Analyzing the fired-clay ceramic of EBA Canaanite pottery using FT-IR spectroscopy and LA-ICP-MS

Shlomo Shoval[1,2,*] and Yitzhak Paz[3,4]

[1] Geology Group, Department of Natural Sciences, The Open University of Israel,
The Dorothy de Rothschild Campus, 1 University Road, Raanana, 43537, Israel
[2] The Freddy and Nadine Herrmann Institute of Earth Sciences, The Hebrew University of
Jerusalem, Edmund J. Safra Campus, Jerusalem, 91904, Israel (at sabbatical year status)
[3] The Department of Bible Archaeology, Ancient Near Eastern Studies
Ben-Gurion University of the Negev, Be'er Sheba', Israel
[4] Israel Antiquities Authority
* Corresponding author: *shovals@openu.ac.il*

Abstract

The fired-clay ceramic of EBA (Early Bronze Age) Canaanite pottery is mineralogically and chemically analyzed by using FT-IR spectroscopy and LA-ICP-MS. Spectral analysis by second-derivative and curve-fitting techniques is applied to the FT-IR spectra in order to improve the identification of the compositional phases. In the firing of ceramics at temperatures no higher than 950 °C, the initial clay of the raw material is transformed into fired-clay, which is then defined as meta-clay. The meta-clay is characterized by a pseudo-amorphous, short-range ordered structure. The clay minerals kaolinite, smectite (montmorillonite) and illite are thermally transformed into metakaolinite, meta-smectite and meta-illite, respectively. In the present study, the fired-clay ceramic is analyzed in two specific classes of EBA Canaanite pottery: Metallic Ware (a group of ceramic) and holemouth cooking pots. The FT-IR spectroscopy and LA-ICP-MS results demonstrate that the major constituent of Metallic Ware is metakaolinite with quartz, indicating that kaolinitic raw material containing quartz was utilized for their manufacture. On the other hand, the major constituent of holemouth cooking pots is meta-smectite, indicating that smectitic raw material was used. An observation of both meta-clays in parts of the ceramics indicates that raw material consisting of a mixture of kaolinite and smectite was employed. The kaolinitic raw material was utilized for the manufacture of high-quality Metallic Ware because it does not swell or shrink upon wetting and drying, and can be fired to high temperatures to form impermeable, thin-walled durable

vessels. However, for the manufacture of cooking pots a raw material that is stable in cooking directly over fire was required, and for this purpose smectitic raw material was utilized.

Key words: Canaan; Early Bronze Age; Holemouth cooking pots; Metakaolinite; Meta-smectite; Metallic Ware.

Introduction

Archaeological ceramics were produced from clay raw materials by sintering the clay in a firing process (Rice, 1987; Grimshaw, 1971; Heimann, and Maggetti, 2014). Two main types of ceramics were produced in ancient times: non-calcareous ceramic and calcareous (calcite-rich) ceramic (Fabbri et al., 2014). Their compositional phases depend on the type of raw material used and the temperature of the firing (Maggetti et al., 2011; Shoval et al., 2011a).

During the firing of non-calcareous raw material, the primary clay of the raw material is transformed by a series of reactions to fired-clay ceramic (Maggetti, 2009; Maggetti et al., 2011). In the firing of raw material to ceramic at temperatures no higher than 950 °C, the initial clay is transformed into fired-clay, which is then defined as meta-clay (Shoval et al., 2011a). This transformation occurs through a thermal process called dehydroxylation. In this process, the kaolinite clay dehydroxylates at approximately 450-500 °C (Frost and Vassallo, 1996; Dion et al., 1998) forming metakaolinite, which is characterized by a pseudo-amorphous short-range ordered structure (Freund, 1974; Shoval et al., 2011b). The smectite (montmorillonite) clay dehydroxylate at approximately 600 °C forming meta-smectite with a pseudo-amorphous structure (Heller, 1962; Heller-Kallai and Rozenson, 1980; Shoval, 1988; Muller et al., 2000). In addition, illite clay dehydroxylates at approximately 550-900 °C (Gualtieri and Ferrari, 2006) forming meta-illite. The consolidation of the ceramic body by sintering of the fired-clay usually occurs in firing nearly 900 °C

(Rice, 1987; Grimshaw, 1971). In this process, the meta-clay grains stick to each other. In the elevated heating of kaolinite, above 950 °C, the meta-clay progressively transforms to a defect spinel-type phase, and at higher temperature to poorly crystallized cubic mullite (Shoval et al., 2011b). The formation of well-crystallized mullite is observed in heating at approximately 1200 °C. The major compositional phases formed by the progressive heating of smectite have been identified as spinel, mullite, cordierite, and cristobalite (Seyama and Soma, 1986).

In the firing of calcareous raw material, the presence of calcite affects the thermal reactions (Shoval, 2003). The calcite decomposes through a thermal process called decarbonation. During the decarbonation, carbon dioxide gas (CO_2) is released, and free-lime (CaO) is formed (Fabbri et al., 2014). Under prolonged firing of ceramic, the decarbonation takes place at temperatures between 600 and 800 °C, depending on the form of the calcite, the impact of the clay and the firing conditions (Shoval et al., 1993; Maggetti et al., 2011). In parallel to the decarbonation, a process of dehydroxylation of the clay to form the pseudo-amorphous phase of meta-clay takes place (Shoval, 1988). In ceramic firing above 800 °C, the free-lime of the decarbonated calcite reacts with the fired-clay and generates firing silicates. Among these firing silicates are the minerals gehlenite, anorthite, larnite and diopside-wollastonite (Maggetti, 1982; Shoval, 1988; Dondi et al., 1999; Cultrone et al., 2001; Trindade et al., 2009, 2010). After firing, recarbonation of the excess of the free-lime takes place by the reaction with water vapour and carbon dioxide from the air, and fine

reformed (recarbonated) calcite is crystallized within the ceramic material (Shoval et al., 2011a; Fabbri et al., 2014). Over time, some reformed (rehydroxylated) clay is reconstructed from the fired-clay (Shoval et al., 1991; Wilson et al., 2009; Shoval et al., 2011a; Shoval and Paz, 2013).

In addition to the fired-clay, archaeological ceramics usually consist of coarse granules from rocks and minerals which are incorporated within the fine ceramic paste (Maggetti, 1982; Heimann and Maggetti, 2014). The coarse granules in the ceramic are known as "temper", "non-plastic constituent", and "inclusions". They are of significantly larger average size than the fine fired-clay of the ceramic matrix. The coarse granules can be inherited from the raw material utilized, for example, basalt fragments in pottery manufactured from basaltic soil (Shoval et al., 2006). Temper granules may be added by the potters for tempering the raw material during the production of vessels. An example would be the temper of mono-crystal calcite in cooking pots (Shoval et al., 1993; Fabbri et al., 2014).

