place at about 600 °C due to the microcrystalline structure of the calcite in the calcareous pottery, the presence of clay and the extended firing duration [4, 22].

The rehydroxylated clay

The reconstruction of clay minerals in the pottery material demonstrates that the pottery was fired below 800 °C [3]. In firing above this temperature non-reversible dehydroxylation takes place [3] and the meta-clay reacts with the free-lime to form gehlenite [19]. Some studies relate the presence of clay in the pottery material to the initial clay of the raw material and concluded that the pottery was fired below the dehydroxylation temperature of this mineral. Nevertheless, the clay in the pottery material is usually formed by rehydroxylation of the meta-clay, and is not the initial clay [3, 23]. Thus, the presence of clay in the pottery material cannot be used as higher limit of the firing temperature.

The absence of gehlenite

Gehlenite is formed by the reaction of the free-lime from the decomposition of the calcite and the meta-clay at about 900 °C and pottery containing this phase was fired above this temperature [19, 20]. The absence of gehlenite in the calcareous pottery examined is in agreement with firing below 900 °C.

The location of the SiO-stretching band

Figure 3 gives the location of the SiO-stretching band in the IR spectra of heated kaolinite and heated smectite as a function of the firing temperature. The SiO-stretching bands of the meta-kaolinite and the meta-smectite are progressively shifted to higher frequencies as the firing temperature increases. Figure 3 is used for estimation of the firing temperature of the pottery. According to the location of the SiO-stretching band of the meta-smectite, the calcareous pottery was fired at 600–675 °C (Table 2). The determination according to the location of the SiO-stretching band of the meta-kaolinite showed higher firing temperature, 670–780 °C (Table 2). Both results reveal that the calcareous pottery was manufactured with a low firing temperature. It should be noted that the exact location of the main SiO-stretching band of the meta-smectite and of the meta-kaolinite may be effected by the presence of recarbonated clay and quartz, respectively. The main SiO-stretching bands of these minerals are located at about 1,030 and at 1,084 cm^{-1} , respectively (Table 2).

The production of vessels using lime technology

The consolidation of the ceramic body by sintering of the clay usually occurs in firing above 900–1,000 °C [28, 29]. In this process, the meta-clay grains stick to each other. The results reveal a low firing temperature of the calcareous pottery (Table 2), which seems to be lower than that required for the sintering of the clay. Lime is considered to be a flux material and vessels prepared from this clay are sintered at lower temperatures [30]. Nevertheless, the large amount of recarbonated calcite in the pottery material (between 40 and 58%, Table 2) and the relatively low-firing temperature indicates that instead of sintering the clay, lime technology was used for the cementation of these vessels [1, 6]. In this technology, the calcite was decarbonated in firing of the pottery above 600 °C and the cementation took place after the firing by recarbonation and recrystallization of microcrystalline calcite in the pottery material. Consolidation of the pottery by lime technology required lower firing temperature than that necessary to complete the sintering of the clay. Firing above 600 °C is sufficient for decomposition of the calcite

in calcareous raw material [4]. It seems that after the firing, the vessels were carefully stored over a period in order to complete the solidification by recrystallization of the re-carbonated calcite. It should be noted that the use of lime technology was already known from the Neolithic period and was applied for cementation of lime-based plasters and mortars [31, 32] and for production of Vaiselle Blanche (“Whiteware”, [33]). Mixtures of free-lime and meta-clay have some pozzolanic activity and such a process was used for the cementation of ancient plasters and mortars [34].

Summary

The thermal phases in the composition of calcareous Iron Age pottery from the Galilee were analyzed using FT-IR spectroscopy and micro-Raman spectroscopy and the application of second-derivative and curve-fitting techniques. FT-IR spectroscopy has advantage in analysis of the pseudo-amorphous meta-clay in the composition of the pottery material. Applying the spectral analysis improves the identification of the individual phases in the composition of the pottery.

The results demonstrate that the principal thermal phases in the composition of the calcareous pottery are pseudo-amorphous meta-clays and microcrystalline-re-carbonated calcite. Both phases are mixed in the pottery material. The type of meta-clay is defined by the second derivatives and the curve fitting of the IR spectra as meta-smectite and meta-kaolinite. The Raman spectroscopy confirms the presence of disordered phases in the pottery material.

