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COMBINED USE OF THERMAL AND SURFACE ANALYSES
Study of the smelting process of iron ores from Monte Ferru (Sardinia)

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Abstract

In order to attempt the location of the iron ore sources exploited at Tharros (Sardinia) during the Phoenician-Punic period and to elucidate some chemical aspects of the iron ore smelting process, the iron ore outcrops of Monte Ferru located near to this archaeological site, have been first sampled and then, differential thermal analysis (DTA) and thermogravimetry (TG) have been used for simulating and studying the iron ore smelting process under a carbon monoxide atmosphere. Furthermore, in order to obtain a qualitative identification of minerals present in the iron bearing rocks and for obtaining some thermochemical data, the smelting process has been carried out also under air and Ar–5% H_2 atmospheres. The microchemical aspects involved during the smelting process of the iron ore to crude iron, the formation and the chemistry of new no metallic phases that results from the smelting, i.e. the slags, and the final product of the pyrometallurgical process have been identified *via* small area X-ray photoelectron spectroscopy (SA-XPS), X-ray induced Auger electron spectroscopy (XAES) and scanning electron microscopy + energy dispersive spectroscopy (SEM + EDS). These results are compared with those obtained from the characterisation of the smelting slags found during the excavation of the archaeological site of Tharros and a relationship is found.

Keywords: iron ore smelting process, iron smelting slags, pyrometallurgy, XPS

Introduction

A large amount of smelting slags produced during pyrometallurgical activities have been found in many Sardinian archaeological sites inter alia Tharros, S. Antioco, Guspini [1]. These latter materials, dating back to the Phoenician-Punic (VIII-II BC) and Roman period (II BC–IV AC), are of considerable importance because they can give direct information on the metallurgical processes that have produced them and further, on the technological competencies of the ancient civilisations [2–4]. The microchemistry of the pyrometallurgical

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materials found at Tharros has been carefully studied and the results indicate that the slags can be really associated with the smelting process of iron ores [1]. The evidence for such an important technological breakthrough puts forward the question about the technological and chemical aspects involved during the iron ore smelting process and about the iron ore provenance. In order to gain a further insight into the iron pyrometallurgical activities in this area and to locate the iron ore geographical sources [5–8], we have sampled some iron ore outcrops located near the archaeological site of Tharros at Sa Remita (Monte Ferru, Oristano). Then, the iron ore smelting process has been simulated in a DTA+TG equipment adopting experimental conditions similar to those of an early iron smelting furnace, for obtaining thermochemical information as well as for identifying the different thermal and chemical steps of the process. The microchemistry of new no metallic phases that results from the smelting, i.e. the slags, and the final product of the pyrometallurgical process have been identified *via* small area X-ray photoelectron spectroscopy (SA-XPS), X-ray induced Auger electron spectroscopy (XAES) and scanning electron microscopy+energy dispersive spectroscopy (SEM+EDS) [2–4]. The results have been compared with those obtained from the characterisation of the iron smelting slags found during the excavation of the archaeological site of Tharros in oder to attempt the location of the iron ore sources.

Experimental

The iron ore smelting process was carried out in the DTA-TG equipment using flowing CO (99.99%, Matheson). The gas flow rate was kept constant at 0.3 l h^{-1} in the temperature range between room temperature and 970 K and at 1.5 l h^{-1} from 970 to 1770 K in order to minimise the carbon deposition on the iron oxides. The heating rate was 50 K min^{-1} from r.t. to 970 and 20 K min^{-1} from 970 to 1770 K. The weight of the iron ore sample was about 15 mg. Fluxing compounds have been added during the smelting process in order to better reproduce the chemical conditions of an antique furnace, in particular, ash produced by the combustion of wood charcoal and a low amount of lime (about 0.75 mg) were added for increasing the content of Na_2O, K_2O and CaO, and therefore, for inducing the formation of a liquid slag at about 1400 K. Furthermore, in order to better characterise the thermal behaviour of the iron ores the DTA-TG measurements have been carried out also under Ar-5% H_2 and air atmospheres [9] adopting the following conditions: flow rate 1.5 l h^{-1} and heating rate 10 K min^{-1}. The smelting products for SA-XPS, SA-XAES and SEM characterisations, have been obtained by heating, in the DTA-TG equipment, the iron ore up to the selected temperature and then, subjecting the sample to an isothermal treatment for 30 min, under reducing condition. The temperatures of these treatments were selected on the base of the DTA-TG curves and were

