

A STUDY OF THE FIRING TECHNIQUE OF POTTERY FROM KAMAN-KALEHÖYÜK, TURKEY, BY SYNCHROTRON RADIATION-INDUCED FLUORESCENCE X-RAY ABSORPTION NEAR-EDGE STRUCTURE (XANES) ANALYSIS*

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Fe K-XANES spectra of a series of pottery sherds excavated from the archaeological site of Kaman-Kalehöyük, Turkey, were measured to reveal the firing technique of the pottery. The analysis disclosed relationships among the chemical form of the iron, the firing conditions and the colour of the pottery. The pottery referred to as 'Grey Ware' found at this site was classified into two groups according to the chemical form of the iron. Also, it was revealed that the Iron Age pottery referred to as 'Cream Ware' was produced first under reducing conditions, and then fired under oxidizing conditions.

KEYWORDS: IRON AGE, XANES, SYNCHROTRON RADIATION, POTTERY, FIRING TECHNIQUE, TURKEY, NON-DESTRUCTIVE ANALYSIS

INTRODUCTION

Chemical state analyses of archaeological materials can provide information on their manufacturing processes. For example, X-ray photoelectron spectroscopy (XPS) was applied to glass in order to investigate the origins of the colour (Lambert and McLaughlin 1976) and Mössbauer spectroscopy has been used to study the firing technique of ceramics (Hess and Perlman 1974; Makundi *et al.* 1989; Wagner *et al.* 1997, 1999). The recent development of synchrotron radiation (SR) technology has brought large advances in the X-ray fluorescence analysis (SR-XRF) of archaeological materials. SR-XRF has several remarkable advantages over the conventional XRF technique. For example, it is easy to obtain a microbeam using slits (beam size about $100 \times 100 \mu\text{m}^2$) or focusing optics (beam size less than a few μm^2). SR-XRF can be used for the transformation of a small or complicated artistic pattern (e.g., a pattern on pottery or a figurine) into a two-dimensional chemical composition image (Nakai 1996). Also, highly polarized and energy-tunable intense radiation allows us to analyse a trace amount of a desired element (Mommensen *et al.* 1996).

Not solely a compositional analysis, SR-XRF also enables chemical state analyses using the fluorescence X-ray absorption near-edge structure (XANES). XANES derives from electronic transitions from a core level to the first empty bound state and from multiple scattering resonance, where low-energy photoelectrons are backscattered by the surrounding atoms (Calas *et al.* 1988). XANES provides information on oxidation states and coordination numbers, as well as site symmetry around the absorbing atoms (Bianconni *et al.* 1985). Since the intensity of a fluorescent X-ray is proportional to the absorption coefficient of an element when the

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sample is thin enough or when it is dilute, the XANES spectrum can be measured using fluorescence detection (Sakurai *et al.* 1988). Fluorescence XANES is suitable for the chemical state analysis of a trace element in a sample. Moreover, a combination of an S.S.D. (solid state detector) and an X-ray microbeam allows us to carry out the non-destructive two-dimensional or spatial measurement of a XANES spectrum (Hayakawa *et al.* 1991). This is a technique that is unique to fluorescence XANES and cannot be done by Mössbauer spectroscopy, although individual sampling may allow partial spatial analysis by Mössbauer. However, when the absorber atom in the sample is in a mixture of several chemical states, the resultant XANES spectrum is the sum of the spectra of each state, and therefore only provides limited information about the individual components. In this respect, Mössbauer spectroscopy provides more quantitative information about the ratio of the components, such as the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio.

