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LETTER

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First lead isotopic data for cinnabar in the Almadén district (Spain): implications for the genesis of the mercury deposits

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Abstract The Almadén district constitutes the largest and probably the most intriguing mercury concentration in the world. Two types of mineralization are recognized: 1) stratabound, of Lower Silurian age, well represented by the large Almadén deposit; and 2) fully discordant mercury deposits of minor importance in terms of size, and exemplified by the deposit of Las Cuevas. The latter ones can be found at different positions along the Almadén stratigraphic column. Both types of deposits are always associated with the so-called *frailesca* rocks (diatremes of alkali basaltic composition). This paper reports the first lead isotope compositions of cinnabar in the district. Whole samples and stepwise leaching cinnabar aliquots display relatively homogeneous isotopic compositions ($^{206}Pb/^{204}Pb$ = 18.112–18.460; $^{207}Pb/^{204}Pb$ = 15.635–15.705; $^{208}Pb/^{204}Pb$ = 38.531–38.826). Taken together with Jébrak et al.'s (2002) pyrite lead isotope results, the new cinnabar isotopic data define a steep array trend on the $^{207}Pb/^{204}Pb$– $^{206}Pb/^{204}Pb$ diagram, indicating a mixed contribution of lead and probably mercury from different sedimentary sources in the Almadén basin. The Almadén Hg deposits are related to a contemporaneous mafic magmatism that might have provided part of the mercury. Hydrothermal leaching of organic matter from sedimentary rocks and formation of Hg organic complexes enhanced metal solubility, promoting transport from and within the volcanic units.

Keywords Mercury · Almadén · Lead isotopes · Upper continental crust · Mantle

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Introduction and geological setting

The Almadén mining district (Fig. 1) constitutes one of the largest mercury geochemical anomalies on the Earth crust. The different mines of the district produced almost one-third of the total historic production of Hg, which is more than any other production by any other mercury-mining district in the world. Mercury ore bodies are hosted by sedimentary and volcanic rocks belonging to a Lower Palaeozoic sequence that unconformably overlies the pre-Ordovician basement of the Central Zone of the Iberian Variscan Chain (Higueras1995; Hernández et al. 1999) (Fig. 1). The volcano–sedimentary rocks, ranging from Ordovician to Upper Devonian in age, comprise several packages of black shale and sandstone/quartzite units and include frequent intercalations of submarine mafic volcanics including the so-called *frailesca* rocks. The latter represent diatremes that locally cut the sedimentary and volcanic units (Saupé1990; Higueras1995). Mafic volcanism in Almadén was by far more important than elsewhere in the region. Magmatic activity was almost continuous and evolved from early basanitic/nephelinitic and alkali–olivine basaltic extrusions, mostly into the Silurian–Devonian part of the section, to late tholeiitic intrusive dolerites, which are scattered throughout the whole sequence (Higueras and Munhá1993; Higueras1995). Basalts and dolerites underwent long-lasting (427–365 Ma; Hall et al. 1997; Higueras et al. 2000a) regional hydrothermal alteration,