In the present study, the fired-clay ceramic of EBA Canaanite pottery is mineralogically and chemically analyzed by using FT-IR spectroscopy (Fourier Transform Infrared Spectroscopy) and LA-ICP-MS (Laser-Ablation Inductively Coupled Plasma Mass Spectrometry). FT-IR spectroscopy is one of the methods used for the mineralogical analysis of archaeological ceramics and artefacts (Roberts et al., 2008; Kurap et al., 2010; Nel et al., 2010; Rutherford et al., 2012; Izzo et al., 2013; Ravisankar et al., 2011; 2014; Weiner, 2010; Barone et al., 2003, 2008, 2011a-b; Shoval et al., 2011a). The major advantage of FT-IR spectroscopy is its ability to identify the composition of crystalline minerals in the ceramic (De Benedetto et al., 2002, 2005; Barilaro et al., 2005, 2008; Akyuz et al., 2007, 2008) as well as the pseudo-amorphous thermal phases of the fired-clay ceramic (Shoval et al.,

2011a). Although the XRD (X-ray diffraction) method is traditionally utilized for mineralogical analysis of the crystalline minerals in the ceramic (Maggetti, 1981; Heimann and Maggetti, 1981), this method is unsuccessful for observing the pseudo-amorphous phases of the fired-clay ceramic because of the lack of distinct XRD peaks. Therefore, FT-IR spectroscopy and spectral analysis by second-derivative and curve-fitting techniques (De Benedetto et al., 2002; Shoval et al., 2011a) are applied here in analyzing the fired-clay ceramic.

LA-ICP-MS is one of the methods used for chemical analysis of archaeological ceramics and cultural heritage samples (Speakman and Neff, 2005; Giussani et al., 2009; Neff, 2012). The LA-ICP-MS method provides quantitative chemical data regarding major elements, as well as of minor and trace elements (Eckert and James, 2011; Niziolek, 2013). In the present study, we use this method for analyzing the composition of the major elements of fired-clay ceramic. The advantage of this method lies in the ability to target the laser on the fired-clay ceramic itself, thus eliminating the influence of the coarse granules within the ceramic on the results (Wallis and Kamenov, 2013).

In the present study, we analyzed the fired-clay ceramic in two specific classes of EBA Canaanite pottery: Metallic Ware and holemouth cooking pots. Metallic Ware is group of ceramic, sometimes termed Abydos Ware or Combed Ware. This specific class of high-quality pottery is identified by its pink/orange colour, thin walls, hard fabric and distinctive metallic resound when struck (Greenberg and Porat, 1996; Greenberg, 2000; Paz et al., 2009). Metallic Ware vessels were utilized for storage or serving, and comprise a full range of household forms, excluding cooking pots. Typical Metallic Ware exhibits a unity of typology and chronology, *floruit* in EB-II (3050-2700 BCE) and decline in EB-III (2700-2300 BCE). According to Greenberg and Porat,

1996, Metallic Ware was manufactured from raw material collected from Lower Cretaceous sediments, which are exposed in the Hermon Mountain foothill (including the Hula Valley margin, near Qiryat Shemona) and the south of Lebanon. In view of its stylistic affinity to contemporary Canaanite pottery, According to Greenberg and Porat, 1996, the Metallic Ware was produced in a pottery production centre at workshops located near the upper Jordan Valley region and distributed from there, in large quantities, to sites as far as 100 km away.

Holemouth cooking pots are also a specific class of Canaanite pottery, commonly identified by their brown colour (Paz and Iserlis, 2009). Their production reached its peak at the same EBA stage as Metallic Ware, especially the EB II. These pots were used for cooking foods. They are brittle, massively built and well fired and well suited for cooking. According to Paz and Iserlis, 2009, the holemouth cooking pots were produced from raw material collected from basaltic soil, which covers basalt rocks in the Golan and in parts of the Galilee.

The aim of the present study

In the present study, we utilize FT-IR spectroscopy and LA-ICP-MS in mineralogical and chemical analyses of the fired-clay ceramic of EBA Canaanite pottery - Metallic Ware and holemouth cooking pots. The mineralogical and chemical methods are utilized here to distinguish between a composition of metakaolinite and/or quartz and a composition of meta-smectite in the fired-clay ceramics. Thus, they are used to distinguish between pottery manufacture from kaolinitic or smectitic raw material. The analyses of the fired-clay ceramic are used here as criteria for identification of the manufacture technology and for sourcing the pottery. The advantages of using kaolinitic and smectitic raw materials in the manufacture of these classes of pottery are discussed.

Materials and methods

Pottery

Table 1 lists EBA Canaanite pottery studied here, their archeological sites, vessel types and dates. The samples of Metallic Ware and holemouth cooking pots were collected in Canaanite sites (Leviah, Mitzpe Zevulun and Gamla).

Reference standards. Reference standards of clay minerals typical of ceramic raw materials, as well as compositional phases typical of fired-clay ceramic were also analyzed by FT-IR spectroscopy and LA-ICP-MS and are presented here:

Reference standards of clay minerals. Reference standards of clay minerals were purchased: reference kaolinite (KGa-1) from Washington County Georgia, USA, by the Source of Clays Repository of The Clay Minerals Society Source; reference smectite (montmorillonite, Ward's No. 25) from Uptown Wyoming (Wyoming Bentonite), USA, by the Wards Scientific Establishment; and Reference illite (Ward's No. 36) from Morris Illinois, USA, by the Wards Scientific Establishment.

Reference meta-clays and firing silicate. Metakaolinite and meta-smectite were sensitized by heating reference standards of kaolinite and smectite in an electric kiln at 800 °C for 6 hours. Reference of firing silicate (gehlenite) was obtained from the geological collection of the Hebrew University.

Relevant local raw materials. Relevant local raw materials were collected in the field: local Lower Cretaceous kaolinitic sediment from the margin of the Hula Valley; and local smectitic basaltic from the margin of the Sea of Galilee. Quartz was obtained from the geological collection of the Hebrew University.

Table 1. List of the EBA Canaanite ceramics studied here, their archeological sites, vessel types and dates. The samples were collected in Canaanite sites.