570 K, 870 K, 1170 K and 1520 K, sample a, b, c, and d, respectively. It is worth noting that 1520 K is the highest temperature supposed to be attainable in an ancient iron furnace. After each thermal treatment, the sample was exposed to the air and immediately inserted into the XPS spectrometer and after this characterisation into the SEM microscope, in order to minimise the ambient surface contamination.

SA-XPS and SA-XAES measurements were performed in a XPS spectrometer equipped with a concentric hemispherical analyser (CHA) using $MgK_{\alpha_{1,2}}$ radiation as excitation source ($h\nu=1253.6$ eV). The $SiKL_{2,3}L_{2,3}$ and $AlKL_{2,3}L_{2,3}$ Auger peaks were excited by the Bremstrahlung continuum above the characteristic MgK_{α} radiation. The hemispherical electron analyser was operated in fixed analyser transmission mode (FAT) by selecting a constant pass energy of 20 eV throughout the measurements. Under these conditions, the full width at half maximum (FWHM) of Ag $3d_{5/2}$ line for Ar^+ ion cleaned material was 1.0 eV. The size of the analysis area was about 0.15 mm in diameter. All measurements were performed at pressure of 5×10^{-10} mbar in the analysis chamber. Binding energies (BE) were referenced to the Fermi level of the analyser and confidence in the linearity of the BE scale was based upon setting the position of the Au $4f_{7/2}$, $CuL_3M_{4,5}M_{4,5}$ and Cu $2p_{3/2}$ peaks at 84.0 eV, 344.9 eV and 932.7 eV, respectively. Correction for the energy shift due to the steady-state charging effect were accomplished by assuming the C 1s line, resulting from the ubiquitous surface layer of absorbed hydrocarbons, as lying at 284.6 eV. Reproducibility in the results was 0.15 eV, which was also the estimated uncertainty in the BE locations. SEM + EDS analyses were performed by means of a Cambridge 360 microscope.

Results and discussion

Petrography observations, X-ray diffraction and chemical analyses have evidenced that the iron bearing rocks of Sa Remita, Monte Ferru (Oristano, Sardinia) are composed of haematite (Fe_2O_3), whose content ranges from 70 to 80%, quartz and complex alumino-silicates such as kaolinite, $Al_2Si_2O_5(OH)_4$ and montmorillonite, $Al_{1.67}Mg_{0.33}[(OH)_2Si_4O_{10}]_{0.33}\cdot Na_{0.33}(H_2O)_4$, 20–30 %.

On the base of the chemical analyses, we have selected for the DTA-TG experiments under CO, Ar-5% H_2 and air atmospheres, the iron ore characterised by the highest content of Fe_2O_3 with respect to the other. In Fig. 1, the DTA-TG curves obtained under CO, Ar-5% H_2 and air atmospheres, are reported.

Figure 2 shows some selected Fe $2p_{3/2}$-Fe $2p_{1/2}$ photoemission spectra for the iron ore in as received condition (a.r.) and after different thermal treatments carried out at 870 K, 1170 K and 1520 K, spectra b, c and d, respectively. From the BEs and line shape analysis [10, 11] of the spectra, the iron oxidation state can be assigned to Fe^{3+}, as in γ-haematite (γ-Fe_2O_3, spectrum a.r.), to a

