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THE EXTRACTIVE METALLURGY OF COPPER FROM CABEZO JURÉ, HUELVA, SPAIN: CHEMICAL AND MINERALOGICAL STUDY OF SLAGS DATED TO THE THIRD MILLENIUM B.C.

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Abstract

The archeological excavations at Cabezo Juré, near Alosno, Huelva Province, in southwestern Spain, have recently revealed the vestiges of an ancient community of workers specialized in the metallurgy of copper (Cu); they were active between 2873 and 2274 B.C. (calibrated radiocarbon age). Evidence of their metallurgical activity has been found in remains of various furnaces, as well as large quantities of slag and copper products, both worked and as raw material. The results of the archeological, geochemical, mineralogical and textural studies performed on slags found in the area show that the recovery of copper was a two-stage process. Primary fusion was obtained in furnaces at relatively high temperatures (~1200°C) with the addition of mafic rocks as a flux. Further refinement of the metal in crucibles produced slags with a mineral composition simpler than that at the furnace stage. The abundance of copper oxides in both smelting and refining slags suggests a highly inefficient metallurgical procedure, with only partial liberation of the copper from the ores.

Keywords: copper, extractive metallurgy, archeological excavations, Iberian Pyrite Belt, Cabezo Juré, Spain.

Sommaire

Les fouilles archéologiques à Cabezo Juré, près d'Alosno, province de Huelva, dans le sud-ouest de l'Espagne, ont révélé récemment les vestiges d'une ancienne communauté de travailleurs spécialisés dans la métallurgie du cuivre. Ces gens étaient actifs entre 2873 et 2274 avant Jésus-Christ, selon les datations calibrées au radiocarbone. L'activité métallurgique se voit dans les débris des fours de traitement de minerai, ainsi qu'une grande quantité de laitier et de produits de cuivre, soit épurés ou bien à l'état brut. Les résultats d'études archéologiques, géochimiques, minéralogiques et texturales montrent que l'extraction du cuivre se faisait en deux étapes. Il y avait d'abord une fusion primaire dans un four à température relativement élevée (~1200°C), en présence de roches mafiques utilisées comme fondant. Une épuration ultérieure du métal dans des vaisseaux en céramique produisait un laitier ayant une composition minéralogique plus simple qu'au stade primaire, dans le four. La proportion des oxydes de cuivre dans les laitiers issus des processus de traitement de minerai et d'épuration témoigne d'une extraction métallurgique très inefficace, menant à une libération partielle seulement du cuivre dans le minerai.

(Traduit par la Rédaction)

Mots-clés; cuivre, extraction métallurgique, fouilles archéologiques, Ceinture Pyriteuse Ibérique, Cabezo Juré, Espagne.

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INTRODUCTION

The commencement of extractive metallurgy represents an essential step forward in the development and structuring of prehistoric societies (Tylecote 1987, Craddock 1995). The production of specialized metallic objects played a fundamental role in the creation of commercial trade networks and the birth of urban superstructures (Frank & Gills 1990, Nocete 2001).

The Iberian Pyrite Belt represents one of the largest concentrations of massive sulfides known on Earth (Sáez *et al.* 1996, 1997). The weathering of these deposits produced important supergene enrichment of the copper ore. It was these high-grade zones that were selectively mined (Sáez *et al.* 1999) from the third millennium B.C. onward (Pinedo Vara 1963, Leblanc *et al.* 2000, Chopin *et al.* 2003) and, in some cases, until today.

The recent excavations at Cabezo Juré (Nocete *et al.* 1998), in southwestern Spain, have revealed the remains of an ancient community specialized and dedicated to the mining, processing and production of copper objects and utensils in the period 2873 to 2274 B.C. (calibrated radiocarbon age). This ancient metallurgical community used raw materials from the zones of supergene enrichment in the massive sulfide deposits that outcrop in the Tharsis mining district (Sáez *et al.* 1999), located about 5 km north of Cabezo Juré (Fig. 1). For a detailed geological and metallogenic description of the Tharsis mining district, see Strauss *et al.* (1977) and Tornos *et al.* (1998).

The study of the archeological remains has revealed the existence of slags related to two different metallurgical processes. The most abundant type of slag appears to be associated with circular combustion structures (furnaces) approximately one meter in diameter, similar to those described at other chalcolithic sites (Rothenberg 1990, Craddock 1995). The furnaces are located on the highest part of the hill at Cabezo Juré and are oriented to favor the dominant direction of the wind. In these furnaces, primary fusion of the copper ore, containing malachite [$Cu_2CO_3(OH)_2$], azurite [$Cu_3(CO_3)_2(OH)_2$], chalcocite [Cu_2S] and tenorite [CuO], was achieved to produce a material rich in copper, chiefly in the oxide form cuprite [Cu_2O] and delafossite [$Cu^{1+}Fe^{3+}O_2$], but also with globules of metallic copper. The refinement of this material was then achieved in baked clay ovoid crucibles approximately 10 cm in diameter. The slags related to this refinement process are much scarcer than the first, and occur as centimetric fragments containing high amounts of iron and copper oxides. In this paper, we present the results of a comparative study of the two types of slag and provide some conclusions concerning the ancient metallurgical processes used for copper production. In addition, we emphasize the importance of Cabezo Juré in the development of metallurgical technology in the western Mediterranean some 5000 years ago. We thus contribute to the debate about the technological dependence on western Europe with respect to the emergent cultures in the Eastern Mediterranean during the early history of Mediterranean regions (Cunliffe 1994, Nocete 2001).