Pottery Number	Excavation details	Vessel type	Date
Metallic Ware			
LEV-1	LAWI 91/186 L-194-6	MW J	EBIII
LEV-B-3	LEW (TL)-3	MW J	EBIII
LEV-B-5	LEW (TL)-5	MW J	EBII
LEV-B-6A	LEW-6 (LW-1)	MW P	EBII
LEV-B-17	LEW-17 (LW-2)	MW Pi	EBII-III
LEV-16	97 1064 L.937 2		EBII
LEV-24	97/2485 L-734-6	MW P	EBIII
ZEV-4	16-23/ 99/01/4	MW P	EBII
ZEV-7	16-23/ 99/01/7	MW P	EBII
ZEV-10	16-23/ 99/01/10	MW B	EBII
ZEV-12	16-23/ 99/01/12	MW P	EBII
GAM-1 G-2	24-83-1781 6330-2	MW P	EBII
GAM-1A G-2	24-83 L.1784 6406-1	MW P	EBII
GAM-3 G-2	24-83 L.1781 6330-3	MW P	EBII
GAM-3A G-5	24-83 L.1781 6334-3	MW P	EBII
GAM-4 G-2	24-83 L.1781 6330-4	MW P	EBII
GAM-4A G-5	24-83 L.1781 6331-4	MW P	EBII
GAM-5 G-5	24-83-1781 6334-5	MW B	EBII
GAM-5A T-13	35-84 4188 1211-1197-5	MW P	EBII
GAM-19 G-2	24-83 L.1781 6333-19	MW P	EBII
GAM-20 G-2	24-83-1781 6333-20	MW P	EBII
Holemouth Cooking Pots			
LEV-9	LAWI 93-446-L.819-9	HCP	EBIII
GAM-3A T-19	75 4016 1353-1355-1420-3	HCP	EBII
GAM-10B B-25	35-84 1251 737-749-10	HCP	EBII
GAM-11 T-19	75 4016 1353-1355-1420-11	HCP	EBII ?
GAM-12a B-22	35-84 1251 763-12	HCP	EBII
GAM-14 T-20	35-84 4039 1196-14	HCP	EBII?
GAM-17A G-2	24-83 1781 6406-17	HCP	EBII
GAM-19D B-22	35-84 1251 763-7	HCP	EBII
GAM-23 G-1	24-83 1781 6356-23	HCP	EBII
ZEV-3	16-23/99/01/3	HCP	EBII
ZEV-6	16-23/99/01/06	HCP	EBII
ZEV-8	16-23/99/01/8	HCP	EBII
ZEV-8-10	16-23/99/01/8-10	HCP	EBII
ZEV-14	16-23/99/01/8	HCP	EBII-III
ZEV-15	16-23/99/01/15	HCP	EBII-III

Leviah (LEV), Mitzpe Zevulun (ZEV), Gamla (GAM), Metallic Ware (MW), Jar (J), Platter (P), Pithoi (Pi), Bowl (B), holemouth cooking pot (HCP), Early Bronze Age (EB).

Methods

The following methods were utilized:

FT-IR spectroscopy. The mineralogy of the fired-clay ceramics was analysed using a Jasco FTIR spectrometer (Series 4000) with Spectra Manager software. Since a small amount of sample was required for the FT-IR analysis, a little chip was taken from the pottery. In the preparation of the samples, a zoom stereomicroscope was used for the separation of the coarse granules (including temper) from the fine fired-clay of the ceramic matrix, thus eliminating the influence of the latter constituent on the results. A KBr (potassium bromide) disk was used as IR transparent carrier material for the analysis of the sample in the apparatus. For this purpose, 1 mg of the picked fired-clay sample was dispersed with 1500 mg of KBr by grinding it in an agate mortar, and then pressed into the disk. The pressed disk sample was analyzed by the FT-IR spectrometer. The wavelength range 1800-400 cm^{-1} of the spectra is presented in the figures. The characteristic bands within this range are used as fingerprints for the identification of the mineral composition of ceramics (Freund, 1974) and minerals (Farmer, 1974).

Spectral Analysis by Curve-Fitting and Second-Derivative. In order to improve the identification of the compositional phases of the ceramic, spectral analysis by curve-fitting and by second-derivative was applied by using "GRAMS/AI 32 software package" of ThermoScientific Corporation. The curve-fitting of the spectra were carried out with the "Peak-Fitting Function" of the software. The band-components were fitted by using Lorentzian band shape, and in several cases by using Gaussian band shape in order to obtain the best fit. Second-derivatives of the spectra were obtained with a derivative "Gap" function of the "Grams" software.

LA-ICP-MS. The major elemental compositions of the fired-clay ceramic were quantitatively analysed by using an LA-ICP-MS of the Institute of Earth Sciences, The Hebrew University of Jerusalem. The analyses were obtained using an ICP-MS AGILENT Technologies 7500 CX series ORS quadrupole mass spectrometer for high-precision measurements of elemental concentration. The ablation was carried out with a New Wave Research UP-193FX Excimer laser ablation (LA) system with an ArF-Excimer laser emitting 15 ns-long pulses at a wavelength of 193 nm. The samples were positioned in a sealed ablation cell, using a standard new wave cell (60 cc round cell) equipped with an inlet nozzle. The cell was constantly flushed with 0.8 L/min helium gas that carried the ablated material into the ICP-MS. The analysis of the ceramic was done on fresh sections by targeting the laser on the fired-clay of the ceramic matrix only, eliminating to a large extent the influence of the coarse granules on the results (Wallis and Kamenov, 2013). We employed line (scan) analysis, 2 lines per sample, with intensive laser ablation (5.04 J cm^{-2}). The dimension of the laser beam was 100 μm-diameter spot and 1100 μm line, measured at 36 μm/sec. Data reduction was completed with the SILLS software package (Guillong et al., 2008). This software displays the time-resolved spectrum for each analyzed mass, and permits the selection of the most homogenous part of the spectrum for calculating element concentrations. The software enables the filtration of most single channel "spikes" that appear during the analysis.

Parameters of the LA-ICP-MS system

The isotopes chosen in the analysis of the major elements are: Si29+28, Ti48+Ti47, Al27, Fe57, Mn55, Mg24+Mg25, Ca42, Na23 and K39. The LODs (μg/g) are: 40.92955, 0.44404, 0.952482, 3.525916, 0.086 068, 0.340944, 21.18302, 1.664711 and 1.972755, respectively. The data was calibrated against a SRM NIST610 glass standard (commonly used in geological studies), which was mounted adjacent to the sample in the ablation cell. Testing the data

obtained with the standard SRM NIST 610 was done by analyzing the standard SRM NIST 612 as a sample. For example, in testing with the standard SRM NIST 610, the concentration of K in the analysis of the SRM NIST 612 (64.000 µg/g K) was found to be 65.001, 64.589 and 65.006 µg/g. Similarly, the concentration of Fe (51.000 µg/g Fe) was found to be 53.321, 52.723 and 53.110 µg/g. The calibration curves are utilized using the SILLS software package (Guillong et al., 2008).

Results

FT-IR spectra and spectral analysis

The term 'absorption bands' is used here for the "peaks" in the original FT-IR spectra, and the term 'components' for the "items" obtained in the spectral analysis.

Spectra of reference standards. Attribution of the absorption bands in the FT-IR spectra of the ceramics and their assignment to different compositional phases is accomplished with the support of both the literature (Freund, 1974; White, 1974; De Benedetto et al., 2002; Shoval et al., 2011a) and reference standards of minerals presented here. Figure 1 demonstrates the FT-IR spectra and second-derivatives of reference silicate phases typically found in archaeological ceramics: metakaolinite and meta-smectite (both sensitizing at 800 °C), quartz and firing silicate (gehlenite). The characteristic bands of these reference standards are used as fingerprints for the identification of the mineral composition of the ceramics.