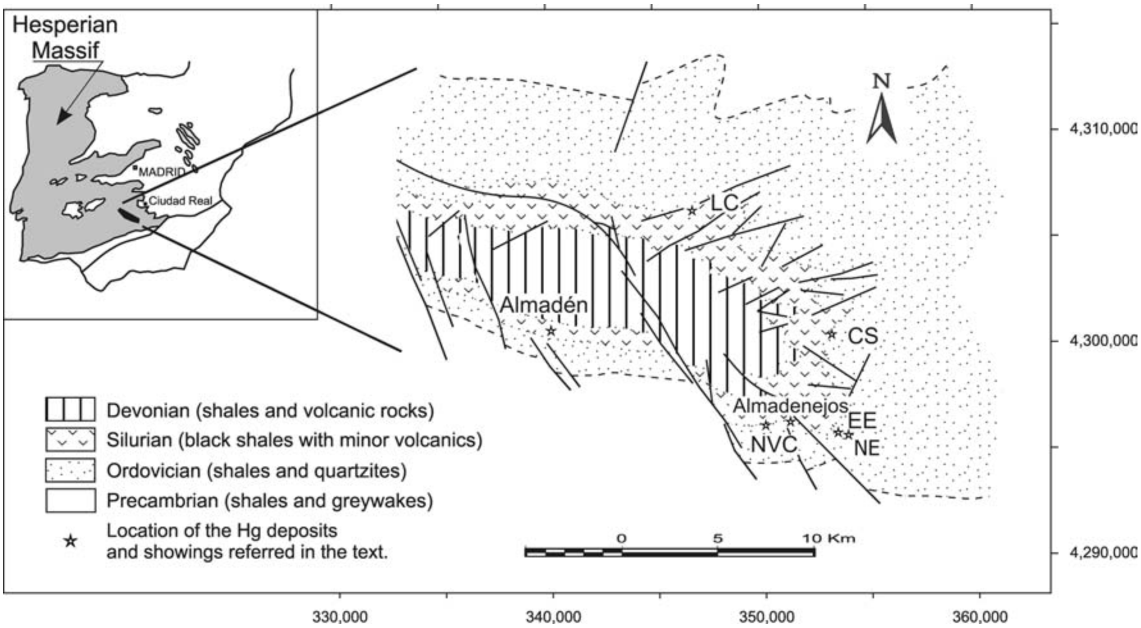


Fig. 1 Regional geological map of the Almadén mercury district, including location of main deposits (LC—Las Cuevas; EE—El Entredicho; NE—Nuevo Entredicho; NVC—La Nueva Concepción)

contemporaneous with water-cooling on the sea floor, being pervasively transformed to albite-chlorite-carbonate-rich spilites (Saupé1990; Higueras1995; Higueras et al. 2000a). Subsequently, the whole sequence was folded, weakly metamorphosed (Higueras et al. 1995), and intruded at 305 Ma (Leutwein et al. 1970) by felsic plutonic rocks during the Variscan deformations.

Two main types of Hg deposits have been described in the district (Hernández et al. 1999): stratabound and fully discordant mineralizations. The former corresponds to the well-known Almadén- type deposits, including the Almadén mine and the "El Entredicho" open pit, where the ore (cinnabar: HgS) is disseminated in lower Silurian quartzites (the so-called *Criadero quartzite*). The second type (fully discordant orebodies) is quite varied in the detail, and comprises small vein-type deposits in quartzitic rocks, as well as larger deposits that can be described as epigenetic replacements in mafic volcanoclastic rocks such as those at the Las Cuevas (Higueras et al. 1999a) and Nuevo Entredicho (Jébrak et al. 2002) mines. Despite the many differences in size and morphology between these two types of deposits, both of them occur in close spatial association with the *frailesca* rocks. The nature of mineralizing brines, and the ultimate origin of mercury, has remained a matter of controversy. Saupé (1990) and Saupé and Arnold (1992) proposed the Ordovician black shales as the source of mercury, whereas Hernandez (1984), Ortega (1986), Borrero and Higueras (1991), Higueras and Monterrubio (1992), Higueras (1995), and Jébrak et al. (2002) suggested a relationship between the source of mercury and the alkali basalt volcanism in the area.

This paper constitutes the first report of lead isotopic compositions of cinnabar from different deposits (Almadén, El Entredicho and Las Cuevas) in the Almadén district. The results, coupled with the previously available data, yield new insights on the origin and genetic processes of the ore formation.