Taking advantage of these considerations, we have established experimental procedures for using the SR-XRF technique for archaeometric analysis and applied it to various practical problems in archaeology and art (e.g., Nakai and Iida 1992; Nakai 1996; Nakai *et al.* 1999). In this study, we applied the fluorescence XANES technique to study pottery found at the archaeological site of Kaman-Kalehöyük, Turkey. The excavation at Kaman-Kalehöyük was begun in 1986 by the Middle Eastern Culture Center in Japan (MECCJ) and so far four main cultural layers—Early Bronze Age (Level IV), Bronze Age (Level III), Iron Age (Level II) and Islamic Period (Level I)—have been confirmed (Omura 1998). Since the colour of a pottery sherd is one feature that is often characteristic of a cultural layer, they are considered as important indexes for the dating of architectural remains at the site (Matsumura 1994). The colour of pottery is presumed to reflect its manufacturing technique, but the relationship between the colour of pottery and firing techniques is complex. Therefore, it is important to find a scientific relation between the colours and the firing techniques on the basis of experimental data. Furthermore, it is not unusual to find pottery that exhibits different colours between the surface and core, and that is not well evaluated by the archaeological classification. Since iron is sensitive to firing conditions and the colour of the pottery is closely related to the chemical form of iron, we measured the iron K X-ray edge (Fe K-XANES) spectra of the samples. We also applied the micro-XANES technique when two-dimensional resolution was necessary. First, the Fe K-XANES spectra of iron minerals and fired clays were measured to obtain basic information on the chemical form of iron in the samples. On the basis of this knowledge, we continued our study to reveal the firing techniques of several important ceramic classes found at Kaman-Kalehöyük.

SAMPLE PREPARATION

Thirty-six pottery sherds excavated from Kaman-Kalehöyük, an archaeological site in central Anatolia with Early Bronze Age, Assyrian Trade Colony, Hittite, Phrygian and Ottoman occupation levels were used in this study. Several fired clay samples collected near Kaman-Kalehöyük were also examined. Small pottery fragments were obtained by cutting the sherds at an edge with a diamond-cutter after washing in water. Sections of the fragments were used in this experiment. Firing experiments were carried out using clays collected from the region surrounding Kaman-Kalehöyük. The clays were levigated for two days and then dried in the sun. After adding water, the clays were moulded into blocks ($1 \times 1 \times 1.5 \text{ cm}^3$) and dried. The blocks were fired at 300, 600, 900 and 1200°C in air or with graphite powder in a nitrogen gas flow ($50 \text{ cm}^3 \text{ min}^{-1}$). The firings were carried out at a rate of 200°C h^{-1} , with a baking time of 4 h at the peak temperature. Reference samples used as standards for iron in various oxidation

states included iron metal, pyrite, magnetite, hematite, goethite, augite, diopside, epidote, almandine, spinel, aegirine, olivine, kaolinite and montmorillonite.

MEASUREMENT OF XANES SPECTRA

The Fe K-edge XANES spectra were measured in the fluorescence mode using the BL-7C and BL-4A beamlines of the Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan. BL-7C is a beamline dedicated to XAFS (X-ray absorption fine structure) and provides X-rays of medium (about $1 \times 6 \text{ mm}^2$) beam size (Nomura *et al.* 1991). BL-4A is a beamline designed for microbeam X-ray fluorescence analysis (Gohshi *et al.* 1988). BL-7C was used for analyses of the clay samples and the pottery fragments with homogeneous colours. BL-4A was selected when the two-dimensional measurements of XANES spectra were required. The reference iron minerals were measured at both beamlines. Monochromatized 2.5 GeV SR X-rays, obtained from a Si (111) double-crystal monochromator, were used as an excitation source throughout the measurement. The experimental conditions of the XANES spectra are as follows: with BL-7C, the beam size, the step size of the monochromator and the number of data points were $1 \times 6 \text{ mm}^2$, 0.88 eV and 173 steps, respectively. The intensity of the Fe K X-ray was measured with a Lytle-type fluorescence detector (Lytle *et al.* 1984). On the other hand, a Si(Li) solid state detector was used with BL-4A, where the beam size, the step size of the monochromator and the number of data points were $100 \times 100 \text{ }\mu\text{m}$, 0.61 eV and 121 steps, respectively. The XANES spectra were calculated by normalizing the intensity of the fluorescent X-ray (I_f) with that of the incident X-ray (I_0) and by plotting against the X-ray energy. The reproducibility of the energy scale is less than one monochromator step (about 0.6–0.9 eV). The energy resolution of the Si(111) monochromator is 0.98 eV at the Fe K edge. The energy of the absorption edge (E_0) is defined as the mid-point of the edge crest in the normalized absorption curve throughout this paper.