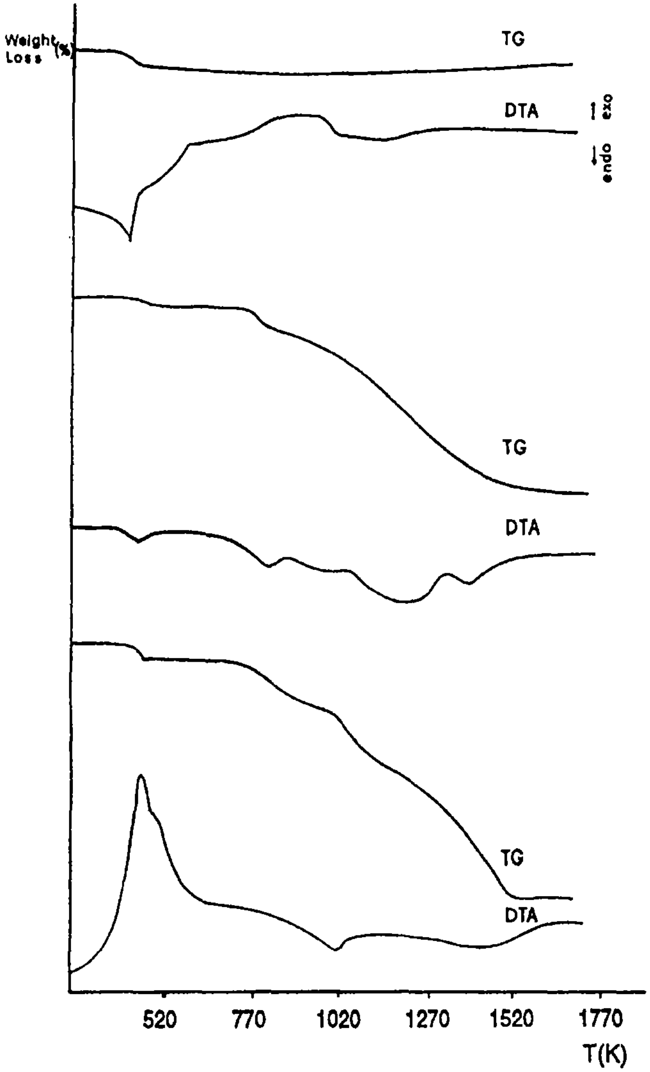

Fig. 1 DTA and TG curves of the iron ore from Sa Remita, Monte Ferru (Oristano, Sardinia) carried out under a CO, Ar–5% H_2 and air atmospheres, curves a, b and c, respectively

mixture of Fe^{3+} and Fe^{2+} oxides, as in magnetite (Fe_3O_4, spectrum b) and to a mixture of Fe^0 and Fe^{2+} (spectra c and d). In particular, the Fe 2*p* spectrum for the as received iron ore shows relatively narrow peaks with a small broad satellite peak centred around 719.1 eV, that is typical of the Fe(III) oxidation state [10, 11]. When the temperature is increased to 870 K, there was a significant broadening of the Fe $2p_{3/2}$ peak that is also shifted to a lower BE. This finding indicates the presence of a mixture of Fe(II) and Fe(III) oxides, both of which