Spectra of the pottery. Figure 2 demonstrates FT-IR spectra and spectral analysis by curve-fitting and second-derivative of representative fired-clay ceramics of Metallic Ware and holemouth cooking pots. Figure 3 shows variations in the FT-IR spectra and second-derivatives of the fired-clay ceramics. The

figures illustrate the different compositional phases of the ceramics according to their indicative bands or components. Diagnostic bands are of metakaolinite (MK), meta-smectite (MS), quartz (Q), firing silicates (FS; gehlenite) some water (H_2O) and calcite (C). Table 2 depicts the positions (in cm^{-1}) of bands and components diagnostic for silicate phases in the FT-IR spectra and in the second-derivatives of the fired-clay ceramics of the Metallic Ware and holemouth cooking pots**.**

The LA-ICP-MS major elemental composition

The major elemental composition by LA-ICP-MS is used here to confirm the identification of the type of the meta-clay composing the fired-clay ceramic. In addition to the composition of Al_2O_3 and SiO_2 of the fired-clay, the ceramic contains other oxides, such as CaO of calcite. Therefore, we use the ratio Al_2O_3/SiO_2 for differentiating between the composition of metakaolinite and meta-smectitic.

Reference standards of clay minerals and local raw materials. Table 3 demonstrates the major elemental composition of reference kaolinite, smectites and illite, and of relevant local kaolinitic and smectitic raw materials (for the sources of the samples see "materials and methods" paragraph). The ratio of Al_2O_3/SiO_2 in the reference kaolinite (0.90) is significantly higher than that in reference smectite (0.36) and in reference illite **(**0.34, Table 3). The ratio of Al_2O_3/SiO_2 in the local kaolinitic raw material (0.59, kaolinitic Lower Cretaceous sediments of the Hula Valley margin) resembles that of reference kaolinite, and confirms a kaolinitic composition. The lower Al_2O_3/SiO_2 ratio in the in the local kaolinitic raw material relative to the reference kaolinite arises from the contribution of SiO_2 from the presence of quartz, and possibly mixing with some smectite. The ratio of Al_2O_3/SiO_2 in the local smectitic raw material (0.30, smectitic basaltic soil of Sea of Galilee margin)
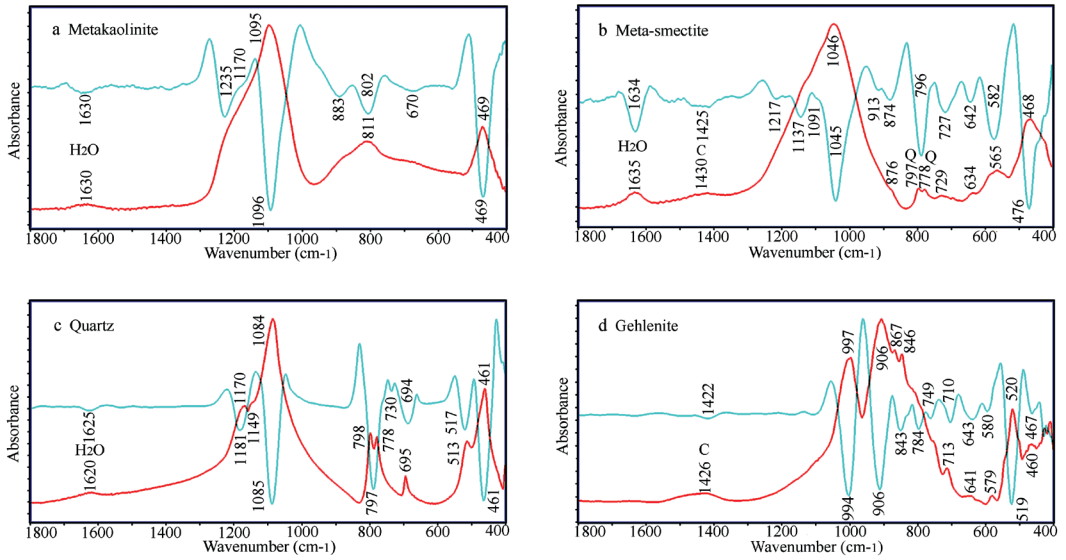
Figure 1. FT-IR spectra and second-derivatives of reference silicate phases typically found in archaeological ceramics: (a) metakaolinite (sensitizing at 800°C), (b) meta-smectite (sensitizing at 800°C), (c) quartz and (d) firing silicate (gehlenite). Bands of some water (H_2O) and accessory calcite (C) are also identified.

Figure 2. FT-IR spectra and spectral analysis by curve-fitting and second-derivative of representative fired-clay ceramics of (a) Metallic Ware (LEV-24) and (b) holemouth cooking pots (LEV-9). Diagnostic bands are of metakaolinite (MK), meta-smectite (MS), quartz (Q), some water (H_2O) and calcite (C).

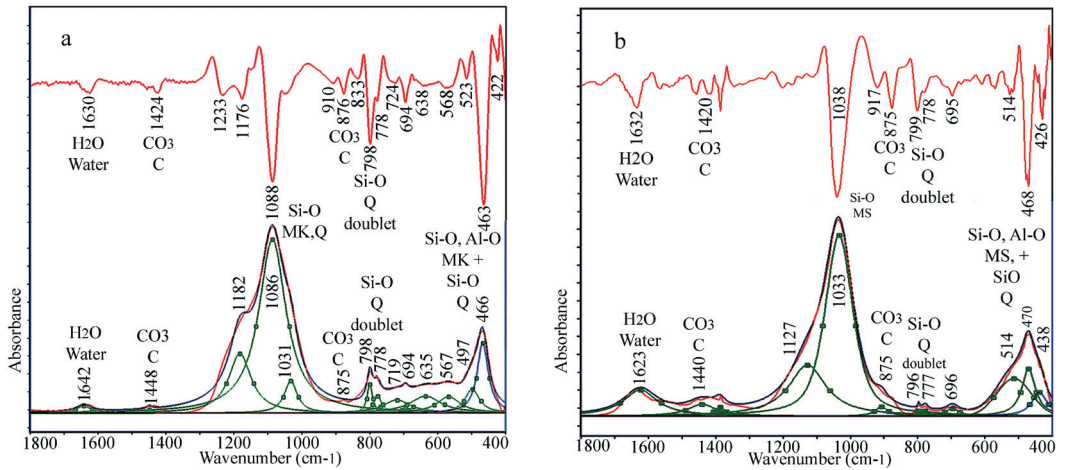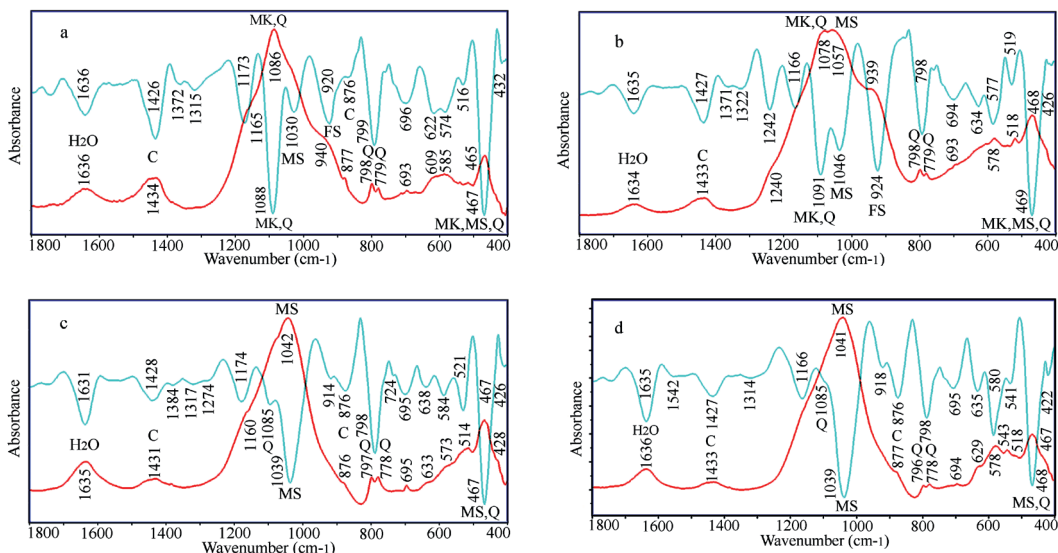Figure 3. Variation**s** in the FT-IR spectra and second-derivatives of the fired-clay ceramics: (a-b) Metallic Ware (GAM-19 G-2 and GAM-4 G-2) and (c-d) holemouth cooking pots (GAM-14 T-20 and GAM-10B B-25). Diagnostic bands are of metakaolinite (MK), meta-smectite (MS), quartz (Q), firing silicates (FS; gehlenite) some water (H_2O) and calcite (C).