Lead isotope geochemistry

Analytical procedures

Pb isotope analyses of cinnabar and hydrothermally altered volcanic rock samples were carried out at the *Centro de Pesquisas Geocronológicas* of the University of São Paulo (Brazil). Powdered whole-rock volcanic samples were washed by HCl + HNO_3 and then totally dissolved in a mixture (2:1) of HF + HNO_3 using Parr-type bombs. Ore samples were crushed and sieved to the appropriate grain size (60–100 mesh) and cinnabar separates (>99% pure) were obtained by electromagnetic separation, followed by handpicking under a binocular microscope; for each sample, 300 mg cinnabar was ultrasonically washed in triple distilled water and then dissolved using 3 ml of 6N HCl plus 2 ml of HNO_3, on a hot plate, at 100°C, for 24 h. Pb was separated using ion exchange resin (Dowex 1×8 AG) in hydrobromic acid medium, following the procedures described by Babinski et al. (1999). After separation, Pb was loaded onto zone-refined rhenium filaments using the silica gel technique and analysed for isotope ratios on a VG 354 Micromass multicollector thermal ionization mass spectrometer. Special care was taken to avoid the problem produced by the interference of ^{204}Hg on the ^{204}Pb signal during mass spectrometric analysis. To increase Pb purification, ion-exchange separation procedures were repeated twice, and careful filament heating procedures were implemented in order to eliminate any residual Hg (by differential evaporation) before Pb spectrometric analysis. Analyses of the "National Bureau of Standards" SRM 981 standard yield a mass discrimination and fractionation correction of 1.0024 (^{206}Pb/^{204}Pb), 1.0038 (^{207}Pb/^{204}Pb) and 1.0051 (^{208}Pb/^{204}Pb); the combination of these uncertainties and within-run uncertainties are typically 0.15–0.48% for ^{206}Pb/^{204}Pb, 0.13–1.07% for ^{207}Pb/^{204}Pb and 0.10–0.45% for ^{208}Pb/^{204}Pb, all at a 2σ (95%) confidence level. The total Pb blank contribution, <1 ng, is not relevant compared to the amount of lead in the samples.

Two ore samples from the El Entredicho mine were further analysed by stepwise leaching (Gulson1977; Frei and Kamber1995; Frei et al. 1997; Chiaradia and Fontboté2003; Marschik et al. 2003) in order to assess the Pb isotope behaviour within cinnabar grains. Pure cinnabar (1.0 g) was submitted to the analytical procedures indicated in Table 1. Leached solutions were brought to dryness and then subjected to the Pb ion exchange separation procedures described above.

Results and discussion

Jébrak et al. (2002) reported lead isotope data on pyrite, and sulphur isotope data on pyrite and cinnabar from Nuevo Entredicho and El Entredicho deposits (Fig. 1). Lead isotope data on pyrites from Nuevo Entredicho mine are characterised by relatively high ^{207}Pb/^{204}Pb ratios (15.70–15.75; Jébrak et al. 2002), which have been interpreted as lead that was mobilised from the upper continental crust during Silurian–Devonian volcanic activity. Sulphur isotopic values (δ^{34} S = + 1.0^{0} $/_{00}$to + 10.8^{0} $/_{00}$) of cinnabar reported by Jébrak et al. (2002) are similar to those measured by Saupé and Arnold (1992) for the Almadén deposit. The δ^{34} S values correlate with the mercury/sulphur contents of the samples (Jébrak et al. 2002), suggesting that sulphur in the analysed cinnabar represents mixing of a low δ^{34} S magmatic source with a high δ^{34} S sedimentary source (Jébrak et al. 2002).