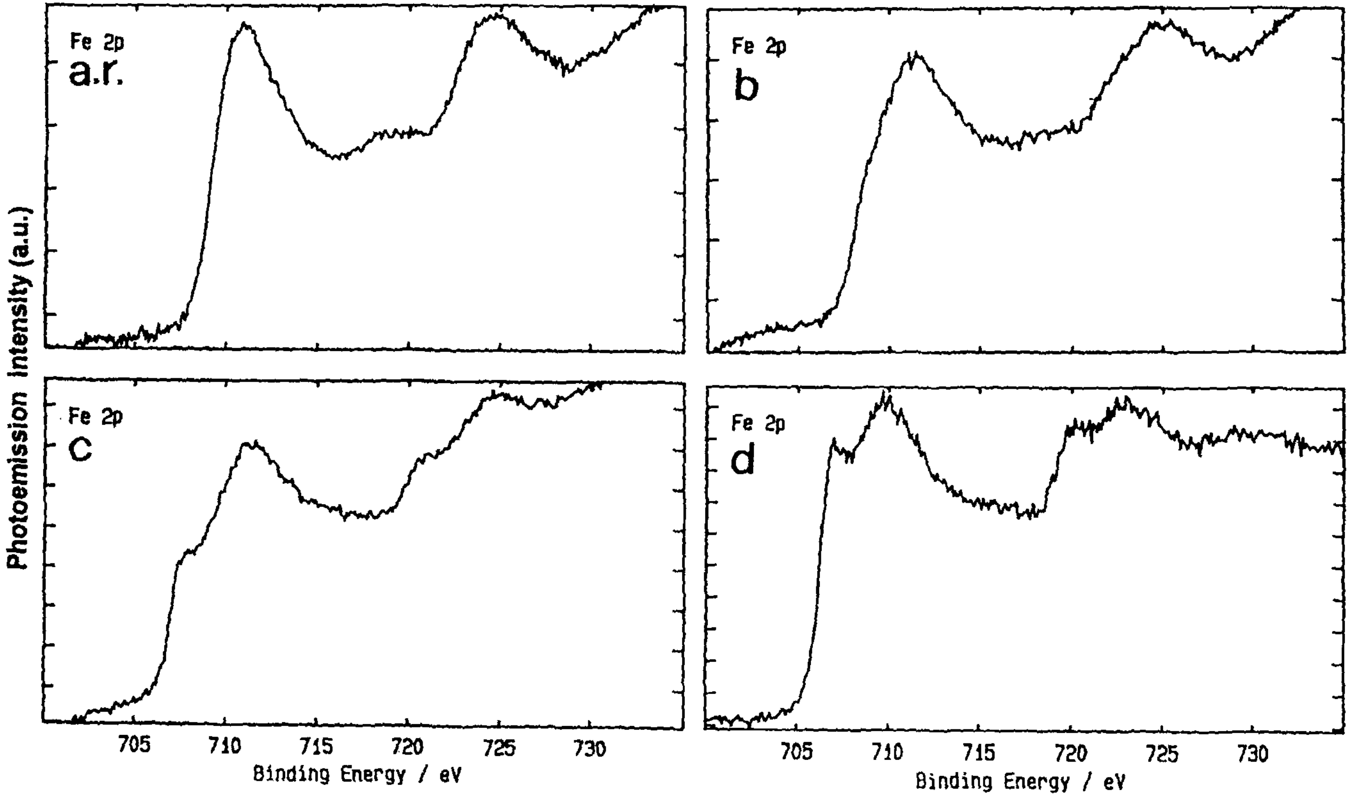

Fig. 2 Small-area XPS spectra of Fe $2p_{3/2}$-Fe $2p_{1/2}$ peaks for the iron ore from Sa Remita, Monte Ferru (Oristano, Sardinia), in the as received conditions (a.r.) and after different thermal treatments carried out in the DTA-TG equipment under a CO atmosphere at 870 K, 1170 K and 1520 K, sample a.r., b, c and d, respectively

contribute to the Fe $2p_{3/2}$ signal with their two overlapping components and therefore, that some reduction of Fe^{3+} state to Fe^{2+}, has taken place according to the following reaction: $Fe_2O_3 + CO \rightarrow 2FeO + CO_2$. Owing to the complexity of the Fe $2p$ spectrum and to the exposure of the sample to the air contamination, that causes a partial re-oxidation of Fe(II) to Fe(III), no quantification was attempted as to the partitioning of the Fe(II) and Fe(III) species. Starting from 1170 K (spectrum c of Fig. 2), in the Fe $2p$ peaks the presence of metal iron is disclosed, thus demonstrating the occurrence of the reduction of Fe^{2+} to Fe^0. The amount of Fe^0 increases at increasing temperature as shown by the spectrum d of Fig. 2, even though, the presence of Fe(III) oxide is also shown. This contribution is due to the exposure of the sample to the air contamination, indeed, after a mild argon ion etching carried out at 2 keV for 5 min, the pres- ence of the oxidised iron completely disappears.