RESULTS AND DISCUSSION

Spectra of standard samples

Figure 1 shows the Fe K-XANES spectra of metallic iron, magnetite (Fe_3O_4), hematite ($\alpha\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeOOH}$) and kaolinite measured with the BL-7C beamline. The characteristic energies for the XANES spectra of each sample are summarized in Table 1. It is known that the absorption edge shifts to a higher energy as the valence state of the absorber atom in

Table 1 *The energy of Fe K-edge features in reference minerals*

Sample	Energy (keV)		
	Pre-edge	E_0	Edge crest
Metallic iron	–	7.115	7.131
Magnetite	7.112	7.118	7.128
Hematite	7.114	7.122	7.128, 7.133
Goethite	7.114	7.124	7.131
Kaolinite	7.114	7.124	7.132

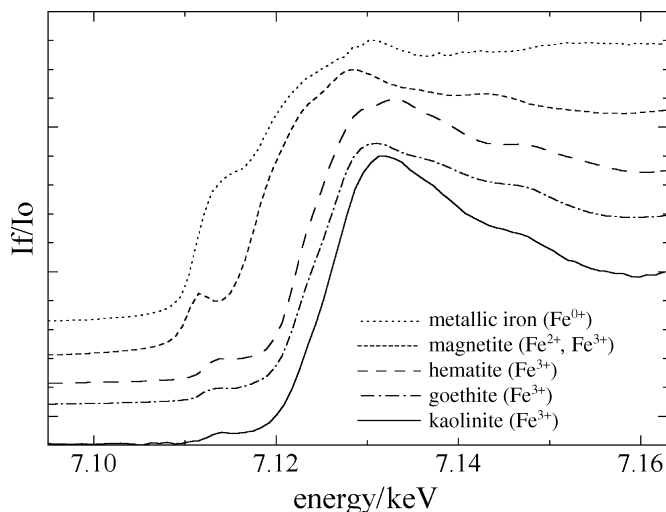


Figure 1 Fe K-XANES spectra of iron reference minerals.

a sample increases (Calas *et al.* 1988). It was found that the absorption edge energy (E_0) of metallic iron is located at the lowest energy level among the reference compounds (Table 1). Similarly, E_0 and a pre-edge peak of magnetite (Fe^{2+} , Fe^{3+}) are located at lower positions than those in compounds containing trivalent iron. Furthermore, it is observed that the magnitude of this pre-edge peak varies among the iron minerals. Transition elements exhibit a small pre-edge peak on the lower-energy side of the absorption edge, corresponding to transitions from 1s to 3d-like levels (Calas *et al.* 1988). This pre-edge absorption is strictly dipole forbidden if coordination about iron has octahedral symmetry with a centre of inversion. When the symmetry of the ligand is lowered, the pre-edge absorption becomes dipole allowed due to d-p orbital mixing (Wong *et al.* 1984). The pre-edge peak also shifts to a higher energy with an increase in the valence state of the absorber atom (Calas *et al.* 1988). The magnitude of the pre-edge peak increases with increasing site distortion or decreasing coordination number (Waychunas *et al.* 1983). Magnetite has a strong pre-edge peak at 7.112 keV, because it has iron with tetrahedral coordination due to the oxygen atoms. Hematite also has a rather weaker pre-edge peak at 7.114 keV, which reflects a distortion of the octahedral coordination, and a splitting of the edge crest into 7.128 and 7.133 keV, which originates from the two Fe–O distances (at 2.115 Å and 1.945 Å) at the distorted site (Paris *et al.* 1991). Thus, it is found that each iron compound has its own characteristic XANES spectrum.

The characterization of fired clay by XANES spectra

Fe K-XANES spectra obtained for the unfired clay and test samples fired in oxidizing conditions are shown in Fig. 2 (a). The characteristic energies for the XANES spectra of each clay sample are summarized in Table 2. The spectrum of the unfired clay is characterized by fine structures with a pre-edge peak at 7.113 keV, an E_0 at 7.124 keV, and the edge crest at 7.132 keV. The oxidation state of iron in this clay was determined to be entirely trivalent, since the energies of the pre-edge peak and the absorption edge are close to those of hematite, goethite and kaolinite, all of which contain trivalent iron. Furthermore, the shape of the spectrum is