MATERIALS AND METHODS

The slags were produced during the extraction of copper at Cabezo Juré. The morphology of the slag remains shows two distinct types. (1) Slags related to the furnace stage are found as “cake-like” pieces weighing up to one kilogram, or lightweight fragments with a sponge-like texture, given the high abundance of gas vesicles present. (2) Slags related to the crucible phase are more massive and occur as accumulations of small fragments never exceeding one hundred grams in weight. Representative samples of slags, ores and fluxes were obtained during the archeological investigation at Cabezo Juré. Samples of ores from the zone of supergene enrichment of the Tharsis mining district have been used to determine the provenance of the copper ores (Sáez *et al.* 1999).

Polished thin sections were prepared and studied using an optical microscope in both transmitted and reflected light and a JEOL JSM–5410 scanning electron microscope (SEM) equipped with energy-dispersion analytical spectrometers (EDAX) and electronic correction (ZAF) (Central Research Services, Universidad de Huelva). The same samples were pulverized for an X-ray diffraction study (XRD). The XRD analysis was done at the Seville Institute of Material Sciences using a Siemens D–501 X-ray diffractometer. The pulverized samples were irradiated with Cu$K\alpha$ radiation (Ni-filter) and graphite monochromator at 36 kV and 26 mA, scanning between 2° and 70° with a step interval of $0.05°2\theta$ at a three-second interval. Semiquantitative proportions of phases have been obtained by addition of an internal standard (fluorite) to the powder used for X-ray diffraction.

Some fragments were also analyzed by X-ray fluorescence at the Department of Mineralogy and Petrology, University of the País Vasco, following the methodology described in Yusta *et al.* (1994). Concentrations of 10 major elements and 23 trace elements were measured for each sample.

Results of both mineralogical and chemical studies are compared with experimental data on phase assemblages (Tylecote & Merkel 1985, Bamberger & Wincierz 1990, Merkel 1990, Happ 1998), which allows us to determine the physicochemical conditions of copper smelting and refining.

SLAG COMPOSITION

A geochemical study of the slags and raw materials has been done in order to identify the primary raw materials, such as fluxes and ores, used in the metallurgical process. The major- and trace-element composition of the analyzed samples is presented in Table 1.

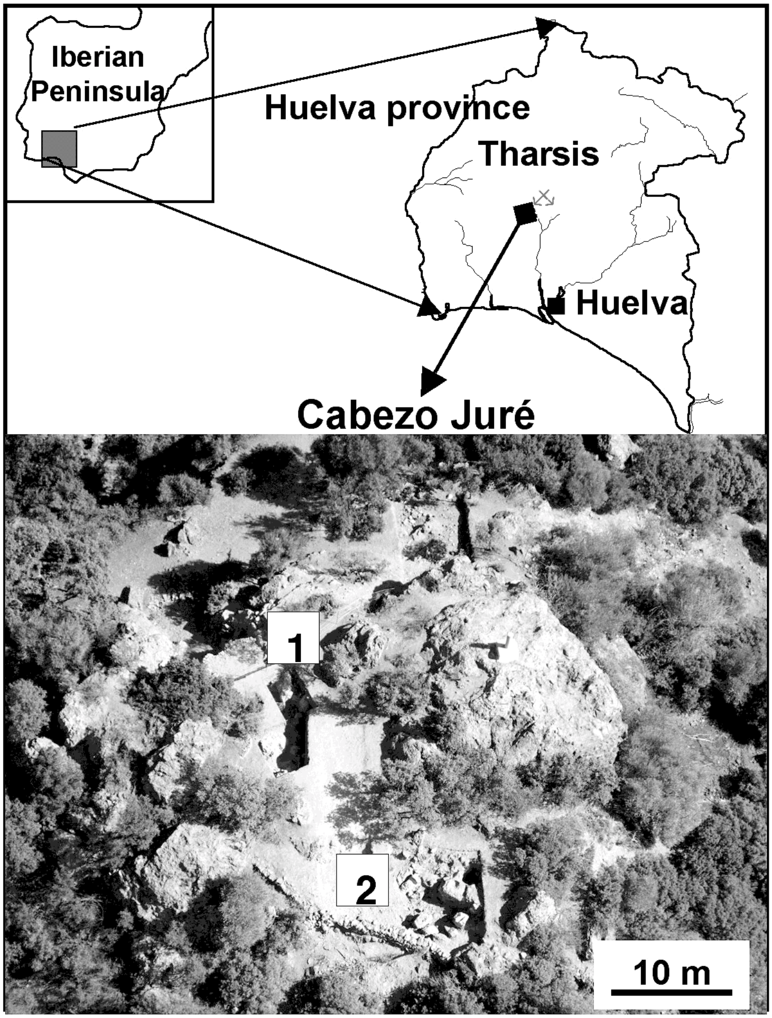

FIG. 1. Location and distribution in space of the Cabezo Juré archeological settlement, in southwestern Spain. 1: Living and copper-refining area. 2: Area of primary smelting in furnaces. Furnace slag and samples of raw materials used in this study were obtained from the furnace area. Crucible slag samples come from the living and refining area.

Samples selected for analysis include furnace and crucible slags. The former are important to understand the composition of the mixture of ore and flux, whereas the crucible slags are roughly indicative of the extent of copper recovery. Three types of ore have been recovered near the furnaces during the excavation at Cabezo Juré. They are 1) supergene copper ore (sample 3494, Table 1) including copper oxide, carbonate and sulfide minerals, 2) copper-rich gossan (sample Cu–N, Table 1), and 3) manganese-rich gossan (sample Mn–J, Table 1). The latter has been included in the study because of 1) its abundance close to the site, and 2) the possibility that it was used as a raw material or flux.

