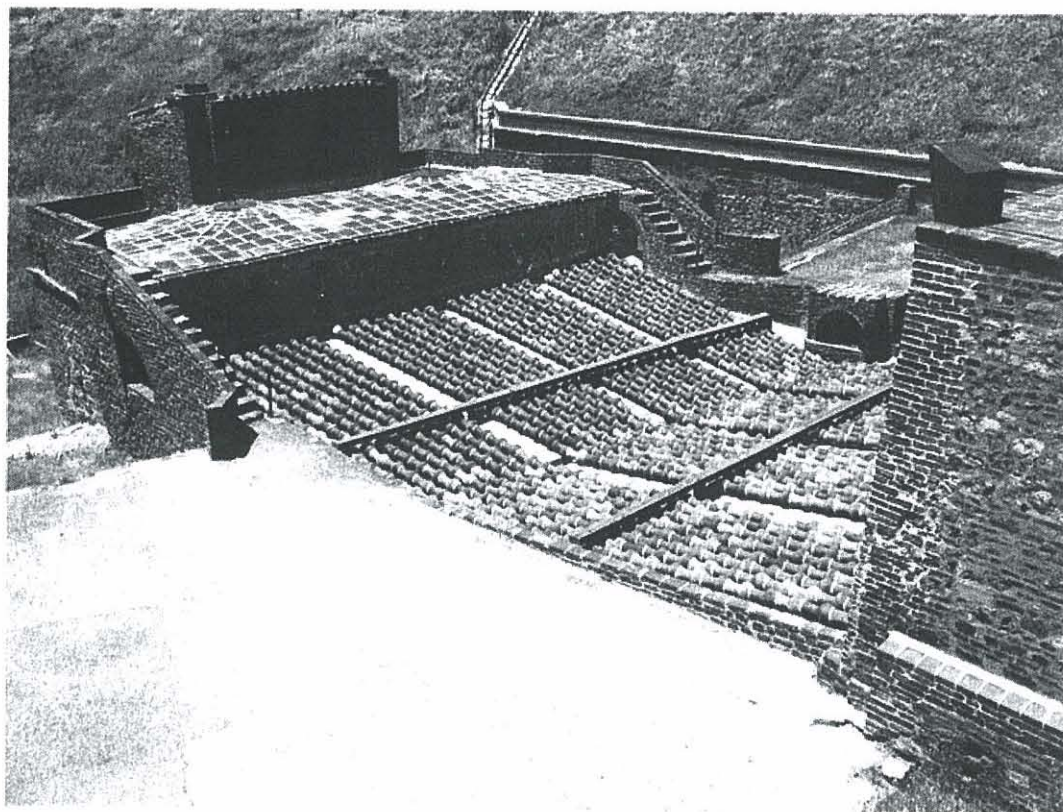


HISTORY OF RESEARCH IN MINERAL RESOURCES



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Edited by: José Eugenio Ortiz
Octavio Puche
Isabel Rábano
Luis. F. Mazadiego



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Instituto Geológico
y Minero de España

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NEOLITHIC AND CHALCOLITHIC –VI TO III MILLENNIA BC– USE OF CINNABAR (HgS) IN THE IBERIAN PENINSULA: ANALYTICAL IDENTIFICATION AND LEAD ISOTOPE DATA FOR AN EARLY MINERAL EXPLOITATION OF THE ALMADÉN (CIUDAD REAL, SPAIN) MINING DISTRICT

