THERMO-FTIR SPECTROSCOPY ANALYSIS AS A METHOD OF CHARACTERIZING ANCIENT CERAMIC TECHNOLOGY

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The Iron Age ceramic technology used in the manufacturing of cooking pots was studied by thermo-FTIR spectroscopy analysis. The pottery was excavated at Tel Hadar on the eastern shore of the Sea of Galilee. The results demonstrate that the cooking pots were manufactured using noncalcareous or slightly calcareous raw material proceeds from soil. The firing was at about 750-850°C and the cementation to ceramic was obtained by low temperature sintering of the clay. The use of soil raw material composed of smectitic (montmorillonitic) clay enabled the low temperature sintering. The clay from soil is relatively poorly crystallized and rich in natural iron oxide, both of which induce earlier sintering. Most of the cooking pots were tempered with broken pieces of large calcite crystals that were added to the clayey raw material from an additional source. Alternative tempering with limestone particles composed of polycrystalline calcite is inappropriate as it brings about earlier and intense decarbonation during the firing, which causes defects in the pots.

Keywords: *cooking pots, firing, infrared spectroscopy, Iron Age, pottery raw material, sintering, Tel-Hadar excavations, temper*

Introduction

The Iron Age pottery was excavated at Tel-Hadar, on the eastern shore of the Sea of Galilee, in the framework of 'The Land of Geshur Archaeological Project, The Institute of Archaeology, Tel-Aviv University' [1]. A study of the material technology of production of ancient pottery done by mineralogical and petrographic methods can focus on the type of the raw material and on the firing process [2, 3]. Two main types of raw materials were used for pottery production, calcareous and noncalcareous clays [4, 5], each of which has different advantages. The firing process of ancient pottery is commonly assessed by investigating the thermal phases, which are temperature-dependent. Several phases are recognizable and their association depends on the mineralogy and chemistry of the raw material, their grain-size distribution, maximum firing temperature, heating rate, duration of the firing, and kiln oxidizing-reduction atmosphere [6].

Different thermal phases are observed when firing calcareous or noncalcareous raw materials [7–9]. The reference data on firing of noncalcareous raw material generally relates to the firing of kaolinite. Kaolinite dehydroxylates at 400–650°C and meta-kaolinite is formed. The thermal transformation from metakaolinite to mullite starts with short-range ordered material. According to Freund [10] at about 900°C the metakaolinite transforms into a cubic phase described as spinel, which is poorly crystallized. Gualtieri and Bellotto [11] stated that after the loss of the residual hydroxyls, metakaolinite transforms into three phases – mullite $[Al_4SiO_8]$, γ-alumina and silica. However, properly crystallized phases of mullite and cristobalite $[SiO_2]$ are observed at about 1200°C [12, 13]. The major thermal phases formed by the heating of smectite have been identified as meta-smectite, spinel, mullite, cordierite and cristobalite [14]. After firing up to 800°C, some rehydroxylation of the clay minerals may take place within the pottery at room temperature [15]. In firing of calcareous clay, the microcrystalline calcite decomposes above 600°C and quicklime (CaO) is formed. Above 900°C, the quicklime reacts with the amorphous phases resulting from the dehydroxylation of clays and Ca-silicates are formed [3, 7, 16]. After the firing, some recarbonated calcite may reform within the pottery [5, 17, 18].

Several techniques were applied to determine the composition, the firing process and the firing temperatures of ancient pottery, mainly X-ray diffraction [19–21], Mössbauer spectroscopy [22], electron microscopy [4, 23] and thermal analysis [24, 25]. While FTIR has been considerably applied in the analysis of polychrome works of art [26], it has not been used extensively in pottery studies [16, 27]. In previous publications we showed that the major advantage of IR

spectroscopy is that it permits the identification of changes in both the crystalline and the amorphous phases, whereas X-ray diffraction is limited to the examination of crystalline phases [28, 29]. IR helps to infer fundamental information such as ceramic matrix and temper composition and firing temperature [17, 27]. In this work, Iron Age ceramic technology in the manufacturing of cooking pots is characterized using thermo-FTIR spectroscopy analysis.