Table 1 Physical–chemical procedures for cinnabar stepwise leaching

Leached	Chemical treatment	Time (h)	Temperature (°C)
L1	10 ml 1N HNO_3	4	100
L2	10 ml 0.7N HBr	4	100
057L3	10 ml 3N HCl	4	100
L4	10 ml 6N HCl	4	100
L5	10 ml 7N HNO_3	4	100
L6	5 ml 6N HCl + 5 ml 7N HNO_3	4	100

In the present study, lead isotope analyses were performed on five cinnabar samples from El Entredicho (ETD 1, 2A, 2B), Las Cuevas (LC-10), Almadén (ALMD-3) deposits and on five samples of hydrothermally altered metamorphic mafic volcanic rocks. Lead isotope results are summarised in Table 2. The cinnabar Pb isotope values are fairly homogeneous, with a total range of ^{206}Pb/^{204}Pb values from 18.112 to 18.460, ^{207}Pb/^{204}Pb values from 15.635 to 15.705 and ^{208}Pb/^{204}Pb values from 38.531 to 38.826. The lowest and the highest ^{206}Pb/^{204}Pb values are those of the Las Cuevas and Almadén cinnabar samples respectively, with the latter also displaying the highest ^{208}Pb/^{204}Pb ratio (Table 2). These subtle isotopic variations probably reflect the different settings of the Almadén and Las Cuevas deposits (see Higueras et al. 1999b), and are consistent with the complex, long-term evolution of the hydrothermal system responsible for ore deposition in the Almadén mining district (Higueras et al. 2000a). Except for the relatively low ^{206}Pb/^{204}Pb value (18.132) of leachate 4 from El Entredicho cinnabar sample 2A (Table 2; Fig. 3a, b), the Pb released during most of the leaching experiments has homogeneous isotope ratios. Residual aliquots (2A6 and 2B6; Table 2) are just slightly less radiogenic than leachates (2A5; 2B1–2B5;

Table 2 Lead isotopic compositions of Almadén district hydrothermally altered mafic volcanic rocks and cinnabar from El Entredicho (ETD), Las Cuevas (LC) and Almadén (ALMD) deposits (ETD-2A, 2B include results for stepwise leaching analysis—L in material column)

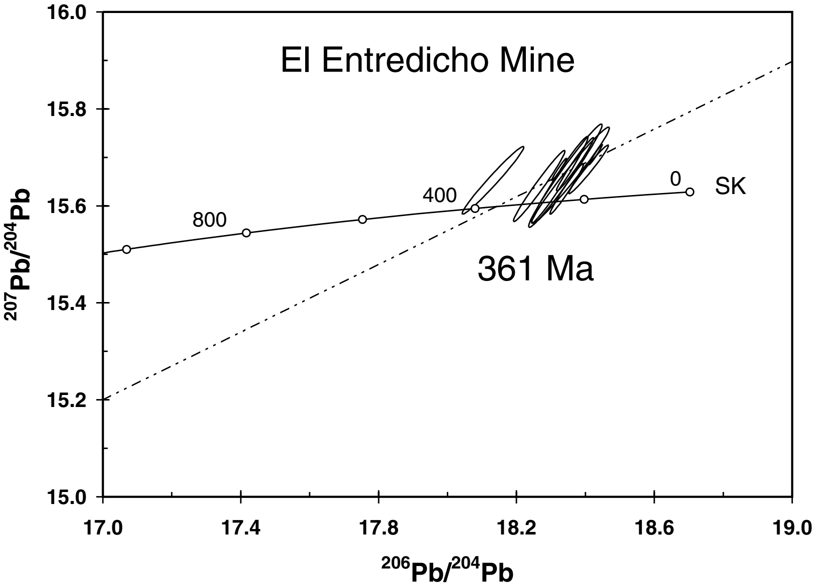
Sample	material	206/204	(2s)	207/204	(2s)	208/204	(2s)
ETD-2	Cinnabar	18.266	0.061	15.641	0.060	38.531	0.062
ETD-2A4	Cinnabar L4	18.132	0.073	15.653	0.057	38.684	0.059
ETD-2A5	Cinnabar L5	18.399	0.006	15.680	0.006	38.667	0.006
ETD-2A6	Cinnabar L6	18.326	0.067	15.654	0.073	38.543	0.069
ETD-2B1	Cinnabar L1	18.429	0.016	15.705	0.017	38.730	0.017
ETD-2B2	Cinnabar L2	18.346	0.040	15.635	0.043	38.555	0.043
ETD-2B3	Cinnabar L3	18.370	0.044	15.686	0.045	38.714	0.046
ETD-2B4	Cinnabar L4	18.409	0.047	15.675	0.041	38.757	0.044
ETD-2B5	Cinnabar L5	18.324	0.018	15.675	0.019	38.654	0.019
ETD-2B6	Cinnabar L6	18.342	0.087	15.662	0.087	38.550	0.088
ETD-1	Cinnabar	18.357	0.092	15.663	0.081	38.577	0.083
LC-10	Cinnabar	18.112	0.096	15.663	0.086	38.643	0.096
ALMD-3	Cinnabar	18.460	0.016	15.681	0.016	38.826	0.017
SVC4/C10	Volcanic	19.364	0.010	15.768	0.011	39.488	0.011
SNC1/C15	Volcanic	19.266	0.012	15.720	0.012	39.419	0.012
LCPL2/17	Volcanic	19.039	0.005	15.794	0.005	39.369	0.005
LCPL4/22	Volcanic	19.440	0.014	15.767	0.014	39.687	0.014
LCPL2/18	Volcanic	19.977	0.009	15.763	0.009	40.236	0.009