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Abstract. This research has been centred on the analytical identification of the use of cinnabar (the red mercury sulphide-HgS-) as a pigment in Neolithic and Chalcolithic archaeological contexts (VI to III millennia B.C.) and in the determination of its possible origin by the application of Lead Isotopes analysis. In order to confront the isotopic results of the archaeological cinnabar pigments, samples from the mercury sulphide mineral deposits of Usagre (Badajoz) and Las Alpujarras (Granada) were submitted to Lead Isotopes analysis. These results were added to those available in the geo-chronological literature referred to the Almadén mining district (Ciudad Real), the largest concentration of cinnabar in the world, although with the oldest evidence of mining dated, at present, to the 8th century BC. The confrontation of the lead isotopic results of the samples from archaeological contexts and of the mineral deposits showed, firstly, the distinguishable lead isotopic composition of the main cinnabar mines studied and, secondly, the consistency of the isotopic composition of the archaeological Neolithic and Chalcolithic cinnabar samples with the Almadén district isotopic field. Based on the currently available isotopic data, it is proposed that the exploitation and the use as a pigment of cinnabar mineral from the Almadén district started, at least, in the late 6th millennium BC, being distributed through long distance exchange networks during the Neolithic and Chalcolithic periods.

1. INTRODUCTION

The use of red pigments for ritual purposes is documented in Europe since the Paleolithic (Alimen and Steve, 1977), being its exploitation of the oldest mining works known (Shepherd, 1980; Wagner and Weisgerber, 1988). With respect to the mining and use of the cinnabar (the red mercury sulphide mineral -HgS-), its exploitation and treatment was documented in the 4th millennium BC in the Suplja Stena mine, near Belgrade (Serbia), dated to the recent phase of Vinca Culture (Jovanovic, 1978; Shepherd, 1980; Mioc et al., 2004).

Focusing on the Iberian Peninsula, the references to the presence of red pigments identified as cinnabar in prehistoric archaeological contexts are not infrequent since the beginning of the 19th century, being identified in diverse Neolithic and Chalcolithic archaeological sites, such as, the Dolmen de Alberite (Villamartín, Cádiz), dated to the 5th millennium BC (Dominguez Bella and Morata Céspedes, 1995), Cueva de los Murciélagos

de Zueros (Córdoba) (Martínez Fernández et al., 1999; Gavilán Ceballos et al., 1999), Dolmen de la Velilla (Osorno, Palencia), dated to c. 3.000 BC (Martín Gil et al., 1994; 1994a; 1995), the dolmens of Marcella (Obermaier, 1919) and Santa Rita (Inácio et al., 2010), both in the Portuguese Algarve, or the Chalcolithic graves (3rd millennium BC) of Paraje de Monte Bajo (Alcalá de los Gazules, Cádiz; Lazarich González, 2007).

In this paper, the preliminary results of the archaeometric characterization of the red cinnabar pigments excavated in Neolithic (Casa Montero) and Chalcolithic (La Pijotilla and Dolmen de Matarrubilla) sites (Fig. 1) are presented, and their possible origin is established through the application, for the first time in this type of archaeological material, of Lead Isotope analysis.

2. ARCHAEOLOGICAL SAMPLES: ANALYTICAL IDENTIFICATION AND CONTEXT

One of the the main objectives of this research has been the basic analytical characterization of red cinnabar pigments recovered from three prehistoric archaeological contexts: the Neolithic flint mine of Casa Montero (Madrid) and the Copper Age burials of La Pijotilla (Badajoz) and Dolmen de Montelirio (Castilleja de Guzmán, Sevilla) (Fig. 1).



Figure 1. Location of sampled archaeological sites (squares) and cinnabar mineral deposits (circles).

2.1 Casa Montero site

The Early Neolithic flint mine of Casa Montero, located south-east of the city of Madrid, covers an extension of 3 hectares. Flint was extracted through more than 4000 mine shafts, 9 meter depth and 1 meter width mean (Bustillo et al., 2009; Capote et al., 2008). The site has been interpreted as a result of a short set of mining events most probably occurring throughout one hundred years, between 5300 and 5200 cal BC. Several objects were deposited together (unit 7985) probably in a petite bundle, more than seven meters down mining pit number 7988. Among these were two small bone tools and 2 *Theodoxus fluviatilis* shells, all coated in ocre, and a flint blade coated with a thin film of cinnabar (Fig. 2).