These methods make it possible to differentiate between calcareous and non-calcareous pottery, to distinguish between pottery manufacture from kaolinitic and smectitic raw material, to observe rehydroxylated clay reconstructed in the pottery material and also to analyze the composition of temper particles in the pottery.

The large amount of re-carbonated calcite in the pottery material and the relatively low-firing temperature indicate that instead of sintering the clay, lime technology was used for the cementation of the calcareous vessels.

The results demonstrate that Iron Age potters had knowledge of raw materials and firing technology thus enabling them to select suitable raw materials according to the advantages of each for the manufacture of the vessels. The potters selected calcareous raw material for the preparation of inferior pottery for daily use such as storage jars and tableware vessels.

Acknowledgements This research was supported by The Open University of Israel’s Research Fund (grant no. 31016). This support is gratefully acknowledged. The assistance of Galina Kaz is also highly acknowledged. The authors acknowledge the “CECOMO (Centre Commun de Microspectrométrie Optique)”, vibrational

spectroscopy platform established by the Institut de Chimie de Lyon and the Rhône-Alpes Région MACODEV program.

References

- Shoval S, Beck P, Yadin E. The ceramic technology used in the manufacture of Iron Age pottery from Galilee. In: Maggetti M, Messiga B, editors. *Geomaterials in cultural heritage*. vol. 257. London: The British Geological Society Publishing House, Geological Society; 2006. p. 101–117 (Special Publications).
- Kochavi M. The Land of Geshur project. *Israel Explor J*. 1989;39:1–17.
- Shoval S, Beck P, Kirsh Y, Levy D, Gaft M, Yadin E. Rehydroxylation of clay minerals and hydration in ancient pottery from the Land of Geshur. *J Therm Anal*. 1991;37:1579–92.
- Shoval S, Gaft M, Beck P, Kirsh Y. The thermal behavior of limestone and monocrystalline calcite tempers during firing and their use in ancient vessels. *J Therm Anal*. 1993;40:263–73.
- Shoval S. The firing temperature of a Persian-Period Pottery Kiln at Tel Michal, Israel, estimated from the composition of its pottery. *J Therm Anal*. 1994;42:175–85.
- Shoval S. Using FT-IR spectroscopy for study of calcareous ancient ceramics. *Opt Mater*. 2003;24:117–22.
- Shoval S, Beck P. Thermo-FT-IR spectroscopy analysis as a method of characterizing ancient ceramic technology. *J Therm Anal Calorim*. 2005;82:609–16.
- Paz Y, Shoval S, Zlatkin O. Canaanite EB-IB ‘Proto-Metallic Ware’—the earliest production of ceramic ‘Metallic Ware’ in the Land of Israel. *Leiden J Pottery Stud*. 2009;24:163–88.
- De-Benedetto GE, Laviano R, Sabbatini L, Zamboni PG. Infrared spectroscopy in the mineralogical characterization of ancient pottery. *J Cult Heritage*. 2002;3:177–86.
- Barilaro D, Barone G, Crupi V, Donata MG, Majolino D, Messina G, Ponterio R. Spectroscopic techniques applied to the characterization of decorated potteries from Caltagirone (Sicily, Italy). *J Mol Struct*. 2005;744–747:827–31.
- Barilaro D, Barone G, Crupi V, Majolino D, Mazzoleni P, Tigano G, Venuti V. FT-IR absorbance spectroscopy to study Sicilian “proto-majolica” pottery. *Vib Spectrosc*. 2008;48:269–75.
- Farmer VC. *The infrared spectra of minerals*. Monograph 4. London: Mineralogical Society; 1974.
- Shoval S, Michaelian KH, Boudeulle M, Panczer G, Lapides I, Yariv S. Study of thermally treated dickite by infrared and Micro-Raman spectroscopy using curve-fitting technique. *J Therm Anal Calorim*. 2002;69:205–25.
- Shoval S, Boudeulle M, Panczer G, Lapides I. Analysis of thermal phases in firing of kaolinite to mullite by Infrared and Micro-Raman Spectroscopy using curve-fitting technique. *Opt Mater*; 2011.
- Legodi MA, de Waal D. Raman spectroscopic study of ancient South African domestic clay pottery. *Spectrochim Acta Part A*. 2007;66:135–42.
- Akyuz S, Akyuz T, Basaran S, Bolcal C, Gulec A. FT-IR and micro-Raman spectroscopic study of decorated potteries from VI and VII century BC, excavated in ancient Ainos, Turkey. *J Mol Struct*. 2007;834–836:150–3.
- Akyuz S, Akyuz T, Basaran S, Bolcal C, Gulec A. Analysis of ancient potteries using FT-IR, micro-Raman and EDXRF spectrometry. *Vib Spectrosc*. 2008;48:276–80.
- Seyama H, Soma M. X-ray photoelectron spectroscopic study of the effect of heating on montmorillonite containing sodium and potassium cations. *Clays Clay Miner*. 1986;34:672–6.
- Shoval S. Mineralogical changes upon heating calcitic and dolomitic marl rocks. *Thermochim Acta*. 1988;135:243–52.

