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Research Article

Presence of bismuth in slag heap upcoming to a copper sample found in a Roman Siete Cuevas (Cerro Muriano, Córdoba (Spain))

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Abstract

The detection, clearly, of the presence of up to 5% by mass of bismuth, in big drops of copper from a Roman era smelter, located near the Cerro de la Coja (Siete Cuevas) in Cerro Muriano (Córdoba); this assumes that some copper produced at this location in Roman times, containing bismuth. In previous studies by our research group, in such samples from the same archaeological site, the presence of this element was not detected. This fact, the presence of bismuth in a sample of copper in Cerro Muriano (Córdoba), it can mean the treatment of minerals from other sources, more or less far away, of this mining localitation.

Introduction

The town of Cerro Muriano is situated 16 kilometers north of Cordoba. In Roman High-Imperial times, Cordoba was the capital of the Roman province called Bética. Despite the relative importance of the seam of copper of archaeological sites of the great metallogenic region of Sierra Morena, the network of Cerro Muriano, both for its size and its high content of copper, it may be regarded as an exceptional case in the Iberian Peninsula [1].

As for his paragenesis, the seams of Cerro Muriano, they must be classified as epigenetic; occurring during the Hydrothermal period, the best conditions for the formation of a copper deposits whose exploitation was the dominant sulfide, namely chalcopyrite (Cu 34% mass). In addition, other associated minerals and copper were exploited malachite (Cu 57% mass), azurite (Cu 55% mass) and chalcocite (Cu 79% mass).

These source of mineral are being exploited from the Chalcolithic period to the present [2]. In all historical periods the site of Cerro Muriano has been self-sufficient, above all, until modern times, possessing [3]:

1. Mining (metalliferous lodes)
2. Forests (wood → coal)
3. Plant for metallurgy (metallurgists)
4. Communication channels (export of metal ingots or manufactured parts)

Since the nineties of the twentieth century, has been investigating the quality of copper in Roman period (first century BC and AD). Has been studied the chemical composition of slag and spills of copper and parts of copper and bronze, already manufactured, produced in Cerro Muriano [4-8].

This article presents analysis of a big drop of copper found in the Roman high- imperial slag heap near the archaeological site of Seven Caves, just 1 kilometer northwest of the town of Cerro Muriano (Figure 1). It is copper with appreciable amounts of bismuth, we think comes from copper ores extracted out of the surroundings; which would mean that in Roman metallurgical facilities of Cerro Muriano were processed, in addition to the minerals belonging to the metalliferous lodes of themselves, minerals brought from outside [9,10] (Figure1).

Experimental technique

Sample collection in the Roman escorial Siete Cuevas was carried

Figure 1. Situation of the Roman slag heap on the site of Siete Cuevas (Cerro Muriano, Córdoba).

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out by an archaeological prospecting with geophysical methods. The metal samples found, were studied by conventional optical microscopy and dark field, and by scanning electron microscopy with EDS-EDX analysis incorporated. Metallographic preparation of the samples was carried out conventionally. First place, samples of the archaeological pieces are pull out, and then, are embedded in epoxy resin of two components.

Then, roughing is done with sandpaper grain 120, 270, 320 and 600 of Buehler, and subsequent, polishing with polishing cloths Buehler with alpha-alumina; both processes in water. Subsequently, an etching is performed during 90 seconds with Nital 4%. For observation on scanning electron microscopy, deposit an sputtering with gold for 30 seconds with a current of 20 mA, and thickness of 3 nm gold, not to interfere with the images obtained.

The scanning electron microscope used is a thermionic cathode microscope with tungsten filament (FEG). The employee for this research is the model JEOL JSM 6400 that provides images and physicochemical data of the surface of the sample.

Results

Most of the samples in the form of drops and spills of copper (Figure 2), presented a chemical composition according to the result obtained in previous studies, scrap metal, slag and artifacts of origin of Cerro Muriano (Córdoba) [4-8].

However, some of the metal spills found in the archaeological projection showed a remarkable bismuth content. It was surprising because the presence of bismuth and mining associated with this metal, are in remote areas of Cerro Muriano, in the region of Pedroches, in the north of the province of Córdoba and Montoro in the Guadalquivir Valley.

Spills copper found are small pieces of copper, between 1 cm and 5 cm in size, showing the typical morphology have been part of the copper smelter (Figure 2). They are products of splashes and spills straining of the first fusion, associated with slags, which are masking, having a high sulfur content and absence of bismuth. Possibly, they are the result of the operations of separation of slag of molten metal. The obtained copper would then an operation of desulfurization and purification.

The metallographic study of these drops show a copper matrix with barely impurities and cooper globules dispersed in it (Figure 3). The amazing thing about this research is the appearance of bismuth in significant amounts in some of the samples prospected in this archaeological site, as in the case shown in Figure 4.

In the chemical analysis by EDS-EDX, the presence of bismuth segregated in interdendritic spaces in the copper matrix, due to its low solubility and to its low melting point (Figure 5) is evident.

Figure 2. Big droppers of copper found in that escorial.