Figure 2. Casa Montero: red pigments on flint blade from Shaft 7988, unit 7985.

The results of the SEM-EDXS analysis of the pigment showed the presence of cinnabar (Fig. 3).

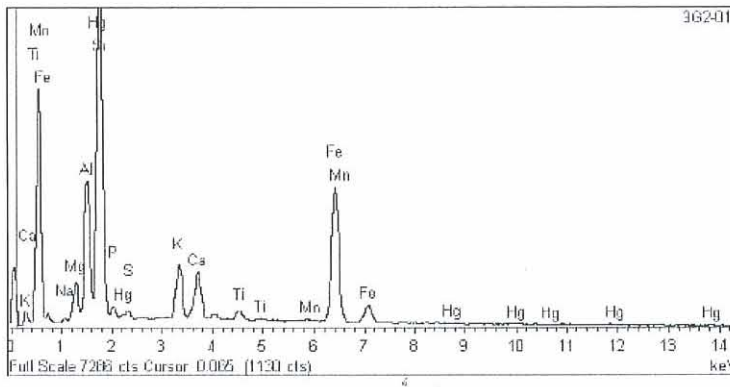


Figure 3. EDXS spectrum of the red pigment covering the flint blade from Casa Montero.

2.2 La Pijotilla site

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From La Pijotilla (Badajoz) site, the presence of red pigments was previously known from the excavation of Tumba 3, a tholos type grave (Hurtado Pérez, 1988). In that case, the pigments were analytically identified as iron oxides (Hunt Ortiz, 2003). In a recent revision of the archaeological register from La Pijotilla's Tumba 1, also a tholos type grave, deposited in the Museum of Badajoz, an accumulation of red pigment in a lithic lamina (n° inv. 11.157) was documented (Fig. 4). Both Tumba 1 and Tumba 3 have been dated to pre Bell-Beaker Chalcolithic times (Hurtado Pérez, 1999: 55).

The analysis of the pigment by XRF showed the presence of cinnabar mineral (Table 1).

| Wt % (nd=not detected) | Al | Si | S | K | Ca | Ti | Mn | Fe | Hg |
|------------------------|------|------|------|------|------|----|------|------|-------|
| Pijotilla 11157 | 1.46 | 1.69 | 4.55 | 0.87 | 2.91 | nd | 0.07 | 0.49 | 87.95 |

Table 1. XRF results of red pigment from La Pijotilla, Tumba 1.

2.3 Dolmen de Montelirio

The Dolmen de Montelirio (Castilleja de Guzmán, Sevilla), a large tholos type grave, is located within the site of Valencina. The corridor, discovered during huge mechanical survey works carried out in 1998, had extensive use of red pigments on the slates forming its internal walls.

Later on, the grave was excavated, confirming the use of red pigments also in the funerary rituals associated with the human remains and grave goods, as well as in the internal walls of the chamber (Fig. 5). The Montelirio dolmen has been dated in the early stages of the 3rd millennium BC (Vargas Jiménez, 2004). A sample from the dolmen, DJ07-32.C46, taken from one of the slates forming the chamber, obtained in the 2007 campaign, was given by its director, archaeologist Álvaro Fernández Flores.

The red pigment, analysed by XRF, contained cinnabar mineral (Table 2).

| Wt % (nd=not detected) | Al | Si | S | K | Ca | Ti | Mn | Fe | Hg |
|------------------------|----|------|------|------|------|------|------|-------|-------|
| Montelirio DJ07 32.C46 | nd | 0.39 | 8.09 | 1.58 | 1.40 | 1.07 | 0.05 | 57.97 | 29.45 |

Table 2. XRF results of red pigment (DJ07.32.C46) from Montelirio dolmen.

3. CINNABAR MINERAL DEPOSITS

As a first step in order to determine the possible origin of the archaeological cinnabar samples, a preliminary approach was carried out on the geographical location and principal characteristics of the most relevant cinnabar deposits in southern Iberian Peninsula (Fig. 1).