20. Maggetti M. Phase analysis and its significance for technology and origin. In: Olin JS, Franklin AD, editors. *Archaeological ceramics*. Washington: Smithsonian Institution Press; 1982. p. 121–33.
21. Trindade MJ, Dias MI, Coroado J, Rocha F. Mineralogical transformations of calcareous rich clays with firing: a comparative study between calcite and dolomite rich clays from Algarve, Portugal. *Appl Clay Sci*. 2009;42:345–55.
22. Shoval S, Yofe O, Nathan Y. Distinguishing between natural and recarbonated calcite in oil shale ashes. *J Therm Anal Calorim*. 2003;71:883–92.
23. Wilson MA, Carter MA, Hall C, Hoff WD, Ince C, Savage SD, McKay B, Betts IM. Dating fired-clay ceramics using long-term power law rehydroxylation kinetics. *Proc R Soc A*. 2009;465(2108):2407–15.
24. Shoval S, Panczer G, Boudeulle M. Study of the occurrence of titanium in kaolinites by micro-Raman spectroscopy. *Opt Mater*. 2008;30:1699–705.
25. Velraj G, Janaki K, Mohamed Musthafa A, Palanivel R. Spectroscopic, porosimetry studies to estimate the firing temperature of some archaeological pottery shreds from India. *Appl Clay Sci*. 2009;43:303–7.
26. Velraj G, Janakia K, Mohamed Musthafa A, Palanivel R. Estimation of firing temperature of some archaeological pottery shreds excavated recently in Tamil Nadu, India. *Spectrochim Acta Part A*. 2009;72:730–3.
27. Barone G, Crupi V, Longo F, Majolino D, Mazzoleni P, Tanasi D, Venuti V. FTIR spectroscopic analysis to study the firing processes of prehistoric ceramics. *J Mol Struct*. 2010.
28. Rice MP. *Pottery analysis—a sourcebook*. Chicago: The University of Chicago Press; 1987.
29. Grimshaw RW. *The chemistry and physics of clays and other ceramic materials*. New York: Wiley; 1971.
30. Maggetti M, Westley H, Olin J. Provenance and technical studies of Mexican majolica using elemental and phase analysis. In: Lambert JB, editor. *ACS advances in chemistry series. Archaeological chemistry III*. vol. 205. American Chemical Society; 1984. p. 151–191.
31. Kingery WD. The beginnings of pyrotechnology, part II: production and use of lime and gypsum plaster in the pre-ceramic Neolithic Near East. *J Field Archaeol*. 1988;15:219–44.
32. Moropoulou A, Bakolas A, Anagnostopoulou S. Composite materials in ancient structures. *Cem Concr Compos*. 2005;27:295–300.
33. Goren Y. The beginnings of ceramic production in Israel, technology and typology of proto-historic ceramic assemblages in Eretz Israel (6th–4th millennia B.E.C.). Ph.D. thesis, The Hebrew University of Jerusalem (1991).
34. Moropoulou A, Bakolas A, Anagnostopoulou S. Evaluation of pozzolanic activity of natural and artificial pozzolans by thermal analysis. *Thermochim Acta*. 2004;420:135–40.