Interesting analytical features are also given by the O 1s spectra (not shown), that evidence some differences between the as received iron ore and the smelted materials. In effect, the O 1s peak for the a.r. sample is characterised by a twofold lineshape, consisting of a component centred at about 530.1 eV along with a component at about 532.0 eV, respectively showing the coexistence of contributions from SiO_4^{4-}, Fe^{3+} and O–H, oxygen bonds. The relative intensity of these components vary with the sampled iron ore and the O–H component drops significantly with increasing temperature, that causes the loss of water. This phenomenon has been also evidenced by the DTA-TG curves, that allow to measure the temperature required to extract the hydration and structural water from the lattices of the mineral. Indeed, the presence of water is frequently indicated by well-defined endothermic reactions in the 370–520 K region. DTA-TG curves, reported in Fig. 1, show broad endothermic peak in the range from 370 to 430 K due to the loss of physically bonded water. In the range from 370 K to 520 K the mass loss due to the release of water is about 3% of the starting mass for curves a, b and c. In the range from 400 to 520 K, the DTA-TG curves obtained under CO atmosphere show a sharp exothermic peak that are interpreted as the formation of a low amount of surface carbon on the iron oxide. Other small endothermic peaks in the range from 770 to 1000 K of the DTA-TG curves indicate the presence of kaolinite [14–15] and in the range from 1270 to 1520 K the probable formation of a new compound. Furthermore, the DTA-TG curves in air show at 540 K, a small and broad endothermic peak that could be interpreted as the transformation of γ-Fe_2O_3 into α-Fe_2O_3. By combining the DTA-TG curves and SA-XPS results, it is evidenced that at about 820 K, the reduction of Fe^{3+} to Fe^{2+} begins to take place, that the reduction of Fe^{2+} to Fe^0 begins at about 1050 K and that is complete at about 1520 K, with an oxygen mass loss of about 24.3%, in the range of temperature from 820 to 1520 K. The microchemical structure and morphology of the smelting products at 1520 K is shown in Fig. 3, where a back scattered electron image and X-ray elemental maps of Si, Al and Fe, are reported. The back scattered electron micrograph shows the presence of iron (white-gray) with dark-gray islands char-