3.1 Usagre mineralization

Cinnabar mineral deposits are not known to exist in the South Portuguese geological zone, and in the Ossa-Morena geological zone the only cinnabar deposits are the ones located in the Usagre (Badajoz) area (Calderón, 1910; Vázquez Guzmán, 1983; Tornos and Locutura, 1989; Mapa Metalogenético de la Provincia de Badajoz, 2006).

In this Usagre mineralization, the exploitation of Mariquita and Sultana mines is documented since the 16th century AD. In the limited field visit carried out to collect mineral samples, outcroppings of the mineralization were observed. Although no clear evidence of prehistoric exploitation was seen in the area (very much altered by recent environmental restoration works), a fragment of a stone axe was found in the surface near one of the modern shafts.

3.2 Las Alpujarras (Tímar-Cástaras) mineralization

The other area visited with mercury mineralizations is located in Las Alpujarras, in the province of Granada, with historical references to mining from, at least, the early 20th century AD (Calderón, 1910). The cinnabar minerali-



Figure 4. La Pijotilla, Tumba 1: red pigment on lithic lamina (11.157).

zation extends from Cástaras to Tímar, impregnating the calcite, and is considered to be of low content, not over 0.5% Hg (Junta de Andalucía, 1986). Of the mineral samples collected in the visit to the area, centred in the mining works located by the ruins of the metallurgical installations in the villages of Tímar and Cástaras, only in one of them was the presence of mercury detected (0.25%). Thus this mineralization was considered not adequate for cinnabar pigment production (Hunt and Hurtado, in press).

3.3 The Almadén district

The major concentration of cinnabar in the Iberian Peninsula is in Almadén (Ciudad Real). More than a single mineralization, it is a mineral district composed of diverse deposits (Fig. 6) that, together, form the richest cinnabar mining area in the world. The composition of the Almadén mineral is defined by some authors as simple, with cinnabar as major constituent and pyrite in minor quantities, with occasional chalcopyrite and galena. It is important to mention that the Almadén district shows a complex geological history, with cinnabar deposits of different ages (Vázquez Guzmán, 1983).

The most ancient evidence known, to date, of cinnabar exploitation in Almadén is of the 8th century BC (Fernández Ochoa et al., 2002). The archaeological remains show extensive Roman workings, as documented in Las Cuevas, El Entredicho, Nueva Concepción and Guadalperal deposits (Domergue, 1987), which confirms the references of classical authors (Pliny, XXXIII).

4. ISOTOPIC RESULTS

In order to establish their possible origin, the characterised cinnabar minerals excavated in archaeological contexts were submitted to Lead Isotopes analysis. In its archaeological application to provenance studies, this method is considered to be contrasted and reliable, with well established extractive and analytical procedures (Rohl and Nee-dham, 1998; Hunt Ortiz, 2003; Santos Zalduegui et al., 2004).

Simultaneously, to define their isotopic composition, the samples of the cinnabar mineral deposits of Usagre (Badajoz) and Las Alpujarras were also analysed by lead isotope analysis. The results obtained were added to those available in the geo-chronological literature referred to the Almadén district (Jébrak et al., 2002; Higuera et al., 2005).

All selected samples were analysed by TIMS in the Department of Geochronology (Universidad del País Vasco). The lead isotopic results are presented in ratios 208Pb/206Pb, 207Pb/206Pb and 206Pb/204Pb, conventionally used in the archaeometallurgical field, and graphically are shown in the bivariable plots



Figure 5. Montelirio: detail of the red pigment covering the slates of the chamber (2007 campaign).