Experimental methods

Ceramic

The studied cooking pots were excavated at Tel Hadar from the strata of the 11th and 9th century B.C.E. [1]. Those from the 11th century B.C.E. stratum were excavated from a large Pillared Building. They were found with many storage and tableware vessels in storage rooms located on the ground floor of the building [1, 5]. The Pillared Building was destroyed by fire at the end of the 11th century B.C.E. and the site was subsequently abandoned [1, 30]. The pottery from the 9th century B.C.E. stratum was excavated from the site of a small village built on the destroyed site [1].

Raw materials

Local basaltic soil and Terra Rossa soil, equivalent to the raw materials used for the production of the investigated cooking pot were examined by thermal analysis. The raw materials were fired in an electric kiln to temperatures between 600–1000°C for 6 h and the thermal transformations were recorded using thermo-FTIR spectroscopy. After the firing, the fired raw materials were left in humid and open-air conditions for a period of one year for rehydration and recarbonation.

Methods

The pottery was investigated by the following methods:

Petrography

Thin sections of the pottery were analyzed under a polarizing microscope.

Infrared spectroscopy (FTIR)

was obtained using a Nicolet FTIR spectrometer and 'Omnic' software. The spectra of the ceramic matrix and those of the temper particles were measured separately. KBr 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 ceramic material. The mixtures were ground manually in an agate mortar and pressed into disks. The disks were heated to 110 and 350°C to remove water bands [15]. Immediately after heating, the disks were repressed (without regrinding) to improve the resolution of the spectra.

Point chemical analyses

The content of the major element in the ceramic matrix (devoid of the temper particles) was determined by point analysis using LINK 1000 EDS (Oxford ISIS) attached to a JEOL (JSM-840) Scanning Electron Microscope (SEM) and ZAF4/FLS program.

Results

The composition of the pottery

The following results were observed:

Petrography

The texture of the pottery material was determined by petrography. The pottery consists of ceramic matrix and temper particles. The cooking pots were divided into three petrographic groups according to the type of ceramic matrix and the assemblage of the temper particles. These groups differ in the type of raw material used in their manufacture.