A first observation regarding the chemical composition of the slags is the great abundance of elements such as Al, Mg, and Ti (Table 1). These elements are generally in low concentrations in the ore used as raw materials, because they come from the supergene alteration of massive sulfides, which are commonly poor in such elements. The only exception among the analyzed ores in Table 1 is sample 3494, which is uncommonly rich in Ti for a supergene copper ore. The abundance of Al, Mg and Ti is also low in the gangue of the copper ore, which is mainly composed of quartz and goethite. Therefore, the type of flux used must have been a rock rich in these elements. Considering the rocks outcropping in the area around Cabezo Juré and their chemical composition, the most likely possibility is a basic volcanic rock, whose average content for these elements in the Iberian Pyrite Belt (1–2% TiO_2, 5–10% MgO, 13–16% Al_2O_3: Mitjavila *et al.* 1997) is sufficient. Close to the site, there are numerous outcrops of diabase and reworked basaltic tuff.

To test the possibility that this rock type was utilized as flux material for the production of copper and to calculate the percentage of flux added, a spilitized basic tuff from the neighboring Tharsis area (Schütz 1985) has been used as representative of the basic volcanic rocks outcropping near Cabezo Juré (Sample BR, Table1). Figure 2 shows two binary variation diagrams in which the chemical composition of the raw materials, the slags and the inferred flux is plotted. Figure 2A shows the composition of the slags analyzed and sorted on a mixing line between the ore materials considered and the basic rocks. The same mixing line is present in all binary diagrams, in which an element typically concentrated in basic rocks, such as Mg, Al or Ti, is plotted as a function of an element typically concentrated in the ore materials, such as Cu, Fe, Zn or Pb. If two elements, concentrated in either the ore material or the basic rocks are plotted, a good positive correlation exists between the two elements, as would be expected. The latter type of data representation allows us to estimate the percentage of each end-member used in the mix. Computing data on Table 1 through the mixing equations of Langmuir *et al.* (1978) by means of the program NewPet (Daryl Clarke, Memorial University of Newfoundland, 1993), we obtain the percentage of flux (basic rock) that was added, for fusion in the furnaces; it attains 50% (from 15 to 50 % depending on the slag sample used in the calculation).

Figure 2B reveals a positive correlation between Al_2O_3 and Ba, suggesting mixing between an Al–Ba-poor component (the ore) and an Al–Ba-rich component (the flux). The hypothetical end-member of this mixture has a Ba content greater than that of the basic rocks considered. A similar result occurs when considering Mn instead of Ba. There is also a good positive correlation between these two elements. All of this suggests that the flux used was not a basic rock of standard composition, as the one shown in Table 1 (sample BR), but one enriched with these two elements. In fact, the reworked basic rocks that outcrop in the immediate surroundings of Cabezo Juré contain quartz veins enriched in both Ba and Mn and whose concentrations progressively increase toward the top of the hill, where there are outcrops of manganese-mineralized rocks that were worked during the middle of the 20th century. From the available data, we conclude that during the fusion process of the copper ores in furnaces, basic rocks mineralized with Mn and Ba were added as a flux; we are confident that this material comes from the immediate surroundings of the settlement. Given the high amount of flux identified in the slags (up to 50%), we can discount the hypothesis of accidental contamination during the fusion process with building or soil material.

PHASES AND TEXTURES

The slags associated with the furnaces are usually composed of quartz, maghemite, magnetite, pyroxene (diopside–hedenbergite), Ca-rich plagioclase, cuprite and delafossite (Figs. 3A, B, C), but domains composed mainly of fayalite, magnetite and minor quartz (Fig. 3D)

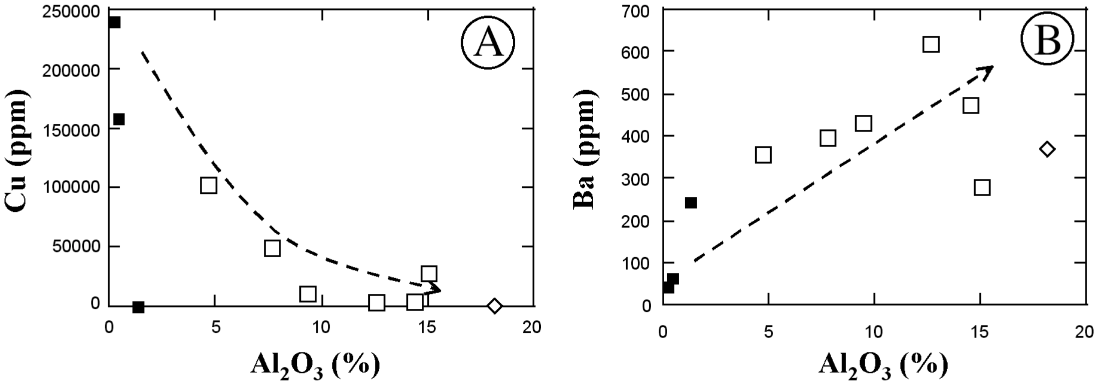

FIG. 2. Binary variation diagrams showing covariation of Al_2O_3 and Cu (A) and Al_2O_3 and Ba (B). See interpretation in text. Black squares: ore minerals collected at the smelting area. Empty squares: furnace slags. Empty rhombs: basic rock representative of those found around Cabezo Juré.