Table 2), indicating that very low amounts of radiogenic lead were produced by the in-situ decay of U and Th within cinnabar. Compared to lead isotope results on pyrites from the Nuevo Entredicho deposit (Jébrak et al. 2002), the analysed cinnabar has lower ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb values, but similar ^{208}Pb/^{204}Pb isotopic compositions (see Fig. 3a, b). Different Pb isotope signatures of pyrite and cinnabar support the mineralogical and geochemical studies of Jébrak et al. (2002), which suggested that these ore minerals might have distinct sources. Cinnabar was the only ore mineral formed by the mineralisation processes, whereas pyrite was present in the sedimentary sequence prior to mineralisation and was subsequently recrystallised and/or neoformed during cinnabar formation.

^{207}Pb/^{204}Pb–^{206}Pb/^{204}Pb cinnabar data plot close to the Stacey and Kramers (1975) model Pb-growth curve and have model ages of ~361 Ma (Fig. 2), which is in agreement with Ar/Ar and Rb/Sr geochronological data (Hall et al. 1997; Higueras et al. 2000a), indicating a clustering of ages at 360–365 Ma for the hydrothermal activity associated with the Almadén Hg deposits.

Hydrothermally altered volcanic rocks (^{206}Pb/^{204}Pb = 19.039– 19.977; ^{207}Pb/^{204}Pb = 15.720–15.794; ^{208}Pb/^{204}Pb = 39.369–40.236) (Table 2) are more radiogenic than both cinnabar and pyrite. The ^{207}Pb/^{204}Pb–^{206}Pb/^{204}Pb isotopic compositions of the Almadén hydrothermally altered volcanic rocks (Fig. 3a) (Table 2) are not compatible with a primary magmatic signature of mantle-derived basaltic rocks, i.e. the volcanic rocks have more radiogenic ^{207}Pb/^{204}Pb values than those that could be explained by mixing arrays between putative mantle components (e.g. Zindler and Hart 1986; Hart 1988). Hydrothermal activity can promote variable changes on the isotopic composition of magmatic rocks. Chiaradia and Fontboté (2003) (see also Marschik et al. 2003) have shown that hydrothermal fluids preferentially leach common lead from mafic volcanics (such as those analysed here) and may precipitate lead that is not in isotopic equilibrium with that of the original rock. Results of qualitative age corrections performed on the Almadén volcanic rocks isotope data (using the average U = 1.4 ppm, Th = 4.1 ppm and Pb = 7.0 ppm contents of Almadén alkaline mafic meta-volcanics; Higueras et al. 2000b) are consistent with the findings of Chiaradia and Fontboté (2003). The estimated Pb isotope ratios at 360 Ma (^{206}Pb/^{204}Pb$_{360\mathrm{Ma}}$ = 18.29–18.68; ^{207}Pb/^{204}Pb$_{360\mathrm{Ma}}$ = 15.68–15.75; ^{208}Pb/^{204}Pb$_{360\mathrm{Ma}}$ = 38.65–38.97; excluding the most radiogenic sample LC-PL2/18) considerably overlap those reported by Jébrak et al. (2002) for the Nuevo Entredicho pyrites. This suggests that the Pb isotope compositions of most volcanic rocks were modified during interaction with hydrothermal fluids by the removal of common lead (with lower ^{207}Pb/^{204}Pb values more typical of mantle-derived magmas), and precipitation of non-equilibrium lead (i.e. lead from an external source), in such a way that they became dominated by the same upper continental crust lead reservoir as indicated by Jébrak et al. (2002). Indeed, plotting ore lead data together with age-corrected (360 Ma) compositions of Almadén sedimentary rocks (Nagler1990; Nagler et al. 1993) (Fig. 3a) strongly suggests that lead in both the pyrite ores and in the 'hydrothermal component' of volcanic rocks was mostly derived from post-Tremadocian (upper Llandelian to Fammenian) regional sediments. Cinnabar data plot away from pyrite Pb isotopic values (Fig. 3a, b) (Table 2), implying that cinnabar must have incorporated lead from other sources. Taken together with the data of Jébrak et al. (2002), our lead isotope data suggests mixing between different end member sources of Pb (Fig. 3a). The Pb isotopic data of ore minerals fall along a steep array that trends from the composition of regional, post-Tremadocian sediments, towards a lower ^{207}Pb/^{204}Pb component. This

Fig. 2 ^{207}Pb/^{204}Pb–^{206}Pb/^{204}Pb diagram showing Stacey and Kramers (1975) model age isochron (SK) for El Entredicho cinnabar samples