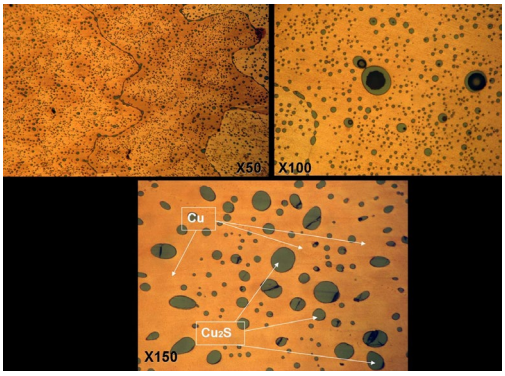


Figure 3. Micrographs by Optical microscopy, at different magnifications, of the overall microstructure of these copper drippers where copper sulfide globules are observed on a copper matrix.

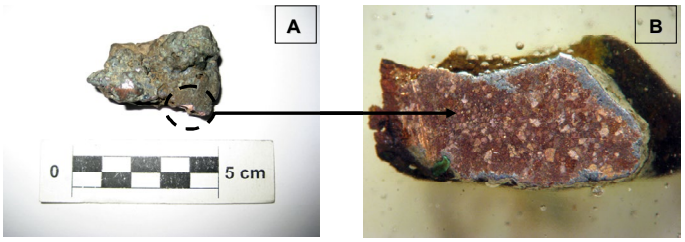
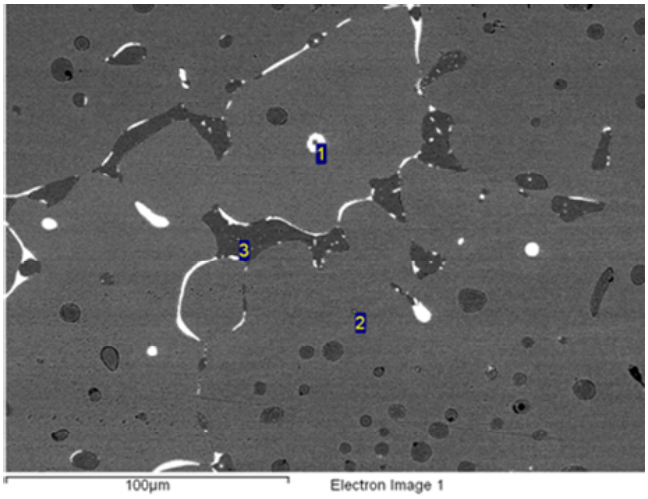


Figure 4. Copper drop that containing bismuth (A), and micrograph of the sample thereof (B).



Spectrum	S	Cu	Bi	Total
1	-	-	100.00	100.00
2	-	100.00	-	100.00
3	38.00	62.00	-	100.00

All results in weight %

Figure 5. Micrography obtained by M.E.B. with analysis EDS-EDX incorporated, in which the presence of bismuth in the drop of copper is identified.

Furthermore, micrographs obtained at M.O. and S.E.M. (Figure 6), a copper matrix is observed, with interdendritic spaces and segregated presence of copper sulfide, and bismuth like all samples studied.

This finding is an important test of the treatment in metallurgical furnaces of Cerro Muriano, in high-Imperial Roman times, minerals from other sites.

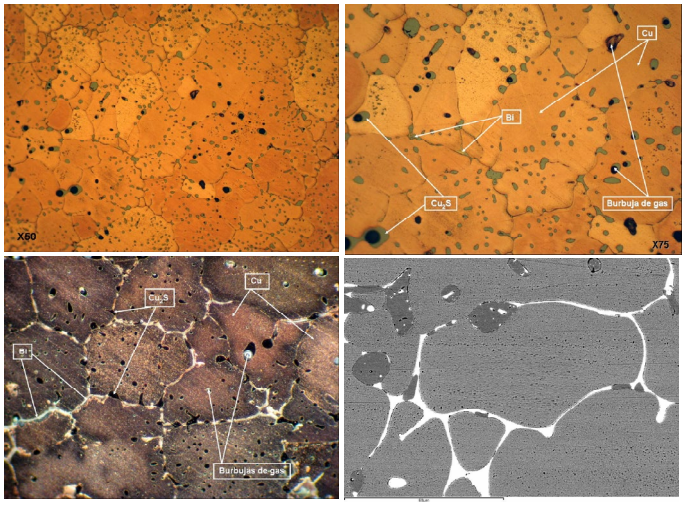


Figure 6. Micrographs obtained by M. O. Conventional (A and B) and dark field (C) of the microstructure of the Figure.4, in which bismuth is observed in light colored, and blue-gray is Cu2S, on a copper matrix. Micrograph (D) is obtained by M.E.B. with backscattered electrons, which is highlighted remarkably light color in interdendritic spaces, bismuth segregated. The Cu2S appears in dark color on a copper matrix (gray color).

Conclusions

The presence of bismuth, in significantly higher quantities, in drops, splashes and spills of copper in found samples by geophysics archaeological survey, in the Roman high-imperial slag heap of Siete Cuevas (Cerro Muriano, Córdoba), confirms the importance of this mining and archaeological site, of Roman Bética. This importance is demonstrated, as the mining and archaeological site of Cerro Muriano, a site that has all the necessary to be, at once, a metallurgical archaeological site top-rated, very complete:

1. Mining (metalliferous lodes)
2. Forests (wood → coal)
3. Plant for metallurgy (metallurgists)
4. Communication channels (export of metal ingots or manufactured parts)

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