TABLE 1. REPRESENTATIVE COMPOSITIONS OF RAW MATERIALS AND SLAGS FROM CABEZO JURÉ, SOUTHWESTERN SPAIN

	Furnace slags							Crucible slags			Raw materials			
	F1		F2			F3		F2		F3	Ores		Fluxes	
sample #	3544	5231	5153	5165	5212	5131	6032	5154	2304	1197	3494	Cu-N	MN-J	BR
SiO_2 wt%	48.7	61.90	65.56	62.37	45.32	68.71	62.31	46.92	32.31	13.81	36.82	10.85	16.11	50.49
Al_2O_3	12.03	14.99	9.36	14.41	4.66	7.66	12.59	1.11	0.01	1.79	0.43	0.18	1.30	18.18
Fe_2O_3	20.78	10.16	6.72	8.72	25.27	9.08	8.35	33.66	32.52	50.6	2.08	50.83	28.45	12.74
MnO	6.553	0.43	1.20	1.56	0.62	1.84	2.45	0.131	0.124	0.026	0.02	0.19	40.30	0.10
MgO	0.53	2.78	1.69	1.98	1.22	0.70	0.74	0.14	0.37	0.2	0.06	0.31	0.25	2.37
CaO	1.09	1.37	7.85	5.15	4.15	2.12	4.16	0.37	0.63	0.2	0.99	1.14	1.91	0.48
Na_2O	0.21	1.25	0.87	0.75	0.51	0.41	0.33	0.11	0.24	0.26	0.57	0.21	0.15	0.92
K_2O	2.68	1.62	2.55	3.05	1.15	1.60	2.11	0.25	0.12	0.01	0.00	0.00	0.56	4.25
TiO_2	0.686	1.66	0.53	0.94	0.36	0.33	0.57	0.107	0.219	0.307	1.50	0.02	0.06	1.79
P_2O_5	0.965	0.18	1.21	0.88	0.85	0.39	2.19	0.135	0.234	0.058	0.66	1.34	0.40	0.08
Cu	n.d.	2.78	1.09	0.14	10.35	5.03	0.14	21.59	28.06	20.16	15.88	23.96	0.06	0.003
As ppm	n.d.	849	235	58	8628	1581	89	7545	3773	223	657	3002	90	13
Ba	545	283	434	476	360	399	623	139	101	53	64	42	244	368
Co	n.d.	91	30	34	180	79	15	180	50	15	134	n.d.	n.d.	n.d.
Cr	276	261	270	237	118	448	237	653	183	442	230	41	93	65
Ni	217	101	64	68	76	76	67	53	81	128	178	96	110	31
Pb	23	249	67	21	4562	1516	16	1042	3672	912	1787	28	25	3
S	n.d.	314	64	258	1354	88	949	219	236	16731	12126	720	753	n.d.
Sn	38	18	21	2	358	78	7	247	513	194	70	160	n.d.	1
Sr	236	127	305	231	170	113	249	25	91	35	78	28	633	74
V	162	210	73	126	53	56	96	49	52	399	39	90	114	n.d.
Zn	207	132	96	89	276	261	58	502	1423	315	1185	370	117	91

F1, F2 and F3 correspond to excavation phases, ordered chronologically from bottom to top. Ore samples come from Cabezo Juré and were recovered as a result of archeological investigations.

also are common (Table 2). The following phases have also been identified: copper, chalcocite (Cu_2S), and minor phases including ferrobustamite [$Ca(Fe,Mn)Si_2O_6$], fluorapatite [$Ca_5(PO_4)_3F$], pyroxmangite [$(Mn,Fe)SiO_3$], titanite [$CaTiSiO_5$], ulvöspinel [$TiFe^{2+}{}_2O_4$], and cassiterite (SnO_2). Secondary phases include Fe–Mn oxides, chrysocolla $(Cu,Al)_2H_2Si_2O_5(OH)_4 \bullet nH_2O$, and conichalcite [$CaCu(AsO_4)(OH)$] and an unidentified copper chloride (Sáez *et al.* 2001). Manganese is a common component in olivine and pyroxene, specially in samples with a high Mn content such as 3544 and also in sample 5212 (Table 1). The olivine-group mineral in these samples ranges in composition from ferrous tephroite [$(Mn_{1.12}Fe_{0.66}Mg_{0.11}Ca_{0.10})SiO_4$] to manganoan fayalite [$(Fe_{1.25}Ca_{0.21}Mg_{0.20}Mn_{0.18})SiO_4$].

TABLE 2. SEMIQUANTITATIVE ESTIMATE OF PHASE PROPORTIONS IN SAMPLES OF FURNACE AND CRUCIBLE SLAG, CABEZO JURÉ, SOUTHWESTERN SPAIN

	Furnace slags								Crucible slags		
Sample #	3544	5090	5231	5153	5165	5212	5131	6032	5154	2304	1197
Quartz	••	•••	•••	•••	•••	•••	•••	•••	•••	•	•
Plagioclase	•	••	•	•	••	••	•	••			
Cpx	•	•	•	•	•	•	•	•			
Olivine	•	•				•					
Magnetite	••	•	•		•		•	•	•	•	•
Maghemite	•	•	•	•	•	•	•		••	••	•••
Cuprite		•		•			•		•	••	••
Delafossite			•	•		•	•		••	••	••
Cu (metal)							•		•	•	
Titanite				•		•					
Ulvöspinel					•						

Estimates are based on X-ray-diffraction data and low-magnification BSE image analysis. Cpx: clinopyroxene.

The main silicate phases (pyroxene and plagioclase) show a microcrystalline intergrowth resembling a common ophitic texture (Fig. 3B). Primary quartz shows evidence of reaction with the glass matrix of the slags (Figs. 3A, C). This textural feature suggests conditions of disequilibrium in which some of the primary phases were partially resorbed by the melt. The remains of non-melted material (mainly quartz) indicate that the system did not achieve full melting due to the high SiO_2 content of the melting load. Also, the coexistence of quartz together with oxidized phases (*e.g.*, magnetite) indicates that temperature conditions for the reaction: $3SiO_2 + 2Fe_3O_4 = 3Fe_2SiO_4 + O_2$ were not maintained long enough for equilibrium to be achieved (Frost 1991).