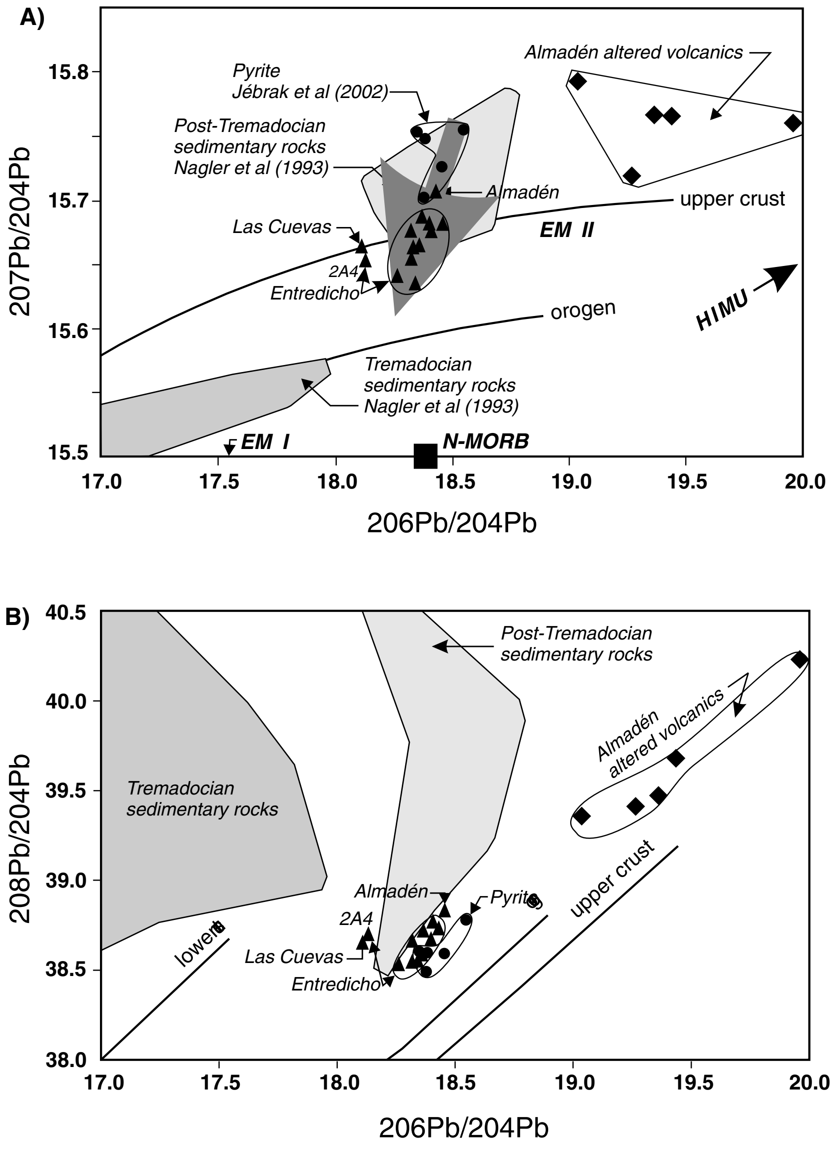


Fig. 3 Diagrams of ^{206}Pb/^{204}Pb versus ^{207}Pb/^{204}Pb (**A**) and ^{206}Pb/^{204}Pb versus ^{208}Pb/^{204}Pb (**B**) for pyrites (*filled circles*; Jébrak et al. 2002), cinnabar (*filled triangles*; Table 2) and hydrothermally altered mafic volcanics (*filled diamonds*; Table 2). Schematic location of the fields for (age corrected —360 Ma) Almadén post-Tremadocian and Tremadocian sediments (Nagler1990; Nagler et al. 1993), N-type MORB, putative mantle components HIMU, EMI, EMII (Zindler and Hart 1986; Hart 1988) and Zartman and Doe (1981) "upper crust", "lower crust" and "orogen" curves are also shown for comparison