- Group 1: Basaltic soil raw material tempered with calcite crystals. This group consists of cooking pots from the 11th and 9th century B.C.E. strata. The composition of basalt fragments (without limestone fragments) within noncalcareous or poorly calcareous blackish-dark matrix, rich in iron oxide and quartz silt is an indication that basaltic soil was the raw material. The pots were tempered with broken pieces of large calcite crystals that were added to the clayey raw material from an additional source.
- Group 2: Terra Rossa soil raw material tempered with calcite crystals. This group consists of cooking pots from the 11th and 9th century B.C.E. strata. The composition of limestone fragments (without basalt fragments) within noncalcareous or poorly calcareous brownish-red matrix, rich in iron oxide and quartz silt is an indication that Terra Rossa soil was the raw material. Similar to group 1, the pots were tempered with particles of calcite crystals from an additional source.
- Group 3: Basaltic soil raw material not tempered with calcite crystals: This group consists of cooking pots from the 9th century B.C.E. stratum prepared from basaltic soil raw material, but not tempered with particles of calcite crystals.
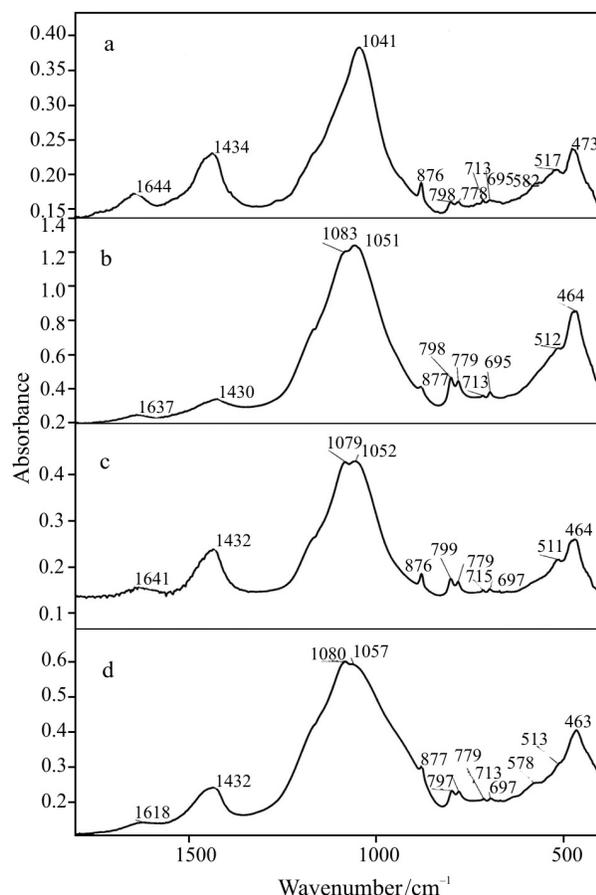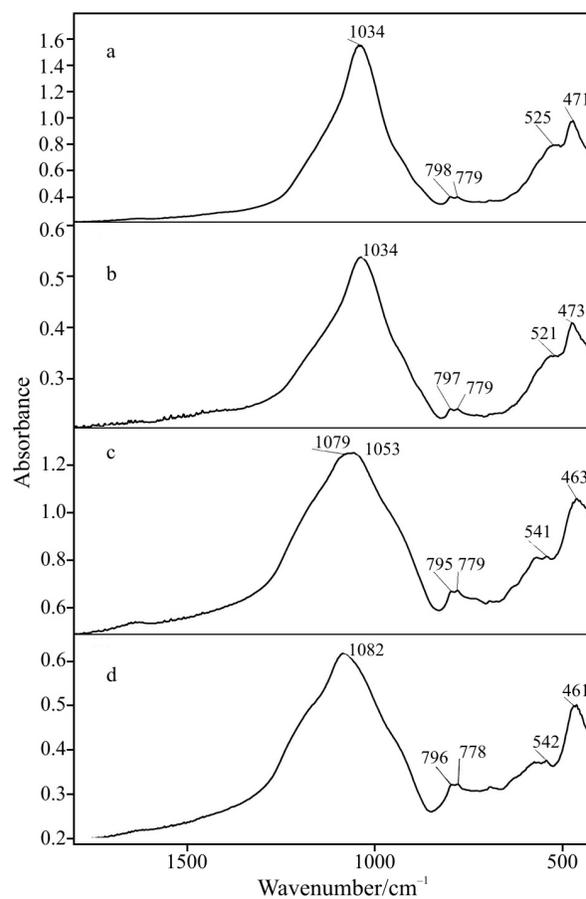
Fig. 1 Representative FTIR spectra in the range of 1800–400 cm^{-1} of the ceramic matrix of cooking pots excavated at Tel Hadar, a – group 1 (TH-31) and b – group 2 (TH-6) of the 11th century B.C.E., as well c – group 1 (TH-118), and d – group 3, (TH-48) of the 9th century B.C.E.

Fig. 2 Thermo-FTIR spectroscopy of basaltic soil raw material after treating at a – 600, b – 700, c – 800 and d – 900°C

FTIR spectroscopy

The mineral composition of the ceramic matrix was observed by FTIR spectroscopy. Representative FTIR spectra in the range of 1800–400 cm^{-1} are shown in Fig. 1. The FTIR data are depicted in Table 1 and arranged according to the petrographic groups of the cooking pots. The spectrum of the ceramic matrix is indicative of slightly-calcareous or noncalcareous ceramic, showing strong SiO vibrations of meta-clay and weak, or an absence of CO_3 vibrations of micro-crystalline calcite. The doublet at about 779 and 798 cm^{-1} indicates that some quartz is present.