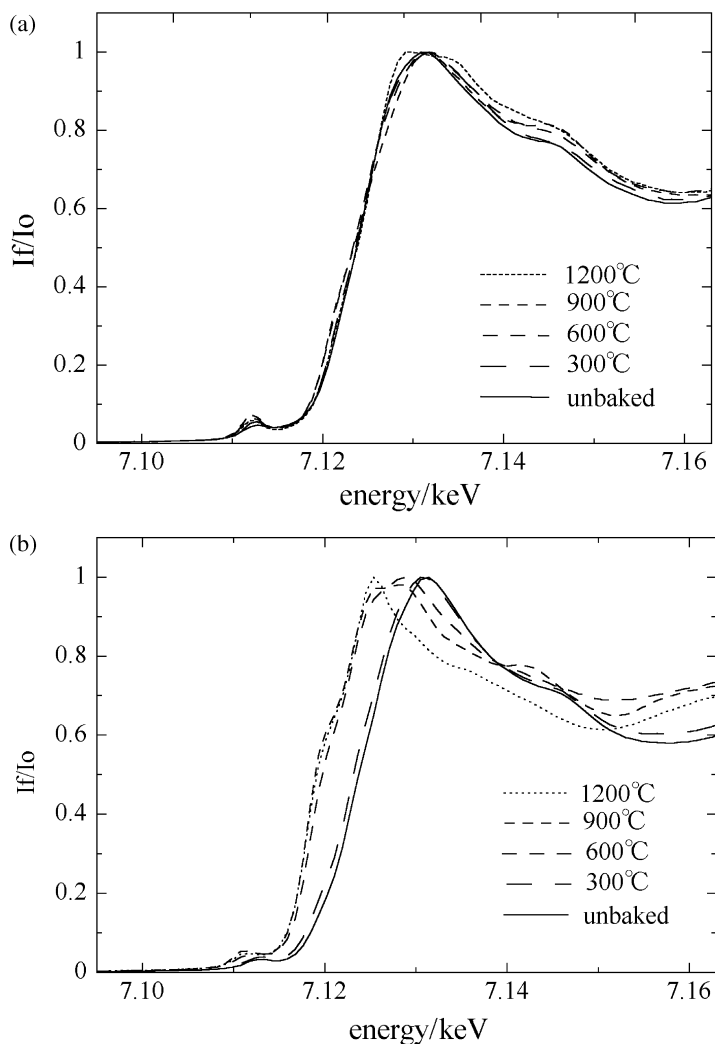


Figure 2 Fe K-XANES spectra of clays fired at various temperatures (a) under oxidizing conditions and (b) under reducing conditions.

very close to those of kaolinite and goethite. The iron atoms in goethite and most of the iron atoms in kaolinite are located in octahedral sites in their crystals (Paris *et al.* 1991). Therefore, it is expected that the iron atoms are also located in octahedral sites in this clay.

Fe K-XANES spectra of the clays fired under oxidizing conditions revealed that the iron atoms remained in the trivalent state after firing, since the chemical shift was negligible between the unfired and the fired clay. It is observed that the intensities of the pre-edge peaks of the fired clays are stronger than those of the unfired ones. Hematite has a rather strong pre-edge peak because the iron atoms occupy distorted octahedral sites. Probably, the observed increase in the intensity of the pre-edge peak after firing suggests the formation of hematite by heating. At 1200°C the clay is partly vitrified, and yields a splitting of the edge crest in the spectrum.

Table 2 The energy of Fe K-edge features in clay samples

Sample	Energy (keV)		
	Pre-edge	E_0	Edge crest
Unfired	7.113	7.124	7.132
<i>Oxidizing conditions</i>			
300°C	7.112	7.124	7.132
600°C	7.112	7.124	7.132
900°C	7.112	7.123	7.131
1200°C	7.112	7.124	7.129, 7.134
<i>Reducing conditions</i>			
300°C	7.113	7.123	7.131
600°C	7.112	7.120	7.129
900°C	7.111	7.119	7.128
1200°C	7.111	7.119	7.125

Fe K-XANES spectra of the clays fired under reducing conditions are shown in Fig. 2 (b). Since the spectrum of the clay fired at 300°C is close to that of the unfired clay, it is assumed that the iron atoms in the clay remain in the trivalent state even after firing. However, above 600°C, the chemical shift was observed to increase with the firing temperature. Furthermore, it was found that the clays fired at 600°C and 900°C gave broader edge crests at 7.128–7.129 keV, while the unfired clay and the fired clay at 1200°C gave sharp edge crests at 7.131 keV and 7.125 keV, respectively. It is known that some compounds exhibit sharp edge crests that are often referred to as ‘white lines’. These are typical of species in which the iron atoms are located at highly symmetric sites and the valency of the absorber atom is expressed as an integer (Waychunas *et al.* 1983). On the other hand, broadened edge crests are often observed in mixed-valence compounds and compounds in which the absorber atoms occupy several different sites. The unfired clay has a trivalent iron and exhibits a XANES spectrum with a sharp edge crest. It is presumed that most of iron in the clay fired at 1200°C under reducing conditions is divalent, since its edge crest is sharp and its E_0 value is lower than those of reference minerals containing trivalent irons. On the basis of the above considerations, the continuous change of the XANES spectra was interpreted as follows: iron in the clay changes from a trivalent state to a mixture of trivalent and divalent states, and then finally the divalent iron becomes dominant as the firing temperature increases.