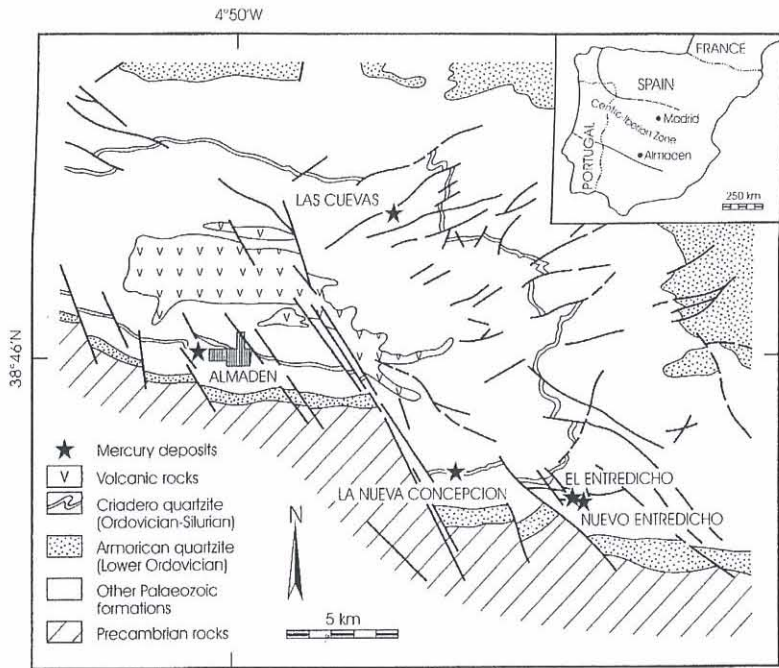


Figure 6. Main deposits of the Almadén district (after Jébrak et al., 2002).

208Pb/206Pb Vs. 207Pb/206Pb and 206Pb/204Pb Vs. 207Pb/206Pb, representing the four lead isotopic ratios defining the isotopic composition of each of the samples (Hunt Ortiz, 2003).

By far, as mentioned, the most important cinnabar mineralization is that of the Almadén district. This mineralization has a long tradition of geological research, which, recently, has also included geo-chronological studies by means of Lead Isotope analysis. The isotopic data available from the Almadén district correspond to the deposits of Nuevo Entredicho (Jébrak et al., 2002) and El Entredicho, Las Cuevas and Almadén (Higuera et al., 2005) (Table 3).

| Deposit | Reference | Pb208/Pb206 | Pb207/Pb206 | Pb206/Pb204 |
|---------------|-----------|-------------|-------------|-------------|
| N. Entredicho | 14 | 2.103530 | 0.85838 | 18.352 |
| N. Entredicho | 15 | 2.090619 | 0.84932 | 18.550 |
| N. Entredicho | 18 | 2.099097 | 0.85652 | 18.386 |
| N. Entredicho | 22 | 2.094118 | 0.85425 | 18.381 |
| N. Entredicho | 23 | 2.090746 | 0.85198 | 18.458 |
| Las Cuevas | LC-10 | 2.133557 | 0.86478 | 18.112 |
| Almadén | ALMD-3 | 2.103250 | 0.84945 | 18.460 |
| Entredicho | ETD-1 | 2.101487 | 0.85324 | 18.357 |
| Entredicho | ETD-2 | 2.109438 | 0.85629 | 18.266 |

Table 3. Lead Isotope results of the Almadén district (after Jébrak et al., 2002; Higuera et al., 2005).

Studying the lead isotopic data available from the four deposits of the Almadén district, represented in the two plots with the isotopic compositions ($^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$) (Fig. 7), the distinct composition of each one of the represented deposits is shown.