Point chemical analysis

The content of the major elements in the ceramic matrix was obtained in the selected pottery by point analysis using an EDS attached to SEM. Data are depicted in Table 2. The composition of the meta-clay in the ceramic matrix is equivalent to that characterizing smectite (montmorillonite), and demonstrates that the precursor raw material was rich in smectitic clay. The amount of Al_2O_3 in the meta-clay, about 15–20%, is equivalent to its content in natural dioctahedral smectite, whereas the amount of Al_2O_3 in pure kaolinite is above 38%. Larger amounts of Al_2O_3 in some pottery are related to the presence of some kaolinite in the precursor raw material. The amount of SiO_2, about 50–60%, is also equivalent to its content in natural dioctahedral smectite, whereas the amount of SiO_2 in pure kaolinite is about 45%. Larger amounts of SiO_2 in some of the pottery are related to the presence of quartz silt. The large amount of FeO is indicative of pottery manufactured from soil raw material.

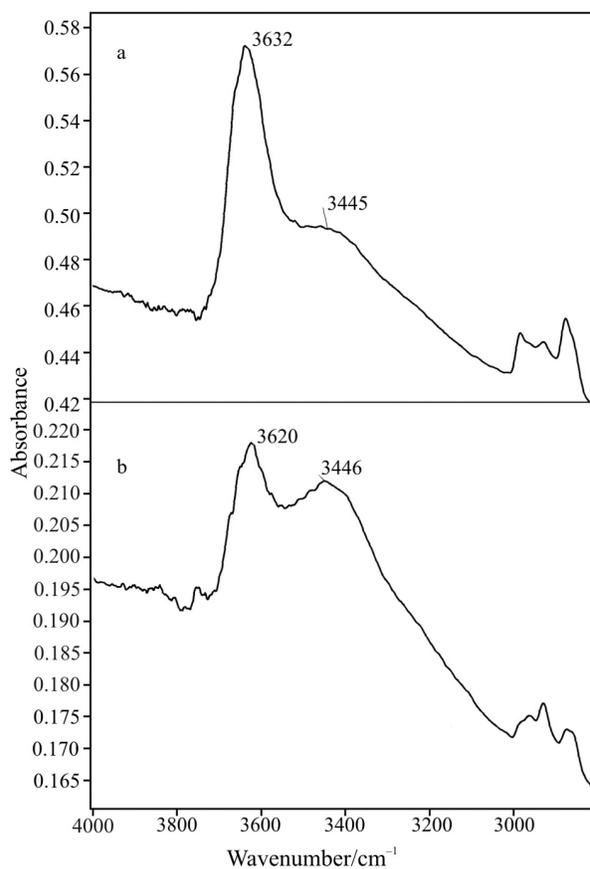### The firing temperature of the pottery