The characterization of pottery sherds by XANES spectra

Fe K-XANES spectra of typical pottery sherds found at the site are shown in Fig. 3. It was found that the differences between the XANES spectra measured on each pottery sherd could be characterized by their E_0 values. The E_0 values obtained from the Fe K-XANES spectra of various pottery sherds excavated from Kaman-Kalehöyük are plotted versus their colours in Fig. 4. The E_0 values of the reference samples are also shown for comparison. As a general tendency, it was observed that the E_0 values increased as the colours of the pottery sherds varied from grey to brown to orange. The E_0 value of the orange-coloured pottery agrees

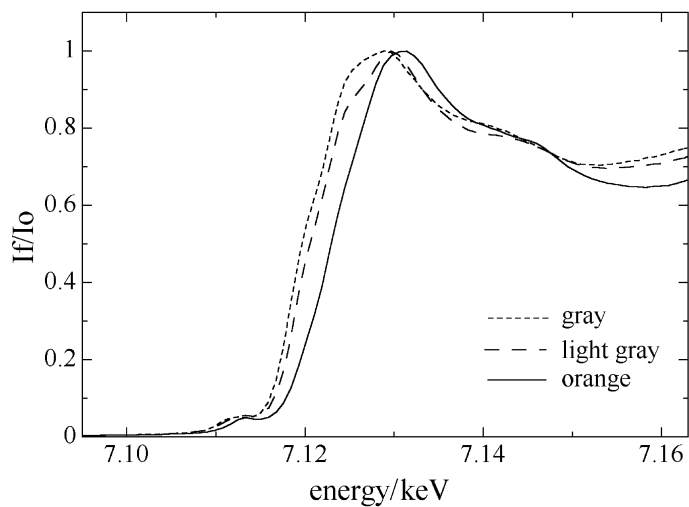


Figure 3 Fe K-XANES spectra of pottery sherds found typically at the site.

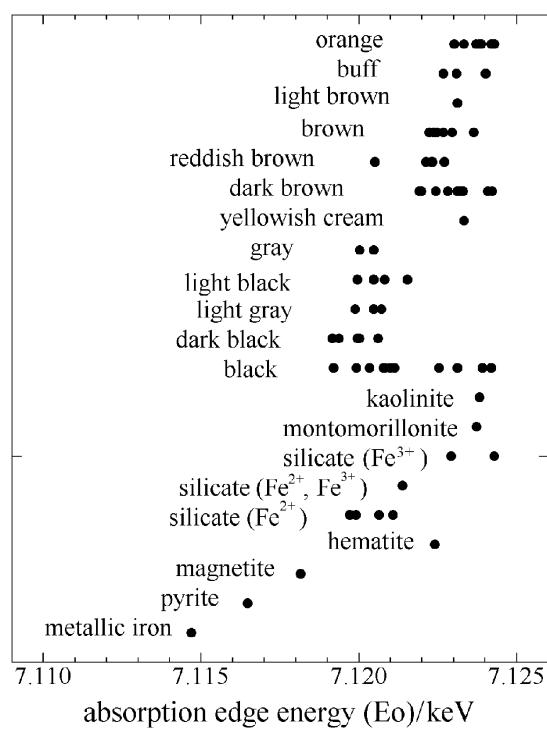


Figure 4 The relationship between the Fe K-absorption edge energy (E_0) of pottery sherds and their colour.