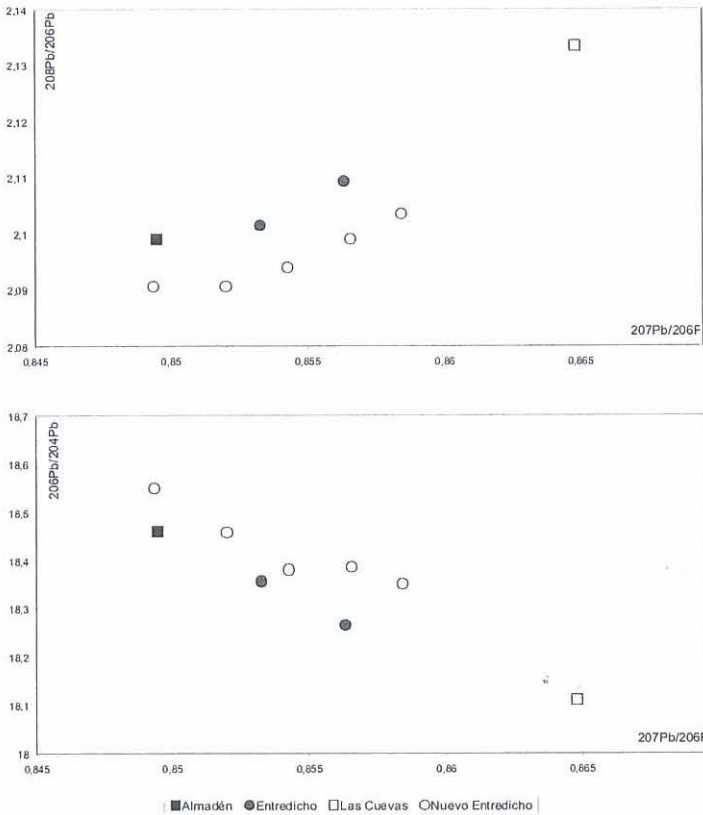


Figure 7. Plots of Lead Isotope results of the Almadén district.

When confronting the isotopic results from the Almadén district with those from the other two mineralised areas analysed, Usagre (Badajoz) and Tímar (Granada) (Table 4), and with those obtained from the archaeological cinnabar samples from Casa Montero, La Pijotilla and Montelirio (Table 5), interesting relations can be established (Fig. 8).

| Mineralization | Reference | Pb208/Pb206 | Pb207/Pb206 | Pb206/Pb204 |
|----------------|-------------------|-------------|-------------|-------------|
| Tímar (GR) | Complejo El Cruce | 2.10801 | 0.85758 | 18.2065 |
| Usagre (BA) | Mina Rampa | 2.13803 | 0.88020 | 17.6452 |
| Usagre (BA) | Pozo Sultana | 2.14354 | 0.88381 | 17.5664 |
| Usagre (BA) | US-1 | 2.11676 | 0.86666 | 17.9823 |

Table 4. Lead Isotope results of Tímar and Usagre mineralizations.

| Archaeological site | Reference | Pb208/Pb206 | Pb207/Pb206 | Pb206/Pb204 |
|---------------------|-------------|-------------|-------------|-------------|
| Casa Montero (M) | 7985.3G-2 | 2.09672 | 0.85284 | 18.3613 |
| La Pijotilla (BA) | T-1,11.157 | 2.07707 | 0.84703 | 18.4791 |
| Montelirio (SE) | DJ07-32.C46 | 2.08951 | 0.84730 | 18.4778 |

Table 5. Lead Isotope results of archaeological cinnabar samples from Casa Montero, La Pijotilla and Montelirio.

With respect to the cinnabar mineralizations, in both plots (Fig. 8), a distinguishable isotopic composition of the Almadén district with the Usagre mineralization can be observed. The composition of the Timar mineralization (as said, considered not to be suitable for pigment procurement), represented with just one sample, is, in any case, also distinguishable from the other two mineralizations considered.

When confronting the isotopic compositions of each one of the archaeological cinnabar samples and with the cinnabar mineral deposits (Fig. 8) it is shown, firstly, that the archaeological samples have a relatively similar composition, closer in the case of the samples from La Pijotilla and Montelirio.