The components of the ceramic materials are the 'fingerprint' of the phases formed during firing and thus the production conditions of the ancient pottery can be derived from their assemblage. The firing temperature of the pottery is assessed by firing clay as similar as possible to the original clay at increasing tempera-
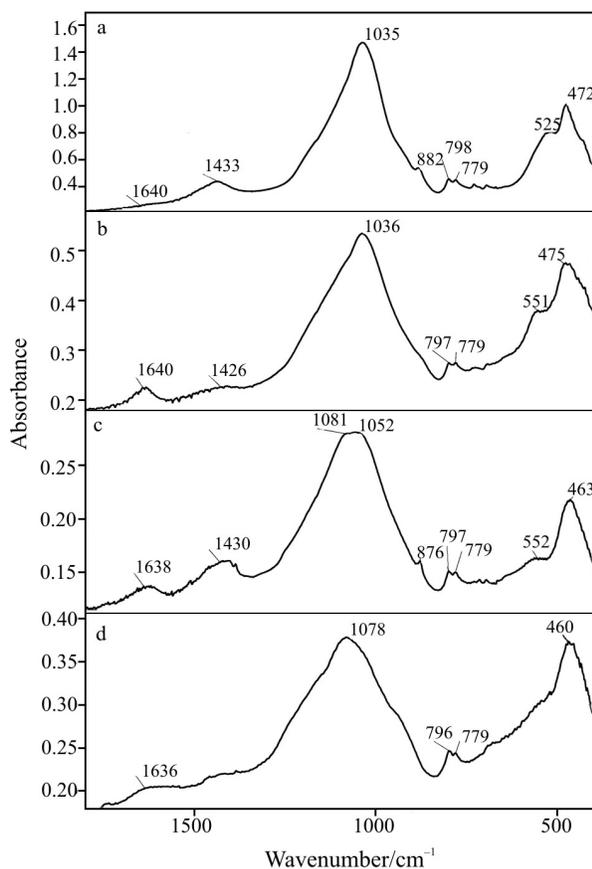
Fig. 3 Thermo-FTIR spectroscopy of Terra Rossa soil raw material after treating at a – 600, b – 700, c – 800 and d – 900°C

Fig. 4 Representative FTIR spectra in the range of 4000–2800 cm^{-1} of the ceramic matrix of cooking pots after heating the KBr disks at 350°C, a – group 1 (TH-31) and b – group 2 (TH-6) of the 11th century B.C.E.

ture until the same properties as seen in the ancient pottery are observed [16, 23]. Thus, basaltic soil and Terra Rossa soil, equivalent to the raw materials used for the production of the investigated cooking pot were fired and the thermal phases were determined. Smectite was found to be the main clay mineral in the basaltic soil and the Terra Rossa soil collected in the vicinity of Tel Hadar.

FTIR spectra in the range of 1800–400 cm^{-1} of these raw materials after firing at 600–900°C for 6 h and after rehydration and recarbonation are shown in Figs 2 and 3. In both figures, the location of the bands of the treated smectite depends on the firing temperature. The main Si–O stretching band is observed at 1034–1036 cm^{-1} after firing at 600 and 700°C. This band shifts and slightly splits to 1052–1053 and 1079–1081 cm^{-1} after firing at 800°C, and appears with one maximum at 1078–1082 cm^{-1} after firing at 900°C. The Si–O, Al–O deformation bands appear as two modes at about 471–475 and 521–525 cm^{-1} after firing at 600 and 700°C and with one maximum at 460–463 cm^{-1} after firing at 900°C. In the spectrum of meta-kaolinite and meta-dickite, a band at about 455–461 cm^{-1} is attributed to a combined Al–O and

Si–O deformation mode resulting from a random arrangement of the silica rings [10, 28]. A similar explanation can be given for the 460–463 cm^{-1} band of the meta-smectite recorded here.

From the following observations it seems that the cooking pots were fired at about 750–850°C:

The main Si–O stretching band

In the FTIR spectra of the cooking pots of group 1 from the 11th century B.C.E., the main Si–O stretching band appears in the range 1039–1048 cm^{-1} (Table 1), and these locations are close to those observed after firing the soil raw materials between 700 and 800°C (Figs 2, 3). In the spectra of the other groups, this band splits to the ranges 1045–1060 and 1076–1083 cm^{-1} (Table 1), and these locations are close to those observed after firing the soil raw materials between 800 and 900°C (Figs 2, 3).