is similar to that in the reference smectite (Table 3), and confirms a smectitic composition.

The fired-clay ceramic. Tables 4-5 demonstrates the LA-ICP-MS major elemental composition of the fired-clay ceramics of Metallic Ware and holemouth cooking pots, respectively. Line (scan) analysis, 2 lines per sample was employed**.** In the fired-clay ceramic of the Metallic Ware, the ratio of Al_2O_3/SiO_2 appears 0.47-0.63 (Table 4), indicating that raw material rich in kaolinite was used for its manufacture. Indeed, Metallic Ware was manufactured from raw material collected from Lower Cretaceous sediments (Greenberg and Porat, 1996), which has an Al_2O_3/SiO_2 ratio of kaolinitic composition (0.59, kaolinitic Lower Cretaceous sediments of the Hula Valley margin, Table 3). In the fired-clay ceramic of the holemouth cooking pots, the ratio of Al_2O_3/SiO_2 is lower, 0.22-0.36 (Table 5), indicating

that raw material rich in smectite was used for their manufacture. Indeed holemouth cooking pots were produced from raw material collected from basaltic soil (Paz and Iserlis, 2009), which has an Al_2O_3/SiO_2 ratio of smectitic composition (0.30, smectitic basaltic soil basaltic soil of the Sea of Galilee margin, Table 3).

Discussion

The fired-clay ceramic of EBA Canaanite pottery (Metallic Ware and holemouth cooking pots) is mineralogically and chemically analyzed by using FT-IR spectroscopy and LA-ICP-MS.

The mineral composition of the fired-clay ceramic

The meta-clay. The FT-IR spectroscopy allows the identification of the pseudo-amorphous phases of meta-clay in the composition of the ceramic (Shoval et al., 2011a). The identified

Table 2. The positions (in cm^{-1}) of bands and components diagnostic for silicate phases in the FT-IR spectra and in the second-derivatives of fired-clay ceramics of Metallic Ware and holemouth cooking pots.

Pottery Number	FT-IR spectra					Second-derivative		
	Si-O str. MK and/ or Q	Si-O str. MS	Si-O and Al-O str. FS	Si-O Q doublet	Si-O/Al-O ben. MK and/or MS + Si-O Q	Si-O str. MK and/ or Q	Si-O str. MS	Si-O/Al-O str. FS and/ or Al-OH ben. RC
"Metallic" Ware								
LEV-1	1086p	1030sh	940m	798,779m	470m	1088s	1030w	931m
LEV-B-3	1081p	1040sh		798,779m	464m	1086s	1037w	908w
LEV-B-5	1085p			798,779m	465m	1086s	1037w	908w
LEV-B-6A	1082p	1050sh		798,779m	463m	1086s	1042w	913w
LEV-B-17	1085p			798,779m	465m	1086s	1038w	910w
LEV-16	1078p	1050p		798,779m	464m	1087s	1037m	913w
LEV-24	1088p			798,778m	466m	1086s	1050w	910w
ZEV-4	1083p	1056p	945m	798,778m	466m	1091s	1032m	923m
ZEV-7	1084p	1040sh		798,779m	461m	1085s	1035w	920w
ZEV-10	1083p	1059p	940sh	798,779m	468m	1090s	1040m	923m
ZEV-12	1079p	1058p		798,779m	469m,461sh	1087s	1033m	913w
GAM-1 G-2	1080sh	1037p		797,778m	467m	1091s	1032s	914w
GAM-1A G-2	1072p	1048p		798,779m	468m	1084s	1039m	914w
GAM-3 G-2	1079p	1036sh	939m	797,779m	465m	1085s	1031m	925m
GAM-3A G-5	1077p	1053p	950sh	797,779m	467m	1093s	1042s	924m
GAM-4 G-2	1078p	1057p	939m	798,779m	469m	1091s	1046m	924s
GAM-4A G-5	1081p	1060p	941m	798,779w	470m	1090s	1030m	925m
GAM-5 G-5	1083p	1050sh	945m	797,779w	467m	1090s	1032m	921m
GAM-5A T-13	1088p			798,779m	468m	1088s	1049w	904m
GAM-19 G-2	1086p	1030sh	940m	798,779m	467m	1088s	1030w	920m
GAM-20 G-2	1080sh	1044p	940sh	798,778w	468m	1093s	1039s	920m
Holemouth Cooking Pots								
LEV-9		1033p		796,778w	470m		1038s	917w
GAM-3A T-19	1072sh	1046p		797,779m	462m	1085m	1040s	917w
GAM-10B B-25		1041p		796,778w	467m	1085w	1039s	918w
GAM-11 T-19	1075p	1051p		797,779m	463m	1085s	1039s	913w
GAM-12a B-22		1045p		798,778w	465m	1086m	1040s	915w
GAM-14 T-20		1042p		797,778m	467m	1085w	1039s	914w
GAM-17A G-2	1077p	1055p	930sh	796,778m	462m, 469sh	1089s	1038s	921m
GAM-19D B-22	1078p	1060p	920sh	796,778m	460m, 468sh	1086s	1037s	918w
GAM-23 G-1	1079p	1052p	935sh	796,779m	464m			
ZEV-3	1073sh	1039p		797,778w	465m	1089w	1040s	914w
ZEV-6	1077sh	1040p	930sh	796,778w	465m	1089m	1034s	914m
ZEV-8	1083p	1050p	930sh	796,778m	460m, 469sh	1086s	1034s	912w
ZEV-8-10	1086p	1040p		798,779m	465m	1086s	1034s	912w
ZEV-14	1084p	1040p		798,779m	461m	1085s	1035s	915w
ZEV-15	1082p	1060p	930sh	797,778s	465m	1085s	1035s	920m

Metakaolinite (MK), meta-smectite (MS), quartz (Q), firing silicate (FS, gehlenite), reformed clay (RC), stretching vibration (str.); bending vibration (ben.), principle band (p), strong (s); medium (m), weak (w), shoulder (Sh).