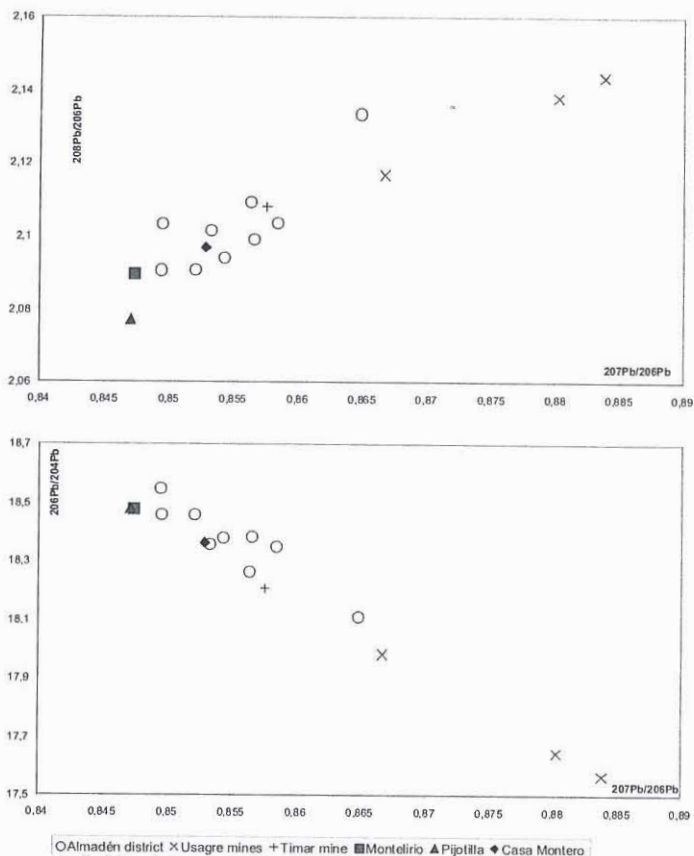


Figure 8. Plots of Lead Isotope results of the Almadén district, Usagre and Timar mineralizations and archaeological cinnabar from Casa Montero, La Pijotilla and Montelirio.

compositions of the archaeological samples are consistent with the Almadén district isotopic composition, but not with those of Usagre and Tímar mineralizations.

5. CONCLUSIONS

Although this research is introductory and more studies and analyses are needed, especially in cinnabar deposits in northern Spain, some relevant conclusions can be made.

In three recently excavated prehistoric archaeological sites the use of cinnabar (HgS) as a pigment in a mining (*Casa Montero*) and funerary (*La Pijotilla* and *Montelirio*) contexts have been analytically documented, reinforcing the importance of the use (and previous mining) of this mineral as a pigment in the Neolithic, since the 6th millennium BC, and Chalcolithic, 3rd millennium BC, periods.

The Lead Isotopic results show that the isotopic composition of the archaeological cinnabar samples from those sites are consistent with the isotopic composition of the mineral deposits of the Almadén district, and are not consistent with the other mineralizations analysed. It can be proposed that the origin of the archaeological cinnabar recovered from Casa Montero (Madrid), La Pijotilla (Badajoz) and Montelirio (Sevilla) was the Almadén district.

Being the Almadén district the origin of the archaeological cinnabar, this pigment may have been distributed to the final deposition places during the Neolithic and Chalcolithic periods through long-distance exchange networks.

This archaeometric approach has demonstrated the applicability of Lead Isotope analysis to provenance studies on cinnabar pigments and has allowed to date the first exploitation of the Almadén district deposits in the 6th millennium BC (5.300 BC), more than 4.500 years earlier than previously stated.