Table 1 Frequencies of the principal vibrations in FTIR spectra of the ceramic matrix and of the calcite temper of Iron Age cooking pot from strata of the 11th and 9th century B.C.E. excavated at Tel Hadar. The FTIR data are arranged according to the petrographic groups of the cooking pots. The sample number includes the excavation symbol of the pottery (such as 1574/1) and the number used for the experiments (such as TH-7, TH=Tel Hadar)

Sample number	Ceramic matrix		Calcite temper	
	Si–O str. cm^{-1}	Si–O, AlO def. cm^{-1}	CO$_3$ cm^{-1}	CO$_3$ cm^{-1}
Strata of the 11th century B.C.E.				
Group 1: Basaltic soil raw material tempered with calcite crystals				
1574/1 (TH-7)	1039	469	1439	1427
1574/3 (TH-27)	1045	471	1431	1425
1778/1 (TH-37)	1048	474	1430	1427
1783/3 (TH-31)	1041	473	1434	1427
1834/2 (TH-8)	1048	473	1431	1426
1844/3 (TH-42)	1046	475	1430	1425
Group 2: Terra Rossa soil raw material tempered with calcite crystals				
1734/1 (TH-2)	1050, 1074	461	1430	1426
1756/1 (TH-6)	1051, 1083 sh.	464	1430	1426
2021/1 (TH-5)	1054, 1082 sh.	466	1430	1427
2264/1 (TH-259)	1056, 1080 sh.	467	1432	1425
Strata of the 9th century B.C.E.				
Group 1: Basaltic soil raw material tempered with calcite crystals				
110/158 (TH-118)	1053, 1080	467	1431	1428
119/158 (TH-117)	1052, 1079sh.	464	1432	1427
1117/256 (TH-105)	1055, 1077	463	1430	1428
Group 2: Terra Rossa soil raw material tempered with calcite crystals				
166/181 (TH-110)	1050, 1080	461	1430	1425
1115/252 (DTH-9)	1045, 1080 sh.	466	1430	1429
1115/252 (TH-113)	1046, 1080 sh.	465	1430	1426
1117/256 (TH-103)	1056, 1079	463	1432	1427
1127/252 (DTH-12)	1060, 1080	463	1430	1426
1227/256 (TH-107)	1050, 1076	465	1441	1428
1250/256 (TH-104)	1051, 1082	465	1431	1426
1672/295 (TH-47)	1053, 1080	465	1432	1429
1672/295 (TH-50)	1045, 1080 sh.	468	1431	1427
1672/295 (TH-51)	1048, 1080 sh.	468	1430	1427
1244/248 (TH-124)	1055, 1081	467	1434	1425
Group 3: Basaltic soil raw material not tempered with calcite crystals				
11/106 (TH-115)	1051, 1079	462	1432	–
171/185 (TH-119)	1059, 1080	465	1434	–
1108/252 (DTH-11)	1046, 1080 sh.	463	1433	–
1115/252 (TH-112)	1057, 1078	461	1435	–
1177/256 (TH-106)	1051, 1080 sh.	463	–	–
1244/248 (TH-126)	1050, 1080 sh.	465	–	–
1244/248 (TH-127)	1045, 1080 sh.	463	–	–
1244/248 (TH-125)	1050, 1083	464	1433	–
1683/295 (TH-48)	1057, 1080	463	1432	–

Table 2 The composition of the ceramic matrix (devoid of the temper particles) in selected of cooking pots. In each sample the results from two measuring points are demonstrated