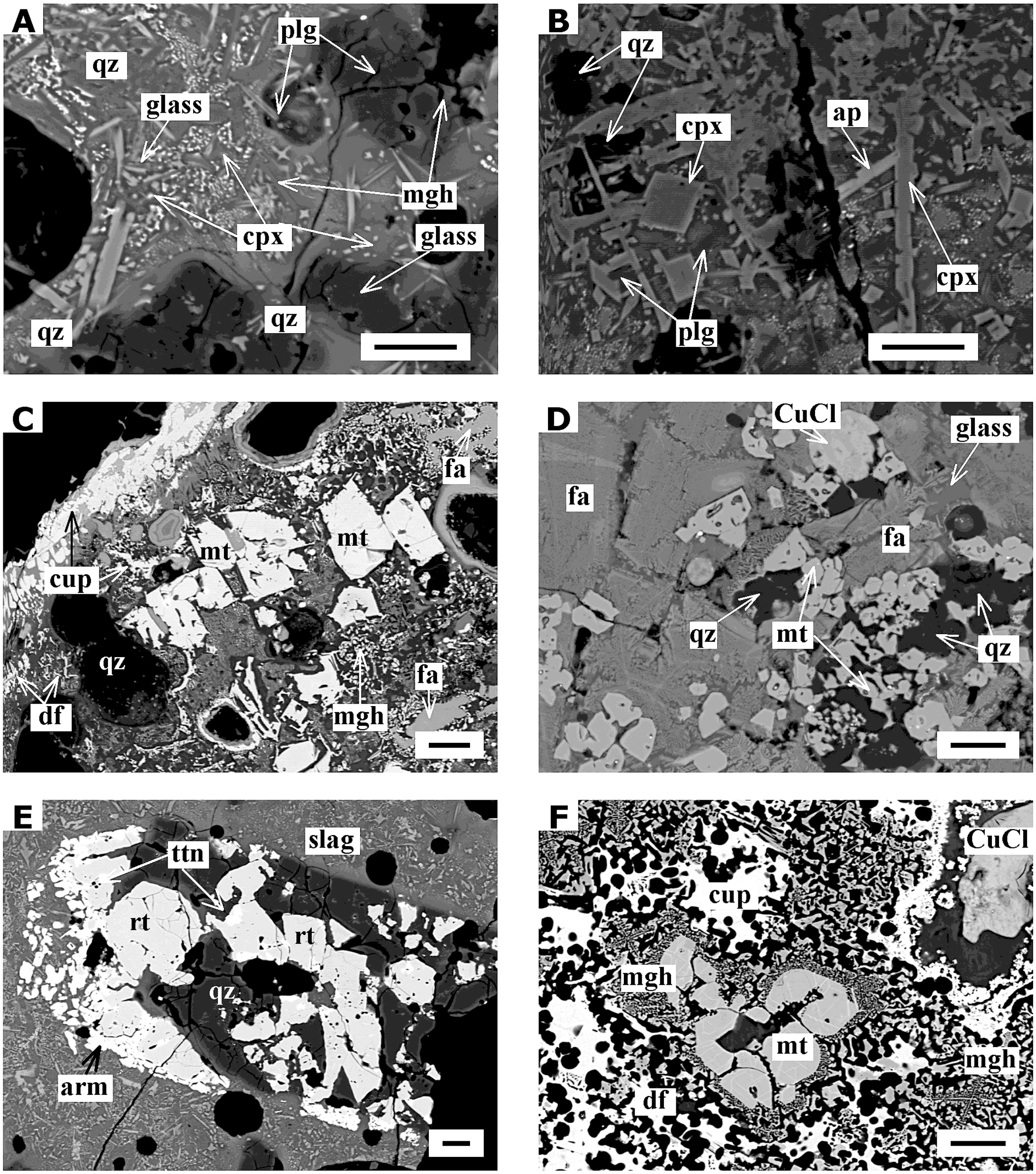

FIG. 3. Back-scattered electron (BSE) images (obtained with a scanning electron microscope) of furnace and crucible slags from Cabezo Juré, showing representative phases and textures. A. Quartz-rich domain (qz) in sample 5153. Relics of quartz grain occur showing corrosion gulfs and assimilation by melt. Clinopyroxene (cpx), plagioclase (plg) and maghemite microcrysts are observed as overgrowths within glass matrix. B. Ophitic texture in sample 5090 is indicated by clinopyroxene (cpx) – plagioclase (plg) intergrowth. Brighter rims of pyroxene crystals are related to an increase in the Fe content of clinopyroxene, whose composition ranges from Di_{80} to Di_{60}. The plagioclase in equilibrium with pyroxene is An_{75}. Quartz (qz) occur as relics of corroded grains. Apatite is also present as acicular crystals related to the pyroxene – plagioclase association. C. Oxide – silicate association in furnace slags (sample 5090). Earlier corroded crystals of fayalite (fa) and quartz (qz) relics are surrounded by an association of pyroxene, magnetite (mt), and cuprite (cp). Fine-grained maghemite and delafossite occur as a skeletal overgrowth within the glass matrix. D. Image of a fayalite-rich domain from a furnace slags (sample 5212). Skeletal laths of fayalite (fa) growing from the glass matrix seem to be in equilibrium with subhedral quartz (qz) and magnetite

Slags corresponding to the crucible stage exhibit a simpler mineralogy, characterized by quartz, which is invariably present, and other scarce silicates (albite and K-feldspar). The slag is composed mainly of quartz, magnetite, maghemite, delafossite, cuprite and copper (Fig. 3F). Copper carbonates and arsenates (malachite, azurite and conichalcite) and an unidentified copper chloride have also been recognized, as secondary minerals, products of the supergene alteration of those originally present during smelting. Metallic copper appears as fine-grained globules within the slag matrix (Sáez *et al.* 2001).

The dominant textures present are dendritic, a feature common to almost all slags (Craig 2001, Ettler *et al.* 2001, Manasse *et al.* 2001). This texture is mostly represented by skeletal growth of both copper and iron oxides (Figs. 3C, F) and usually involve direct precipitation from the melt. These textural features are indicative of rapid cooling at a stage when the melt is saturated in some phase during crystallization (Bard 1980).