could be ascribed either to the primary magmatic lead in the mafic volcanic rocks (as suggested by sulphur isotope data; Jébrak et al. 2002) and/or to lead in Almadén Tremadocian sedimentary rocks (Figs. 3a, b). The age-corrected Pb isotopic compositions of the Tremadocian sedimentary suite plot near to the lower end of the ^{206}Pb/^{204}Pb– ^{207}Pb/^{204}Pb ore array, slightly beneath Zartman and Doe's (1981) orogen growth curve (Fig. 3a). Moreover, there is also a consistent trend between the Tremadocian sedimentary rocks and ore isotopic compositions in the thorogenic diagram (Fig. 3b), where both ores and sedimentary rocks are characterized by thorogenic-rich signatures. Thus, it is likely that hydrothermal fluids leached most of the lead from the sedimentary host rocks. Observed variations in the Almadén ore Pb isotope compositions (Figs. 3a, b) reflect ore forming fluids that have travelled along different aquifers, equilibrated with sedimentary rocks of different isotopic compositions, and finally mixed at the site of ore deposition. Mixing of the different fluids at or near the site of ore deposition is required in order to maintain the Pb isotope distinction between pyrite and cinnabar (e.g. Kesler et al. 1994; Goldhaber et al. 1995), providing further evidence for multiple ore fluid input as previously suggested by Jébrak et al.'s (2002) mineralogical studies. As it should be expected, Pb isotopic compositions of pyrite and cinnabar are intermediate between the two main sedimentary lead sources (Fig. 3a). The ore lead budget was dominated by the post-Tremadocian component but also included subordinate contributions from Tremadocian sediments, which may have been significant in cinnabar from Las Cuevas and El Entredicho deposits (Fig. 3a, b). A rigorous characterisation of the relative contribution (and the nature) of the remaining magmatic (mantle-derived) component(s) in ore lead is precluded by the absence of Pb isotopic data on fresh volcanic rocks from the Almadén district. However, any (minor) magmatic contribution to ore lead should have been swamped by lead from the sedimentary rocks (which are Pb-richer and volumetrically more abundant than magmatic rocks in the Almadén sector), resulting in ore lead isotopic signatures dominated by sediment lead. Therefore, the observed ore lead isotopic compositions do not exclude that the Hg in Almadén deposits could have been partly derived from magmatic sources. This hypothesis has been proposed by several studies (e.g. Higueras and Monterrubio1992; Hernández et al. 1999; Higueras et al. 2000b) that emphasize close spatial and genetic relationships between the mercury deposits and the alkali basalt volcanism in the Almadén basin. A preliminary investigation of Sm/Nd isotopic systematics on seven samples of Almadén district mafic volcanics and ultramafic xenoliths produced ^{143}Nd/^{144}Nd values from 0.512578 to 0.512757, with $\epsilon(\mathrm{Nd})_{360\ Ma}$ ranging from +2.5 to + 5.7. The inferred