Number	Ceramic matrix composition/%							
	SiO_2	Al_2O_3	MgO	FeO	TiO_2	K_2O	CaO	$(CaCO_3)$
Group 1: Basaltic soil raw material tempered with calcite crystals								
1574/1 (TH-7)	56.13	17.84	2.56	11.38	2.00	2.37	7.72	13.74
	55.34	20.12	2.19	11.05	1.50	2.93	6.86	12.21
1778/1 (TH-37)	58.95	12.35	4.77	15.03	1.22	1.43	6.25	11.13
	60.29	17.14	2.08	9.00	1.38	1.74	8.37	14.90
1783/3 (TH-31)	58.95	19.45	2.00	11.15	1.69	3.36	3.39	6.03
	56.98	19.23	5.05	9.33	1.29	2.08	6.04	10.75
1834/2 (TH-8)	55.89	23.37	1.99	8.99	1.27	2.50	5.99	10.66
	58.46	21.25	2.68	10.37	1.19	2.18	3.87	6.89
1844/3 (TH-42)	56.39	20.12	2.42	12.32	2.15	2.09	4.52	8.05
	56.03	19.86	2.85	13.35	2.27	1.94	3.70	6.59
Group 2: Terra Rossa soil raw material tempered with calcite crystals								
1734/1 (TH-2)	61.13	17.78	1.52	8.55	1.31	1.47	8.24	14.67
	50.87	15.59	1.50	16.41	7.19	1.06	7.39	13.15
1756/1 (TH-6)	62.78	17.76	1.41	10.58	2.96	1.79	2.72	4.84
	66.12	16.94	1.27	10.40	1.93	1.81	1.52	2.71
2021/1 (TH-5)	60.89	16.70	1.83	10.54	3.00	2.03	5.01	8.92
	64.89	17.24	1.39	10.03	2.54	1.91	2.01	3.58
2264/1 (TH-259)	60.49	19.57	1.38	10.88	2.09	1.50	4.09	7.28
	55.00	23.21	1.60	10.08	1.73	1.26	7.11	12.66

The Si–O and Al–O deformation bands

In the FTIR spectra of the cooking pots of group 1 from the 11th century B.C.E., the Si–O, Al–O deformation mode appears in the range 469–475 cm^{-1} (Table 1), and these locations are close to those observed after firing the soil raw materials between 700 and 800°C (Figs 2, 3). In the spectra of the other groups, this band appears in the range 461–468 cm^{-1} (Table 1), and these locations are close to those observed after firing the soil raw materials between 800 and 900°C (Figs 2, 3).

The main CO_3 band

In the slightly calcareous ceramic matrix, the main CO_3 band is located above 1430 cm^{-1}. In contrast, in the calcite temper, this band appears at about 1425–1429 cm^{-1} (Table 1). The higher frequency in the ceramic matrix can be related to the presence of reformed calcite [17]. This shift may result from the low degree of crystallinity of the reformed calcite and the existence of impurities of magnesium and iron [16]. It seems that at least the microcrystalline calcite of the matrix was fully decarbonated during the firing and recarbonated calcite was reformed in the ceramic after the firing. Thus, the firing was done above its decarbonation temperature. Shoval *et al.* [17] showed that in the presence of clay, under prolonged heating (6 h), the decarbonation process is completed at about 600°C in microcrystalline calcite of chalk and at about 750°C in large calcite crystals.

The OH stretching band of rehydroxylated clay

FTIR spectra of the ceramic matrix in the range of 4000–2800 cm^{-1} are shown in Fig. 4. The OH stretching bands are very weak and are distorted by bands of highly absorbed water. Therefore, they were observed only after drying the samples inside the KBr disks at 350°C. After removing the water bands, a weak OH band is observed at 3620–3632 cm^{-1} (Fig. 4). Since smectite was found to be the main clay mineral in the precursor raw material, the 3620–3632 cm^{-1} band is related to the presence of some rehydroxylated smectite in the ceramic [15]. The weak intensity of this band indicates that small amounts of rehydroxylated smectite are present in the ceramic matrix. Thus, the firing was done below the entire nonreversible dehydroxylation of the smectite [15]. In smectite, rehydration and rehydroxylation occur at room temperature, after being dehydrated and dehydroxylated by heating to temperatures as high as 800°C [31].

Discussion

Ancient ceramic technology

In a previous publication we showed that calcareous raw material was used for the preparation of Iron Age storage jars [5]. In contrast, the cooking pots were manufactured using noncalcareous or slightly-calcareous raw material proceeds from soil. A higher quality raw material was necessary in order to produce dense ceramic, impermeable and stable in cooking directly over fire and able to withstand repeated heating and cooling. Ceramic is a poor heat conductor, thus the walls of the vessel should be resistant to thermal shock, without damage [32].