Table 3. The major elemental composition of reference kaolinite, smectite and illite, and of relevant local kaolinitic and smectitic raw materials (for the sources of the samples, see "materials and methods" section).

Raw Material	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Al_2O_3/SiO_2
Reference standards of clay minerals:									
Kaolinite (KGa-1)	44.20	1.39	39.70	0.13	0.03	-	0.01	0.05	0.90
Smectite (montmorillonite, Ward's 25)	60.38	0.08	21.78	3.94	2.57	3.40	3.25	0.00	0.36
Illite (Ward's 36)	62.12	1.91	20.94	4.84	2.03	-	0.56	6.40	0.34
Local raw materials									
Kaolinitic Lower Cretaceous sediments of the Hula Valley margin	57.53	2.08	34.11	2.30	0.30	-	0.29	1.28	0.59
Local smectitic basaltic soil of the Sea of Galilee margin	53.31	1.93	16.01	10.17	4.75	9.25	0.67	2.06	0.30

meta-clays in the ceramics are metakaolinite and meta-smectite. The principle band of the meta-clay at 1030-1090 cm^{-1} is assigned to Si-O stretching mode (Freund, 1974). In the FT-IR spectra of the reference metakaolinite and meta-smectite, this band appears at 1095 and 1046 cm^{-1}, respectively (Figure 1 a,b). The presence of the quartz contributes an overlapped component nearly 1084 cm^{-1} (Figure 1c). In the spectra of the ceramics, the location of the principle Si-O stretching band reflects the relative amounts of these contributors (Figures 2, 3, Table 2). When metakaolinite and/or quartz are dominant, the band-maximum appears at higher frequencies (1086 cm^{-1}, Figure 3a) and when meta-smectite is dominant, it appears at lower frequencies (1042 cm^{-1}, Figure 3 c,d). When both compositional phases are dominant, two maxima may be observed in the spectra (1057 and 1078 cm^{-1}, Figure 3b). In addition, a weak Si-O component of some reformed (rehydroxylated) clay (Shoval et al., 1991; Shoval et al., 2011a) may overlap in the range of the principle Si-O stretching band of the meta-smectite. The band at 468 cm^{-1} in the spectra of the reference metakaolinite and

meta-smectite (Figure 1 a,b), is assigned to a combined Si-O/ Al-O bending mode (Freund, 1974). This band appears at 460-470 cm^{-1} in the spectra of the ceramics (Figures 2, 3, Table 2).

Spectral analysis of the meta-clay. The principle Si-O stretching band usually appears in the spectra of the ceramics as a composite-band of mixtures of silicate phases, on which their Si-O stretching bands partially overlap. Characteristics of the composite-band are wideness, asymmetric shape and some shoulders (Figures 2, 3). The spectral analysis by curve-fitting and second-derivative permits the separation of the composite Si-O stretching band into its components - metakaolinite and/or quartz and meta-smectite - and thus enables us to improve the identification of the compositional phases of the ceramic. Through the curve-fitting technique, the composite-band is converted into its quantified components of the compositional phases (Figures 2, 3). The second-derivative technique enables us to determine the exact frequencies (wavenumbers) of the components of the composite-band. The location of the

Table 4. The LA-ICP-MS major elemental composition of the fired-clay ceramic of Metallic Ware. Line (scan) analysis, 2 lines per sample was employed**.**

Pottery Number	Line	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	Al_2O_3/SiO_2
LEV-1	1	45.81	2.50	25.39	7.34	0.09	1.46	15.87	0.09	0.83	0.55
	2	46.75	1.76	26.13	6.66	0.09	1.25	16.06	0.04	0.75	0.56
LEV-B-3	1	56.36	1.91	26.10	7.37	0.05	0.79	6.04	0.26	0.88	0.46
	2	59.04	2.21	25.27	5.33	0.04	0.91	5.41	0.25	1.22	0.43
LEV-B-5	1	47.95	1.88	26.01	7.00	0.07	1.83	13.56	0.17	0.92	0.54
	2	50.73	1.74	23.83	7.17	0.10	1.28	13.69	0.17	0.84	0.47
LEV-B-6A	1	53.25	3.81	25.11	7.76	0.06	0.76	6.18	0.49	2.18	0.47
	2	53.29	4.69	24.49	8.26	0.04	0.85	6.87	0.20	1.01	0.46
LEV-B-17	1	49.15	2.57	25.44	9.66		1.02	8.61	0.23	2.39	0.52
	2	49.44	2.43	21.46	10.74		1.40	10.29	0.02	2.32	0.43
LEV-16	1	53.53	1.52	25.14	6.99	0.10	0.87	9.89	0.18	1.26	0.47
	2	53.18	1.70	22.89	10.40	0.12	0.77	8.93	0.22	1.10	0.43
LEV-24	1	55.59	3.16	35.15	3.45		0.70	0.72	0.13	0.83	0.63
	2	51.62	1.70	30.77	3.22		0.75	9.36	0.34	1.44	0.60
ZEV-4	1	46.59	1.44	28.19	5.72	0.08	0.73	15.66	0.18	1.04	0.61
	2	49.22	1.82	26.44	4.79	0.07	0.66	14.33	0.34	1.74	0.54
ZEV-7	1	47.59	1.95	27.82	12.05	0.06	0.65	8.23	0.22	0.87	0.58
	2	47.55	1.84	28.09	6.75	0.06	0.64	13.78	0.11	0.64	0.59
ZEV-10	1	50.83	1.45	26.79	6.54	0.14	0.92	11.65	0.15	1.07	0.53
	2	46.97	1.49	25.40	8.85	0.15	0.90	15.10	0.15	0.65	0.54
ZEV-12	1	44.37	2.00	26.23	5.91	0.09	0.92	18.91	0.27	0.90	0.59
	2	42.14	1.30	25.17	5.93	0.08	1.07	22.80	0.23	0.88	0.60
GAM-1 G-2	1	46.92	1.29	27.36	5.58	0.07	0.82	16.14	0.28	1.30	0.58
	2	49.07	1.19	25.64	6.02	0.07	0.84	15.28	0.30	1.36	0.52
GAM-1A G-2	1	49.31	1.41	26.67	6.42	0.06	0.93	13.82	0.23	0.94	0.54
	2	51.57	1.66	24.92	6.66	0.13	0.87	12.86	0.18	0.90	0.48
GAM-3 G-2	1	47.32	1.51	27.54	7.38	0.12	1.32	13.07	0.14	0.91	0.58
	2	47.27	1.47	27.17	8.53	0.18	1.29	12.38	0.14	0.94	0.57
GAM-3A G-5	1	45.24	2.14	26.33	7.35	0.06	0.90	15.37	0.21	1.31	0.58
	2	44.79	1.25	25.72	6.64	0.10	1.04	17.26	0.20	1.23	0.57
GAM-4 G-2	1	46.54	1.72	25.57	6.42	0.09	1.05	16.80	0.20	1.08	0.55
	2	47.36	2.18	24.74	7.24	0.19	1.02	15.22	0.20	1.17	0.52
GAM-4A G-5	1	46.57	1.29	25.89	6.46	0.07	0.82	17.31	0.11	1.00	0.56
	2	43.63	1.28	25.00	7.40	0.10	0.92	19.95	0.12	0.99	0.57
GAM-5 G-5	1	46.94	1.42	27.20	7.03	0.08	1.01	14.92	0.12	0.88	0.58
	2	46.20	1.17	26.70	6.93	0.08	0.98	16.62	0.13	0.83	0.58
GAM-5A T-13	1	59.11	2.03	33.48	2.07	0.00	0.61	0.59	0.21	1.77	0.57
	2	55.59	3.16	35.15	3.45	0.01	0.70	0.72	0.13	0.83	0.63
GAM-19 G-2	1	47.59	1.48	26.08	8.44	0.11	0.85	13.84	0.16	0.95	0.55
	2	49.12	1.46	25.94	8.85	0.10	0.82	12.04	0.18	1.05	0.53
GAM-20 G-2	1	50.22	1.86	24.90	6.17	0.05	1.12	13.18	0.41	1.49	0.50
	2	48.42	1.42	22.65	7.30	0.05	0.95	15.60	0.54	2.06	0.47