The quartz, found in either type of slag, is invariably fractured and corroded, although some fayalite-rich slags shows subidiomorphic quartz crystals in equilibrium with magnetite and fayalite (Fig. 3D). The presence of quartz in the primary ore suggests that although it could have behaved as a flux (in fact, it is corroded), its presence in the melting mixture was not intentional. Some slag samples studied contain titanite and ulvöspinel (sample 5231). Ti-rich minerals are common elsewhere in mafic rocks of the Iberian Pyrite Belt, but the more likely source is the basic rocks (basalt, diabase) outcropping in the area (Sáez *et al.* 2001). This finding supports our above inference that basic rocks were added to the mix to improve the fusion process. The high Ti content of sample 5212 seems to be related with micro-enclaves containing quartz, rutile, titanite and armalcolite [$(Mg,Fe^{2+})Ti_2O_5$] (Fig. 3E). Titanite occur along the quartz–rutile interface. The titanite thus could have originated by reaction during heating, the calcium coming from the melt or from decomposed calcium carbonate. Armalcolite is a rare mineral first identified in lunar basalts (El Goresy 1976). In sample 5212, it occurs along the boundary between rutile and the melt, suggesting that armalcolite originated by rutile–melt reaction. Experimental studies indicate that ideal armalcolite ($Fe_{0.5}Mg_{0.5}Ti_2O_5$) is stable at temperature above 1010 ± 20°C under conditions of low oxygen fugacity (Lindsley 1976, El Goresy 1976).

crystals. EDS-derived composition of this glass is plotted in Figure 4. Copper globules altered to Cu chloride and chalcocite granules are common. E. Titanium-rich enclave in sample 5212. Heating under furnace conditions gave titanite (ttn) and armalcolite (arm) as result of a reaction of rutile (rt) with quartz (qz) and silicate melt, respectively. F. Common textural and compositional features of crucible slags (sample 5154). The lighter phases correspond to iron and copper oxides. Symbols: magnetite (mt), maghemite (mgh), cuprite (cup), delafossite (df). Darker ones correspond to K-feldspar and quartz. Metallic copper is altered to Cu chloride. Scale bar for all photographs: 10 μm.

The slags from the furnace fusion systematically contain clinopyroxene (diopside–hedenbergite solid solution) and Ca-rich plagioclase. The formation of pyroxene instead of fayalite (which occurs only sparsely in small domains), as well as the presence of anorthite instead of monticellite and melilite, are not common in slags (Bachmann 1982, Manasse *et al.* 2001), and indicate a high content of silica in the system (Fig. 4). From a chemical point of view, the abundance of pyroxene and plagioclase points to the existence of significant quantities of Ca, Al and Mg (as well as Fe and Si). The scarcity of these elements in the ore material supports the idea discussed before regarding the use of silicate fluxes during the first fusion process. The clinopyroxene in slags shows compositions (Table 3) ranging from hedenbergite ($Di_{25–35}$) to diopside ($Di_{75–80}$). Hedenbergite is not a stable phase in the system FeO–CaO–SiO_2 (Huebner 1980, Bachmann 1982), but seems related to the subsolidus transformation of ferrobustamite or of metastable ferroan wollastonite at temperature conditions close to 950°C (Bachmann 1982). As a result, the mineral association in the furnace slag points to melting temperatures over 1000°C. Samples of furnace slag (Tables 2, 3) showing Mg-rich clinopyroxene ($Di_{75–80}$) in equilibrium with Ca-rich plagioclase ($An_{75–80}$) indicate that even higher temperatures might have been attained.

The most abundant opaque minerals in both types of slag are the iron oxides maghemite (Fe_2O_3) and magnetite (Fe_3O_4), copper oxides, including cuprite (Cu_2O) and delafossite ($Cu^{1+}Fe^{3+}O_2$), and globules of metallic copper. The coexistence of metallic copper (Cu^0) with oxides of the metal (Cu^{1+}) can be interpreted in two ways: a) the oxidation state of the melt was heterogeneous and related to the addition of oxygen by means of forced aeration, and b) equilibrium redox conditions were compatible with the coexistence of both oxidation states. The presence of maghemite and magnetite in the slags indicates that conditions of log oxygen fugacity were close to zero, and thus points to the existence of free oxygen in the system, especially related to the crucible slags (Fig. 5), where magnetite is scarce, although present in most samples.

DISCUSSION

The main difficulties preventing a full discussion of the physicochemical conditions of copper smelting and refining at Cabezo Juré arise from the complexity of working with multicomponent systems, as is the case of archeometallurgical slags. The main source of potential