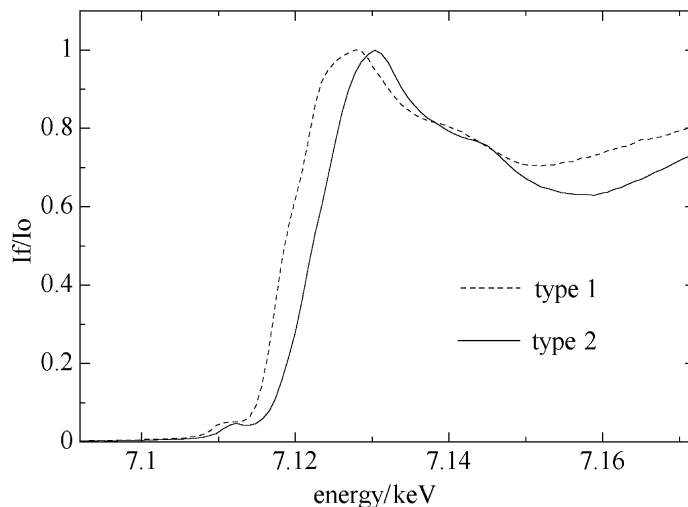


Figure 5 Fe K-XANES spectra of the Grey Ware found at Kaman-Kalehöyük.

with those of the silicates that contain trivalent irons. The E_0 values of the greyish pottery agree well with those obtained from the silicates predominantly containing divalent iron. These observations support the conclusion that most of the iron in the pottery occupies the crystallographic sites of silicates. The E_0 values of the black pottery sherds exhibit a wide distribution of energies and cover an area that corresponds to Fe^{2+} and Fe^{3+} in the silicates. It is known that black pottery was produced by various firing techniques (Makundi *et al.* 1989; Matsumura 1994). The observed variety in the E_0 values may reflect differences in their firing techniques. Close visual observation of present specimens suggests that the sherds with low E_0 energy, indicating a reduced iron state, had a dark grey colour at the core of the sherds. On the other hand, the sherds with high E_0 values, indicating an oxidized iron state, had a black surface with a red or brown core. It is presumed that the former sherds are produced by firing under reducing conditions, while the latter sherds are produced under oxidizing or not strongly reducing conditions, and their black colour is possibly due to the soot during firing or daily use of the vessels in processes that involve heating, such as cooking.

'Grey Ware'

The term 'Grey Ware' has been applied to a type of Anatolian Iron Age pottery that has a grey colour. These wares are commonly found in the IIa and IIb levels at Kaman-Kalehöyük, dated to the Phrygian period of the Iron Age. Two main groups of 'Grey Wares' have been recognized (Matsumura 1994). One group has a grey core and a grey surface (type 1), and the other group has a brown core and a grey surface (type 2). Typical Fe K-XANES spectra of these 'Grey Wares', measured at the surfaces and in the cores, are shown in Fig. 5. A difference was observed between the spectra of types 1 and 2. The XANES spectra of the 'Grey Ware' with a grey core (type 1) are close to those of the clay samples produced under reducing conditions at 600°C and 900°C (Fig. 2 (b)). Also, the Fe K-XANES spectra of the 'Grey Ware' with a dark brownish core (type 2) are found to be close to the spectra of the clays produced under oxidizing conditions, although a slight difference is observed between the surface of type 2 and its core. Chevalier *et al.* (1976) reported that ferrous iron was dominant in clays fired under

reducing conditions. Qin *et al.* (1989), in a study of Chinese terracotta figures, reported that the iron in grey sherds was predominantly ferrous (Fe^{2+}), whereas it was all ferric (Fe^{3+}) in the red sherds examined. It seems appropriate to presume that the former (type 1) is a variety of pottery produced under reducing conditions. Although we cannot define the firing method of type 2, it appears that the type 2 was a variety of pottery produced in relatively reducing conditions, because the iron on the surface is slightly reduced. However, a significant difference was observed in the XANES spectra of the 'Grey Ware' between types 1 and 2. This indicates that the firing environments—that is, the firing techniques—of types 1 and 2 are distinct but are not definable on the basis of the XANES measurements alone.

'Cream Ware'

Besides the 'Grey Wares', pottery sherds with cream-coloured exteriors were recognized at Kaman-Kalehöyük and are referred to as 'Cream Ware' (Matumura 1992). 'Cream Wares' found at the IIc level of the site, dated to the seventh or eighth century BC, have the following characteristics: the exterior surfaces of the pottery sherds are cream coloured, whereas their interiors are light grey. The bodies are coarsely textured and highly tempered. They have no slip layer and they do not contain any organic temper (Tsu 1996). Some of the sherds show colour variations from cream to red on the exterior surfaces (Matsumura 1992). Both the red- and cream-coloured regions of the pottery sherd contain K, Ca, Ti, Mn, Fe, Zn and Sr in comparable quantities, and no detectable compositional differences were observed among them (Tsu 1996). Although it is reported that the colour variations were presumed to be a result of a difference in oxidation states of an iron-rich compound (Tsu 1996), the cause of the cream colour and the estimation of their manufacturing technique have yet to be solved.