Table 5. The major elemental composition of the fired-clay ceramic of holemouth cooking pots. Line (scan) analysis, 2 lines per sample was employed.

Pottery Number	Line	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O	Al$_2$O$_3$/ SiO$_2$
LEV-9	1	38.64	1.77	10.95	12.99	0.23	3.30	28.73	0.29	1.97	0.28
	2	41.63	1.70	12.21	10.71	0.03	3.71	27.06	0.35	2.09	0.29
GAM-3A T-19	1	69.88	2.09	16.20	6.57	0.25	1.49	2.16	0.62	0.54	0.23
	2	64.76	6.58	15.47	8.26	0.26	1.27	2.23	0.25	0.74	0.24
GAM-10B B-25	1	64.49	0.08	14.97	20.04	0.01	0.28	0.07	0.04	0.01	0.23
	2	64.91	0.05	14.21	20.36	0.00	0.29	0.10	0.05	0.01	0.22
GAM-11 T-19	1	63.00	2.56	19.38	8.72	0.23	1.43	2.79	0.32	1.15	0.31
	2	58.86	5.75	17.98	10.71	0.25	1.53	2.77	0.50	1.16	0.31
GAM-12a B-22	1	56.82	1.54	15.49	7.13	0.12	5.25	10.62	0.73	1.49	0.27
	2	53.65	1.63	16.25	7.16	0.09	4.44	14.08	0.54	1.54	0.30
GAM-14 T-20	1	61.55	2.59	20.12	8.87	0.12	1.49	3.61	0.60	0.76	0.33
	2	60.69	2.60	19.31	9.77	0.15	1.64	3.83	1.02	0.69	0.32
GAM-17A G-2	1	63.30	2.60	17.46	10.15	0.12	1.44	2.79	0.84	1.07	0.28
	2	59.92	2.88	19.10	11.55	0.11	1.36	2.80	0.92	1.16	0.32
GAM-19D B-22	1	60.52	2.42	19.17	10.60	0.24	1.83	2.56	1.58	0.82	0.32
	2	54.61	2.83	15.82	10.26	0.23	4.82	8.37	1.64	0.85	0.29
GAM-23 G-1	1	55.14	1.90	14.13	6.71	0.12	7.32	12.30	0.35	1.40	0.26
	2	52.74	1.10	14.43	5.07	0.13	7.14	17.50	0.04	1.34	0.27
ZEV-3	1	58.19	1.76	17.70	12.56		1.75	3.78	1.27	2.58	0.30
	2	56.55	1.84	17.79	11.97		1.81	5.76	1.62	1.55	0.31
ZEV-6	1	55.21	2.69	18.52	14.07	0.43	1.74	4.50	1.67	0.79	0.34
	2	51.54	2.70	18.46	12.39	0.13	2.16	8.68	2.21	0.93	0.36
ZEV-8	1	56.34	1.54	16.44	14.87	0.43	1.53	5.92	0.85	1.53	0.29
	2	57.84	1.40	18.79	11.21	0.09	1.96	5.46	1.14	1.57	0.32
ZEV-8-10	1	59.23	4.45	19.95	8.01	0.15	1.98	4.08	0.78	0.92	0.34
	2	60.05	3.75	20.90	7.72	0.12	2.14	3.78	0.21	1.05	0.35
ZEV-14	1	57.21	2.23	16.62	15.28		1.18	4.76	0.10	1.72	0.29
	2	55.49	2.43	15.93	16.65		1.36	5.37	0.10	1.77	0.29
ZEV-15	1	58.56	2.04	14.50	13.68	0.62	1.08	6.42	0.91	1.89	0.25
	2	61.42	2.39	14.35	12.91	0.17	1.54	3.83	1.02	2.54	0.23

principle component at 1070-1090 cm^{-1} is related to a composition of metakaolinite and/or quartz, whereas the location of the principle component at 1030-1060 cm^{-1} is related to a composition of meta-smectite (Figure 2, Table 2).

The firing silicates. In the spectra of highly fired ceramics, an additional band of firing silicate (gehlenite) may be observed at 920-940 cm^{-1} (Table 2). In the FT-IR spectrum of reference firing silicate (gehlenite), the principle band at 906 cm^{-1} (Figure 1d) is assigned to Si-O/Al-O stretching modes (Henning, 1974). In the spectra of the ceramics, this band appears at 920-940 cm^{-1} on the flank of principle Si-O stretching band of the meta-clay (Figure 3 a,b). This band of firing silicate commonly forms a shoulder, and thus it is better observed by the second-derivative nearly 920 cm^{-1} (Figure 3 a,b). In addition, a weak Al-OH bending mode (Farmer, 1974) of some reformed (rehydroxylated) clay (Shoval et al., 1991; Shoval et al., 2011a) may be observed in the second-derivative at 910-920 cm^{-1} (Figure 2, Figure 3 c,d). The latter band may overlap in the range of the principal Si-O/Al-O stretching band of the firing silicate.

Quartz. In the FT-IR spectrum of reference quartz, the principal band at 1084 cm^{-1} (Figure 1c), is assigned to Si-O asymmetrical stretching vibration ($v3$; Saikia et al., 2008). In the spectra of the ceramics, this band may distorted by the Si-O stretching mode of metakaolinite (Figure 3a). Thus, the band doublet of quartz at approximately 778 and 798 cm^{-1}, which is assigned to Si-O symmetrical stretching vibration ($v1$; Saikia et al., 2008), is preferable for detection of quartz in the spectra of the ceramics. The band of quartz at 461 cm^{-1} (Figure 1c), is assigned to Si–O asymmetrical bending vibration ($v4$, Saikia et al., 2008). In the spectra of the ceramics, this quartz band is distorted by the combined Si-O/Al-O bending mode of the metakaolinite and the meta-smectite at 460-470 cm^{-1} (Figures 2, 3; Table 2).