TABLE 3. COMPOSITION OF REPRESENTATIVE SILICATE PHASES IN SAMPLES OF FURNACE SLAG, CABEZO JURÉ, SOUTHWESTERN SPAIN

	olivine			clinopyroxene					plagioclase				
sample #	5212	5153	5090	3544	5231	5212	5153	5090	3544	5231	5212	5153	5090
SiO_2 wt%	32.4	30.82	31.30	40.87	51.91	49.84	53.67	46.81	56.34	51.92	51.82	51.25	49.34
Al_2O_3	4.77	1.58	n.d.	7.60	4.14	4.57	0.99	5.04	21.65	28.36	28.38	29.58	32.70
TiO_2	n.d.	n.d.	n.d.	1.87	0.61	0.63	0.20	1.61	n.d.	n.d.	n.d.	n.d.	n.d.
FeO(t)	47.45	24.42	57.51	33.87	8.27	10.14	7.27	12.53	2.77	1.49	0.64	1.11	0.49
MnO	4.78	40.67	2.17	11.28	1.47	1.44	1.67	1.24	1.38	0.19	n.d.	n.d.	n.d.
MgO	3.83	0.91	8.44	2.19	10.96	12.09	13.72	11.53	0.14	0.40	0.25	0.61	n.d.
CaO	5.80	1.52	0.98	1.16	21.73	21.23	23.49	20.94	12.02	14.91	14.28	16.34	14.95
Na_2O	n.d.	n.d.	n.d.	0.02	n.d.	0.41	n.d.	n.d.	2.99	1.99	2.01	1.84	2.90
K_2O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.90	1.04	1.23	0.77	1.02
Total	99.03	99.92	100.40	98.86	99.09	100.35	101.01	100.37	101.19	100.31	98.95	101.14	101.40
Si *apfu*	1.01	1.01	0.99	1.74	2.02	1.87	1.98	1.83	2.69	2.42	2.43	2.32	2.23
Al	0.17	0.06	0	0.38	0.19	0.20	0.04	0.17	1.22	1.55	1.57	1.58	1.74
Ti	0	0	0	0.06	0.02	0.02	0.01	0.05	0	0.06	0	0	0
Fe	1.23	0.67	1.52	1.21	0.27	0.32	0.22	0.41	0.11	0.01	0.02	0.04	0.02
Mn	0.13	1.13	0.13	0.38	0.05	0.05	0.05	0.04	0.06	0.03	0	0	0
Mg	0.18	0.04	0.18	0.14	0.64	0.68	0.75	0.67	0.01	0.74	0.02	0.04	0
Ca	0.19	0.05	0.19	0.05	0.91	0.86	0.93	0.88	0.61	0.18	0.71	0.79	0.72
Na	0	0	0	0	0	0.03	0	0	0.27	0.06	0.18	0.16	0.25
K	0	0	0	0	0	0	0	0	0.12	0.06	0.07	0.04	0.06

Structural formulae of olivine, clinopyroxene and plagioclase are calculated on the basis of four, six and eight atoms of oxygen, respectively. Results of energy-dispersion analyses.

uncertainty is introduced by the evidence of disequilibrium as well as the role of some major components (*e.g.*, copper) and minor elements (As, Pb, Zn, see Table 1) whose behavior is not well constrained in silicate systems (Kim & Sohn 1997, 1998, Matsuzaki *et al.* 2000). In spite of this shortcoming, general statements can be made concerning the study of archeometallurgical procedures. The best approach for this approximation is to assume that the smelting and refining processes are comparable to experimental data obtained from well-known multicomponent systems. Usually, the reference system for silicate slags is $CaO–MgO–FeO–Fe_2O_3–Al_2O_3–SiO_2$ (Roeder & Osborn 1966, Jak *et al.* 1998), at atmospheric pressures and different $f(O_2)$ conditions. Phase analysis in this system accounts for the main silicate mineral equilibria observed in the Cabezo Juré furnace slags. Nevertheless, this system is not representative for refining slags because the composition of the smelted phase in these slags is dominated by Fe and Cu. The high silica content of samples 5154 and 2304 (Table 1) is related to unsmelted quartz grains. As a consequence, the main observed phases are Fe and Cu oxides. The compositions of archeometallurgical slags have commonly been represented in the system $FeO–SiO_2–CaAl_2Si_2O_8$ (Merkel 1990, Chernykh & Rovira 1998). This simplified system is considered useful for this study (Fig. 4), as the MgO content of most of the samples is low enough to introduce only a minor modification of the main phase assemblages (Zhao *et al.* 1998). According with these authors, addition of MgO expands the primary field of fayalite toward higher SiO_2 concentrations, increasing the liquidus temperature by 24°C for each weight percent of MgO added. Most of the primary smelting slags plot in the primary field of cristobalite, accounting for the free-silica character of this type of slag. The compositions of crucible slags are diverse, and include samples in the primary fields of wüstite, fayalite and tridymite. This analysis accounts for the predominance of oxidized phases as well as the scarcity of silicates in this type of slag.

Slags composition plotted in the system $FeO–SiO_2–CaAl_2Si_2O_8$ (Fig. 4) account for the incomplete melting of the furnace slags, as the liquidus temperature in the high-silica region is higher than is reasonable for prehistoric procedures of melting. This diagram also accounts for textural features observed in quartz grains, including engulfing and other corrosion-induced features. As a result, the melt composition differs from that of the analyzed slags, which is richer in silica than the smelted phase. Homogenization by mixing could be impeded by the high viscosity of the smelted phase. This factor could account for the phase heterogeneity observed in some of the samples.

The simultaneous crystallization of plagioclase and diopside occurs along a cotectic curve with a thermal minimum over 1130°C for albite in equilibrium with

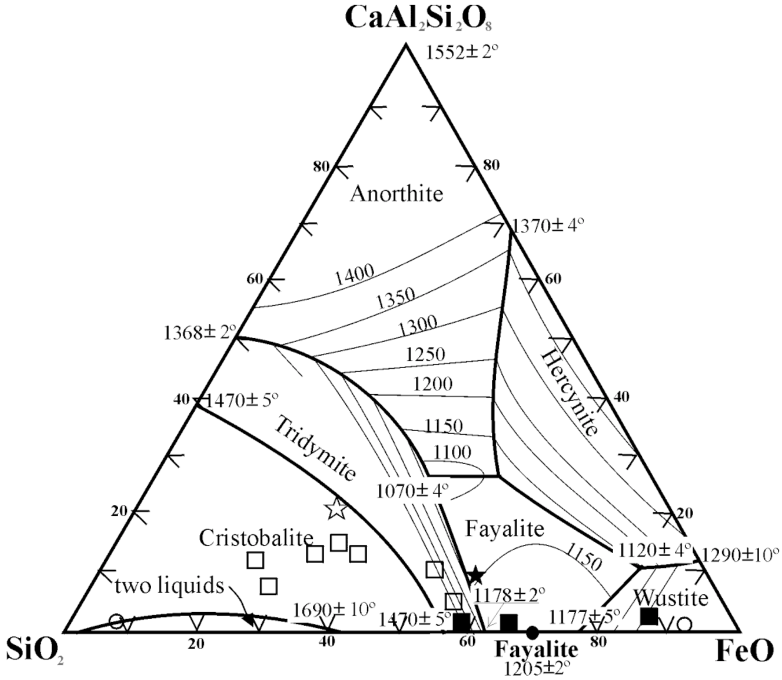

FIG. 4. Plot of the composition of slags and raw materials from Table 1 in the system FeO–CaAl$_2$Si$_2$O$_8$–SiO$_2$ (redrawn after Morton & Wingrove 1969). □: chemical composition of furnace slags, ■: composition of crucible slags, ○: ore samples, ★: EDS-derived composition of glass in the QFM domains, ☆: mean of eight EDS analyses of glass in clinopyroxene–plagioclase slags.