A cross-sectional photograph of a typical sherd of the 'Cream Ware' found at the IIc Level is shown in Fig. 6 (a). Figure 6 (b) shows the Fe K-XANES spectra measured at each point of the sherd. As can be seen from Fig. 6 (b), it is found that the absorption edge shifts towards the low-energy side from the surface of the pottery sherd towards the core (cream (A) → dark orange (B) → grey (C) in Fig. 6 (b)). The XANES spectrum measured in the orange-coloured region (point B) agrees with those of the clays fired under oxidizing conditions, and the spectrum measured at the core (point C) exhibits a good resemblance to those of the clays fired under reducing conditions at 600–900°C (Fig. 6 (b)). On the other hand, the spectrum measured at the surface (point A) exhibits a slightly higher edge energy (E_0) than that of clays fired under oxidizing conditions.

The red colour of pottery is associated with the presence of ferric compounds such as Fe_2O_3 (hematite). If a clay is free of iron and organic materials, it will usually be white when fired (Rice 1987). Furthermore, it is known that some ceramics made from calcareous clays containing iron exhibit a pale cream colour (Rice 1987; Jacobs 1992). The cause of the cream colour is explained as follows. When a calcareous clay is fired between 650°C and 890°C—and, in particular, at temperatures above 750°C—calcium carbonate in the clay decomposes to lime. The lime then reacts with the clay and, at temperatures over 1000°C, calcium silicates or calcium ferrosilicates with a white or pale yellow colour are formed, depending on the composition. It is expected that a similar reaction occurred during the firing of the 'Cream Ware'.

A question remains concerning the firing temperature of the 'Cream Ware'. Generally, it is known that clays fired at temperatures over 1000°C have well-sintered bodies. Ceramics with cream-coloured surfaces have been produced from iron-rich clays at Avanos, a city that is well known for the production of ceramics in modern Turkey. They have partly vitrified surfaces and well-sintered bodies due to firing at high temperatures (Matsumura 2000). On the other