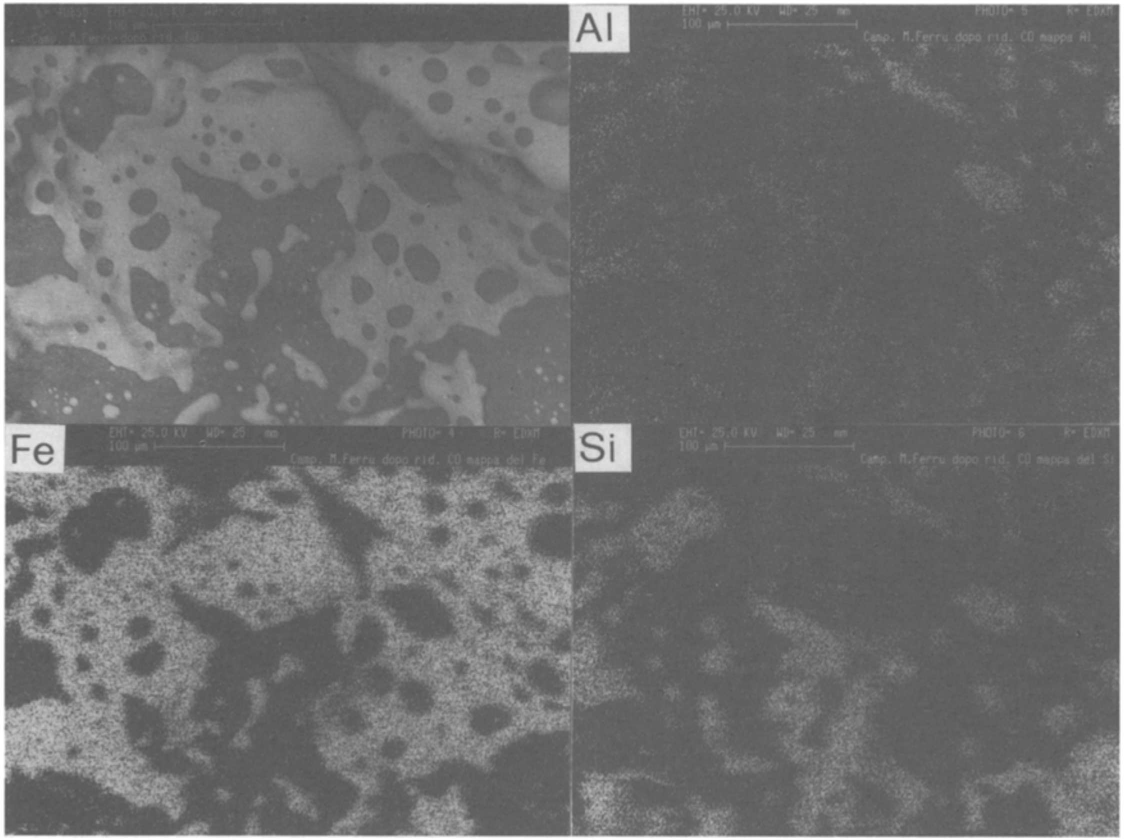

Fig. 3 Back scattered electrons image and X-ray elemental maps of Al, Si and Fe for the iron ore from Sa Remita, Monte Ferru (Oristano, Sardinia) subjected to a smelting process in the DTA-TG equipment at 1520 K$\times$30 min under a CO atmosphere

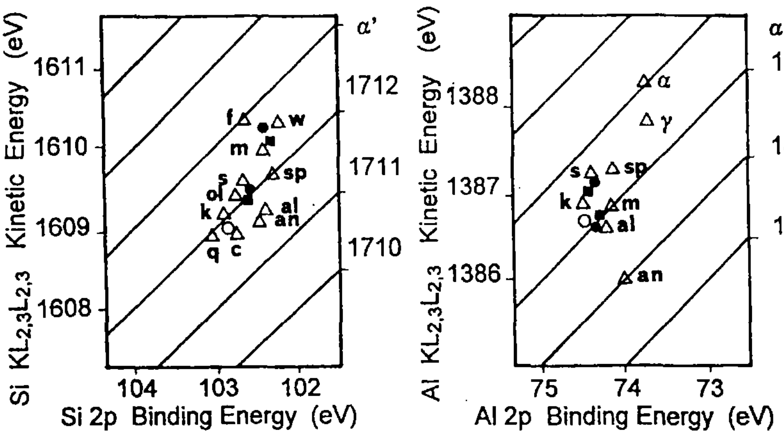

Fig. 4 Two-dimensional chemical state plot for reference silicon and aluminium compounds (Δ), for different phases present in the early iron smelting slags (■) found at Tharros (Sardinia) and dating back to the Phoenician-Punic (VIII-IV BC), for the iron ore from Sa Remita, Monte Ferru (Oristano, Sardinia) in as received condition (o) and after a smelting process carried in the DTA-TG equipment under a CO atmosphere at 1520 K for 30 min (•)
al=albite, $NaAlSi_3O_8$; an=analcime, $NaAl(SiO_3)_2$; f=fayalite, Fe_2SiO_4;
k= kaolinite, $H_4Al_2Si_2O_9$; m=melilite, $Na_2(Ca,Mg)_{11}(Al,Fe)_4(SiO_4)_9$; q=quartz, SiO_2; c=cristobalite, SiO_2; α=α-Al_2O_3; γ=γ-Al_2O_3; w=wollastonite, $CaSiO_3$; sp=spodumene, $LiAl(SiO_3)_2$; st=staurolite, $Fe_2Al_9Si_4O_{24}$; ol=olivine, $(Fe,Mg)_2SiO_4$