pure diopside at atmospheric pressure (Schairer & Yoder 1960, Roeder & Osborn 1966, Ehlers 1972). Consequently, it is reasonable to predict temperatures of about 1200°C for the formation of Ca-rich plagioclase, although the possible effect of other components of the system on the equilibrium temperature is not known (Fig. 4).

The presence of fayalite in equilibrium with quartz and magnetite in some domains of the samples of furnace slag indicates that locally, fusion occurred at conditions where the oxygen fugacity was near the QFM buffer. This fact supports the existence of a heterogeneous melt that was capable of reducing the copper, whereas in others it would remain as oxides.

The slags derived from the crucible-held refinement process have a simpler mineralogy; they contain rare silicate phases, albite and K-feldspar. Crucible refinement was attained at temperatures close to 1000°C, as indicated by the simultaneous (eutectoid) crystallization of delafossite and cuprite (Haupmann *et al.* 1994). The slags derived from the fusion in crucibles do not show evidence of flux addition. The general presence of iron oxides and copper oxides indicate conditions of oxygen fugacity between the quartz – fayalite – magnetite (QFM) and hematite – magnetite (HM) buffers. Changing redox conditions together with the high temperatures of furnace melting suggest forced ventilation in the combustion structures, as have been experimentally tested in other archeological sites (Rothenberg 1990, Rovira 1999). Forced ventilation yielded a double coupled effect. Air input enhances combustion reactions and, as a consequence, temperature can increase up to 1300°C, also in primitive charcoal furnaces (Haupmann *et al.* 1994). The coupled effect leads to an increase of oxygen fugacity, moving the redox equilibrium to oxidized phases. This model accounts for the heterogeneous redox conditions, as deduced from phase equilibria in the analyzed slags. The approximate conditions of smelting and refining have been obtained by several buffer equilibria as a function of oxygen fugacity against temperature. The physical and chemical conditions of smelting might be close to those shown in Figure 5. Furnace slags were obtained by smelting at temperature above 1100°C under oxygen fugacity conditions limited by the QFM and HM buffers. These redox conditions allow copper reduction as well as the coexistence of metallic copper and cuprous oxide, which is observed in the slag samples studied. Slags resulting from crucible refining

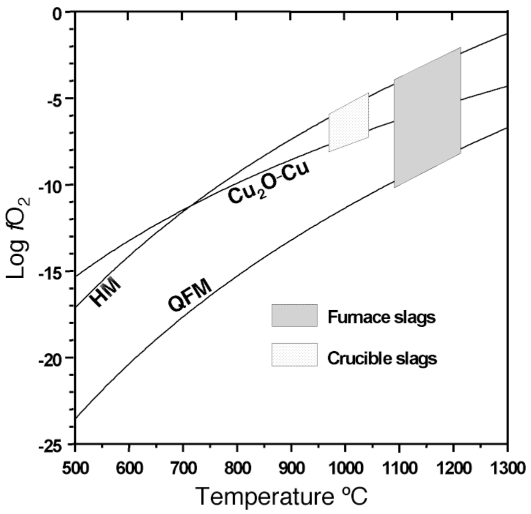

FIG. 5. Diagram showing conditions of *logf*(O_2) *versus* T for primary smelting and copper refining, as deduced from chemical and mineralogical composition of related slags (modified after Haupmann *et al*. 1994). QFM: quartz – fayalite – magnetite buffer; HM: hematite–magnetite buffer; Cu_2O–Cu: cuprous oxide – copper buffer. Data for QFM and HM have been obtained from Frost (1991), and for the Cu_2O–Cu buffer from Eugster & Wones (1962).

of copper were produced at lower temperatures (900–1000°C) at redox condition limited by the Cu_2O–Cu and HM buffers (Fig. 5). We infer both using the magnetite – maghemite and the cuprite – copper equilibria.

The abundance of copper oxide phases suggests an inefficient process where a large part of the copper contained in the ore was never liberated as metallic copper. Difficulties with copper recovery occur not only in prehistoric smelting, but also in modern metallurgical procedures. Nevertheless, the high content of copper (up to 28%) in some of the slag samples analyzed illustrates well this low efficiency, which is related to difficulties in achieving and keeping, for a long-enough time, a high temperature and very reducing conditions in charcoal-burning smelting furnaces.

CONCLUSIONS

The study of metallurgical slags from Cabezo Juré led us to the following conclusions about the smelting and refining procedures for copper extraction during the third millenium B.C. near the Tharsis mining district.

1. Copper was arecovered by means of a two-stage process: smelting in furnaces and refining in baked clay crucibles.
2. Smelting in furnaces was obtained at temperature near 1200°C at redox conditions limited by the QFM–HM buffers.
3. The high silica content as well as relics of corroded quartz grains indicate incomplete smelting of the furnace charge. Inferences of a high viscosity of the liquid phase made the segregation of a metal-rich smelted phase difficult.
4. Local mafic rocks were intentionally added as flux in order to improve smelting procedures. Mixing models suggest addition up to 50% for some of the samples analyzed.
5. Refining in baked clay crucibles was achieved at temperature near 1000°C at redox conditions limited by the HM and the Cu_2O–Cu buffers. There is no evidence of flux addition during copper refining.

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