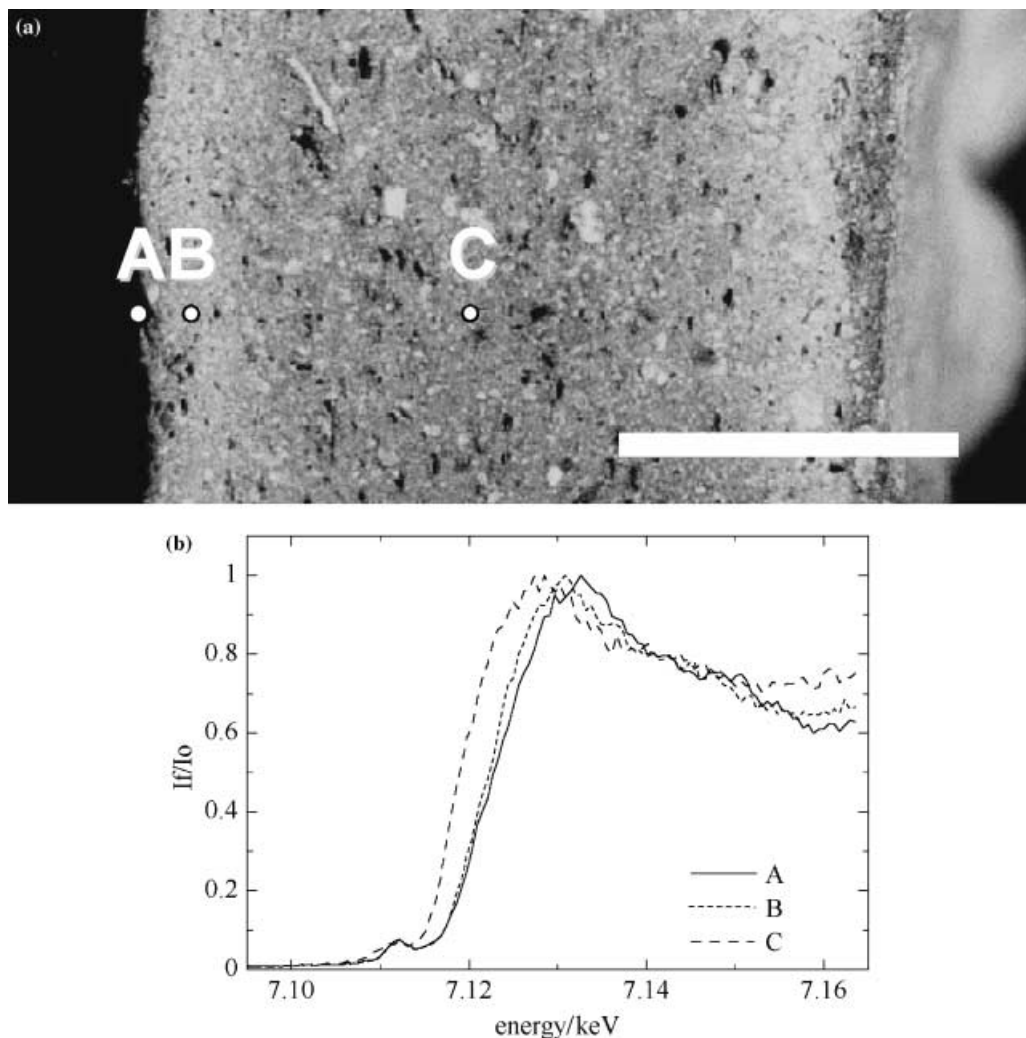


Figure 6 An optical image of a Cream Ware item and its XANES spectra. (a) A cross-section of the pottery sherd; bar = 3.0 mm. (b) Fe K-XANES spectra of the pottery sherd measured at the points shown in Fig. 6 (a): A, cream; B, dark orange; C, grey.

hand, the 'Cream Wares' from Kaman-Kalehöyük do not have well-sintered bodies like those fired to over 1000°C, such as those produced at Avanos.

A key to answering this question might be the differences in the oxidation state of the iron measured in each part of the pottery sherd. The analysis of the XANES spectra of the 'Cream Ware' suggests that the pottery was first fired under reducing conditions, and then it was oxidized (Fig. 6 (b)). It has been reported that melting of calcium compounds is accelerated under reducing conditions when the calcium carbonate is in the form of very fine particles (Tite and Maniatis 1975; Maniatis *et al.* 1983). It is probable that the cream-coloured substance observed on the surface was produced at temperatures less than 1000°C at this stage of firing. A microscopic observation of the cream-coloured sherds suggests that the colour is

made up of a combination of the red-coloured body and the whitish, cream-coloured surface. Oxidation in the final stage of the firing would oxidize the remaining iron compounds that had not formed calcium silicates in the clay, and red ferric compounds would be formed. This would contribute largely to making the surface lighter and more reddish in colour. We can conclude that the 'Cream Ware' from the site of Kaman-Kalehöyük was probably produced by an oxidation–reduction technique as mentioned above, and that the firing temperature was less than 1000°C.

CONCLUSIONS

The XANES analysis disclosed a relationship between the chemical forms of the iron and the colours of the pottery from the site: (a) the chemical state of the iron changes with an increasing firing temperature; (b) the colour of the pottery changes from grey through brown to orange with an increase in the oxidation state of the iron; (c) and most of the iron exists in a silicate matrix. Also, it is suggested that hematite was formed under oxidizing firing conditions. On the basis of these examinations, we could draw some conclusions on the firing techniques used for some Iron Age pottery. It may be difficult to compare our results with other reports, since the analysed pottery was produced in different places and at different times. However, our results are generally consistent with reports based on Mössbauer spectroscopic studies (Chevalier *et al.* 1976; Makundi *et al.* 1989), which can, however, often give more precise identification. Throughout the experiments, no damage caused by X-rays could be observed in the samples. This advantage opens up the possibility that this technique can be applied to many important samples that require non-destructive analysis, although the analysis must be confined to the surface. This does not apply only to pottery; information about the chemical state of an element is useful for the characterization of many archaeological materials. The present analytical method can analyse micro-regions of a sample and can be applied to all elements heavier than aluminium. We anticipate that the present technique will be applied to a wide range of archaeological materials and will contribute to archaeological studies.

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