acterised by a complex chemical composition with different contents of silicon, aluminium and iron. These slag phases that results from the smelting process, appear quite similar to some anorthite-like phases present with fayalite (Fe_2SiO_4) and wustite (FeO) in early iron metallurgy slags found at Tharros (Sardinia) and at Tell Afis (north-western Syria) [1–4]. These results evidence that, a part the reduction of the iron oxide to crude iron, other reactions take place with the formation of new phases whose chemical structure has been identified *via* SA-XPS and XAES. Indeed, the SA-XPS and XAES results reported in Fig. 4, as two-dimensional chemical state plots [12, 13], show remarkable variation of the BEs and α' Auger parameters of silicon and aluminium and allow to propose the chemical structure of the new phases. It is worth noting that the α' parameter is obtained by means of the combined use of both the photoelectron and X-ray induced or Bremstrahlung Auger line according to:

$$\alpha' = \mathrm{KE(Auger\ peak)} - \mathrm{KE(photoelectron\ peak)} + h\nu$$

So conceived α' has the advantages of being independent of photon energy, of always having positive values and is independent of the charge referencing operation. Therefore, α' is found with higher accuracy than the determination of either photoemission line energy alone. The data reported in Fig. 4 show a good dispersion even though, for the smelted treated materials, we have measured only two different values of the α' Auger parameters for silicon and aluminum. In Fig. 4 are reported also the data obtained from the iron ore in as received condition, from the different phases previously found for early iron metallurgy slags [1] and from various compounds presumed to similar to the latter. α' Auger parameters for aluminum indicate that in the as received iron ore is present an aluminosilicate, where aluminium occupies either octahedral + tetrahedral sites (α' is 1461.1 eV) and that also a new phase is formed during the smelting process whose α' value is 1461.7 eV. Both these latter compounds have an α' value similar to that of the phases present in the early iron smelting slags. From the data of silicon plot, we deduce that the a.r. iron ore contains an aluminosilicate similar to kaolinite, that changes its chemical structure during the thermal treatment under CO and that two new silicates are formed during the smelting process. This species could be ascribable to a complex aluminosilicate of iron and to fayalite (Fe_2SiO_4). It is worth noting that the also the α' Auger parameters for silicon of the new phases are similar to those previously measured for early iron metallurgy slags found at Tharros [1]. On the base of these latter results, it is possible indicate that the iron ore source exploited by the local smelters at Tharros in the ancient time, was a high grade hematite ore deposit with a relatively low aluminosilicate content that could be the iron ore outcrop of Sa Remita, Monte Ferru.

Conclusions

The iron ore outcrops of Monte Ferru have been sampled and the smelting process of the most iron rich ore has been studied by the combined use of SA-XPS, SA-XAES, SEM+EDS and DTA-TG techniques. The results have shown the different chemical reactions that take place during the pyrometallurgical process. The first step is the loss of the hydration and structural water, in the range from 370 K to 520 K. With increasing the temperature, at about 820 K, the reduction of Fe^{3+} to Fe^{2+} begins to take place and the further reduction of this latter oxide to metal iron occurs at 1050 K. At higher temperatures, about 1520 K, iron oxides are completely transformed into metal and the gauge forms new compounds whose chemical composition is ascribable to alumino-silicates of iron and to an iron silicate. The microchemical composition of these phases and of the phases present in the early iron smelting slags found at Tharros, allows to propose the iron ore outcrop of Sa Remita, Monte Ferru (Oristano, Sardinia) as probable iron ore source used in the ancient time for the smelting activity. From an analytical point of view, it has been shown that the combined use of SA-XPS, SA-XAES, SEM+EDS and DTA-TG techniques, can be useful tool for an application to the study of early pyrometallurgical investigation and for attempting the location of the metal ore sources exploited at that time.

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