Calcite. In a FT-IR spectrum of calcite, the principal band at 1025 cm^{-1} is assigned to CO_3 asymmetrical stretching vibration ($v3$, White 1974; Fabbri et al., 2014). In the spectra of the ceramics, the principal band of the accessory calcite range from 1430-1450 cm^{-1} (Figures 2, 3). Its weak intensity in the spectra of the ceramics studied demonstrates a non-calcareous or a slightly calcareous composition.

The major elemental composition of the fired-clay ceramic

Chemical analysis of the fired-clay ceramic by LA-ICP-MS (Tables 4, 5) is used here to confirm the identification of metakaolinite and meta-smectite in the composition of the fired-clay ceramic as obtained by the FT-IR spectroscopy. Kaolinite contains a higher amount of Al_2O_3 and has a higher Al_2O_3/SiO_2 ratio than smectite. In their structure, the kaolinite plate consists of a single silica tetrahedral sheet and a single alumina octahedral sheet, whereas the smectite plate consists of two silica tetrahedral sheets with a single alumina octahedral sheet between them (Farmer, 1974). Thus, the content of Al_2O_3 and SiO_2 in the meta-clay and the ratio of Al_2O_3/SiO_2 allow the observation of the types of meta-clay composing the fired-clay ceramics, and the types of initial clay used in the manufacture. The higher Al_2O_3/SiO_2 ratio detected in the fired-clay of the Metallic Ware (0.43-0.63, Table 4) indicates that metakaolinite is the major constituent, whereas the lower ratio observed in the fired-clay of the holemouth cooking pots (0.22-0.36, Table 5) indicates that meta-smectite is the major constituent. The presence of quartz silt in the fired-clay ceramic may increase the amount of SiO_2. In addition, the low content of K_2O in the fired-clay ceramic indicates that illitic raw material was not used for the manufacture (Tables 4, 5). Some content of MgO is related to

a contribution from smectite and some content of Fe_2O_3 to a contribution from smectite and iron oxide.

Identification the type of raw material

The results reveal that specific types of raw materials were used for the manufacture of specific classes of functional pottery. Each of these raw materials has its advantages.

Metallic Ware. was manufactured from kaolinitic raw material. In these vessels the mutual band of metakaolinite and quartz at 1070-1090 cm^{-1} is dominant (Figures 2a, 3a, Table 2). The high Al_2O_3/SiO_2 ratio observed in the ceramic by LA-ICP-MS analysis (0.43-0.63, Table 4) is indicative of a composition rich in metakaolinite. Petrography reveals that such Metallic Ware with quartz sand inclusions were produced from Lower Cretaceous clay sediment (Hatira Formation), which is rich in quartz grains (Greenberg and Porat, 1996). These sediments are exposed in the Hermon Mountain foothill (including the Hula Valley margin, near Qiryat Shemona) and in the region of southern Lebanon. Indeed, the examined Lower Cretaceous sediment of the Hula Valley margin is rich in kaolinite and contains quartz grains (Table 3). Kaolinitic raw material is more suitable for ceramic production, and was selected for the manufacture of the high-quality Metallic Ware. The kaolinite clay does not swell or shrink upon wetting and drying, and can be fired to high temperatures to form high-quality impermeable, thin-walled, durable vessels. Apparently, its superiority was recognized in early times, and it was used wherever available. Due to the high quality of the raw material, the kaolinitic Lower Cretaceous sediment of the Hermon Mountain foothill was utilized in the production and distribution centre of Metallic Ware during the Early Bronze Age (Greenberg and Porat, 1996).

The holemouth cooking pots. were produced from smectitic raw material. In these pots, the band of meta-smectite at 1030-1060 cm^{-1} is dominant (Figure 2b, Figure 3 c,d; Table 2). The low Al_2O_3/SiO_2 ratio observed in the ceramic by LA-ICP-MS analysis (0.22-0.36, Table 5) is indicative of a composition rich in meta-smectite. Petrography reveals that such holemouth cooking pots with volcanic rock inclusions were produced from basaltic soil raw material (Paz and Iserlis, 2009). Nevertheless, temper granules of mono-crystal calcite were not reported in petrography of holemouth cooking pots from Golanite production and distribution centre (Paz and Iserlis, 2009). The basaltic soil covers basalt rocks in the areas of the Golan and parts of the Galilee. Indeed, the examined basaltic soil of Sea of Galilee margin is rich in smectite and contains basalt fragments (Table 3). Smectitic raw material is usually considered less suitable for ceramic production, since it swells or shrinks upon wetting and drying. However, for the manufacture of cooking pots, a raw material that is stable in cooking directly over fire and able to withstand repeated heating and cooling was required. Smectitic raw material was utilized for this purpose (Shoval and Beck, 2005). As ceramic is a poor heat conductor, the pot must be able to tolerate thermal shock during cooking without sustaining damage. For this reason, smectitic basaltic soil raw material was utilized in Golanite production and distribution centre of cooking pots during the Early Bronze Age (Paz and Iserlis, 2009).

Summary

1. The fired-clay ceramics in two specific classes of EBA Canaanite pottery - Metallic Ware and holemouth cooking pots - are mineralogically and chemically analyzed by using FT-IR spectroscopy and LA-ICP-MS. These methods are used here to distinguish between a composition of metakaolinite and/or quartz and a composition of meta-smectite of the fired-clay ceramics. That is, they are used to

distinguish between pottery manufacture from kaolinitic or smectitic raw materials.

2. In the spectra of the ceramics, the type of the meta-clay is distinguished by the location of the principle Si-O stretching band**.** In the second-derivative, the location of the principle component at 1070-1090 cm^{-1} is related to a composition of metakaolinite and/or quartz, whereas the location of the principle component at 1030-1060 cm^{-1} is related to a composition of meta-smectite. The chemical analysis confirms the identification of metakaolinite and meta-smectite as obtained by the FT-IR spectroscopy. A high Al_2O_3/SiO_2 ratio in the ceramic is indicative of metakaolinite composition, whereas a low ratio is indicative of meta-smectite.

3. The results reveal that specific types of raw materials were used for the manufacture of specific classes of functional pottery. The major constituent of Metallic Ware is metakaolinite with quartz, indicating that kaolinitic raw material was used for its manufacture. On the other hand, the major constituent of holemouth cooking pots is meta-smectite, indicating that smectitic raw material was used. An observation of both meta-clays in the ceramic indicates that raw material consisting of a mixture of kaolinite and smectite was employed.

4. The kaolinitic raw material was utilized for the manufacture of the high-quality Metallic Ware, because it does not swell or shrink upon wetting and drying, and can be fired to high temperatures to form impermeable, thin-walled, durable vessels. However, for the manufacture of cooking pots, a raw material that is stable in cooking directly over fire was required, and for this purpose smectitic raw material was used.

Acknowledgments

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