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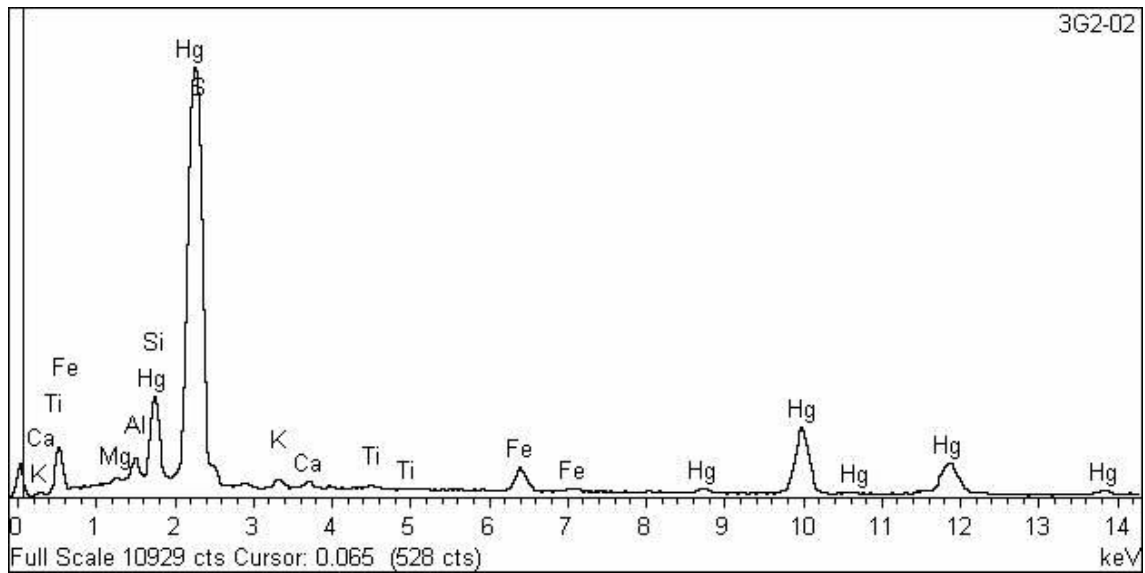
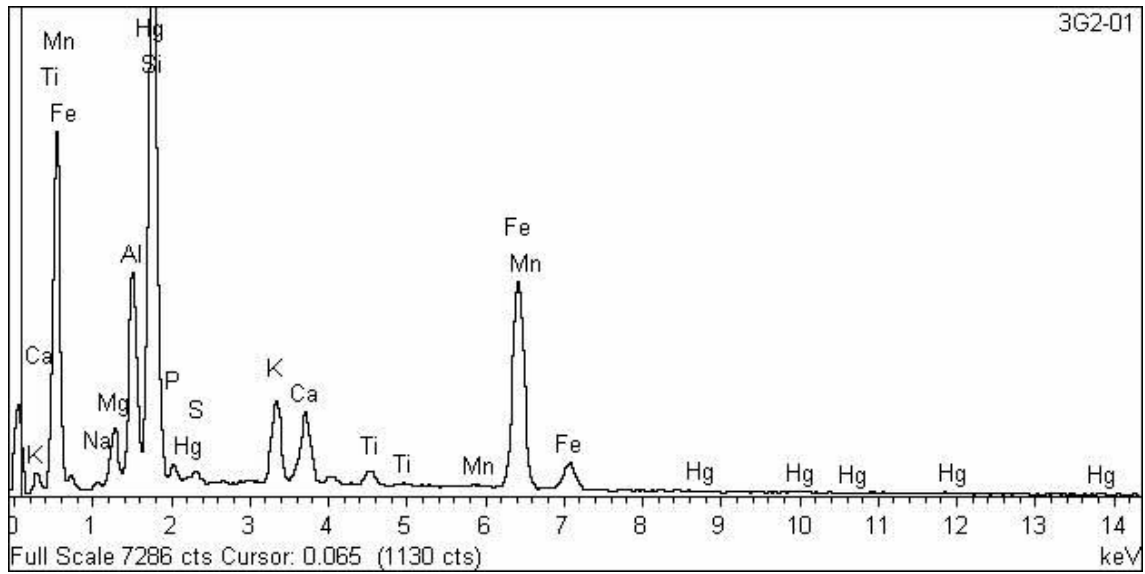


Figure 3 EDXS spectra of the red pigment covering the flint blade from Casa Montero.