The cementation of the ceramic body by sintering of the clay usually occurs on firing above 900–1000°C [33, 34]. The firing temperature of the pots, at about 750–850°C, suggests that the cementation to ceramic was obtained by low temperature sintering of the clay. This low temperature sintering occurred due to the use of soil raw material composed of smectitic clay. The clay from soil is relatively poorly crystallized and rich in natural iron oxide, both of which induce earlier sintering. In very fine textured raw material (such as soil) the sintering begins earlier than in coarse raw material [33]. Moreover, very finely divided ferrous oxide (FeO) in a reduced state may act as flux at temperatures between 800 and 900°C [35]. It seems that the high iron oxide content in the basaltic soil and the in Terra Rossa soil acts as an efficient flux material, which reduces the sintering temperature during the firing.

The tempering of the pots

The investigated cooking pots have high concentrations of temper particles. According to Tite *et al*. [36], the production of pottery with high toughness and thermal shock resistance requires low firing temperatures and high temper concentrations. The routine use of these properties in the production of cooking pots suggests that the requirement for high thermal shock resistance was a factor that at least influenced the technological choice in this case [36]. In the investigated cooking pots the high temper concentration can be related to the use of smectitic clay raw material for their production. Swelling smectitic clay is less suitable for ceramic production than kaolinitic clay. The temper particles were necessary during the manufacturing of the pottery in order to reduce high plasticity and collapse of the smectitic clay during the shaping of the vessels, as well as to prevent shrinking and cracking during the drying of the pots.

Most of the cooking pots were tempered with broken pieces of large calcite crystals that were added to the clayey raw material from an additional source. The large calcite crystals were crushed and mixed for tempering during production [37]. Large calcite crystals are not readily available and therefore potters must have gone to great efforts to collect them. According to Arnold [32], the tempering with calcite crystals prevent cracking and fracturing, which would result from thermal shock during rapid heating or cooling of the vessels. Such prevention was explained by the similarity between the thermal expansion coefficient of the calcite crystals and the surrounding fired clay during the firing. However, this is true only at low firing temperatures, at which calcite crystals do not decompose. If the firing temperature were high enough for decomposition of the calcite crystals to quicklime, the thermal expansion coefficient would no longer be similar to that of the clay [38].

Limestone particles composed of polycrystalline calcite have the same $CaCO_3$ formula and would be expected to have similar thermal expansion coefficients [17]. Although limestone is much more readily available than large calcite crystals, potters usually rejected it for the preparation of cooking pots [32]. The alternative tempering with limestone particles is inappropriate as it brings about earlier and intense decarbonation during the firing, which causes defects in the pots [17]. The polycrystalline calcite of limestone has large specific areas of crystal faces and, frequently, more crystalline defects and impurities, which lead to earlier intensive thermal decarbonation compared to monocrystalline calcite. The fast release of carbon dioxide gas (CO_2) is accompanied by, blowing and fracturing which induces mechanical damage in the pots. Furthermore, after firing the hygroscopic quicklime (CaO) picks up moisture from the air, forming calcium hydroxide $Ca(OH)_2$. The formation of calcium hydroxide is accompanied by volume expansion, which induces stresses in the surrounding clay body, causing defects in the vessels [32]. The tempering with broken pieces of large calcite crystals prevents cracking and fracturing during the firing as it provides higher resistance to thermal decomposition and this seems to be the reason for their use in cooking pots production [17].

Conclusions

The present study demonstrates that thermo-FTIR spectroscopy is a useful method for materials analysis of ancient pottery and for the determination of firing temperatures. The potters in biblical times had knowledge of raw materials and temper particles, thus enabling them to select suitable ones, according to their advantages, for the manufacture of cooking pots.

Acknowledgements

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