long-term LREE depleted mantle source(s) contrasts with the strong incompatible element enrichment seen in the Almadén mafic volcanic rocks (Higueras and Munhá1993; Higueras1995; Higueras et al. 2000b), being consistent with geological and geochemical data (Hernández et al. 1999) suggesting that rifting processes and plume-related mantle metasomatic activity may have shortly predated the extensive mafic magmatism in the Almadén syncline during early Palaeozoic times. Ortega and Hernández (1992) have highlighted the compositional similarities between the ultramafic xenoliths at El Entredicho mine and the ultramafic rocks related to the Californian mercury deposits, and Fedorchuk (1974) has noted connections between mercury mineralization and ultramafic rocks elsewhere. Moreover, many studies on mantle rocks (e.g. Clarke et al. 1977; Irving 1980; Dromgoole and Pasteris1987) emphasised close relationships between mantle metasomatism and sulphide mineralization. Thus, it is feasible that mantle metasomatic activity and the low degrees of partial melting of the Almadén magmas (Hernández et al. 1999) could also provide (either direct or indirect) Hg enrichment in the source rocks of Almadén deposits.

Conclusions

Whole samples and stepwise leaching cinnabar aliquots display relatively homogeneous isotopic composition ($^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$ = 18.112– 18.460; $^{207}\mathrm{Pb}/^{204}\mathrm{Pb}$ = 15.635–15.705; $^{208}\mathrm{Pb}/^{204}\mathrm{Pb}$ = 38.531–38.826), being less radiogenic, relative to uranogenic lead, when compared to lead isotope results reported by Jébrak et al. (2002) for pyrites from Nuevo Entredicho deposit. Isotopic analyses of cinnabar from El Entredicho mine are grouped near to the 360 Ma model age isochron (Stacey and Kramers1975), being consistent with both Ar/Ar illite ages recorded at Las Cuevas and El Entredicho mines (363–359 Ma; Hall et al. 1997), and whole-rock Rb/Sr geochronological data (365 ± 17 Ma; Higueras et al. 2000a) reported for hydrothermal activity associated with the Almadén Hg deposits. The bulk of the lead isotope data defines a steep array trend on the $^{207}\mathrm{Pb}/^{204}\mathrm{Pb}$–$^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$ diagram and suggests a mixed contribution of post-Tremadocian (major) and non-radiogenic Tremadocian (minor) sedimentary Pb for the ores of the Almadén Hg deposits. However, in the absence of data on fresh volcanic rocks, other minor contributions to the less radiogenic reservoir (e.g. magmatic) cannot be excluded.

Direct observation (e.g. Prol-Ledesma et al. 2002) and experimental evidence (Varekamp and Buseck1984; Fein and William-Jones 1997) indicates that mercury transport in hydrothermal systems is largely promoted by reducing conditions under the presence of organic complexes. The close association of mercury mineralization and organic matter at Almadén suggests that mercury may have been transported as an organic complex. The Silurian black shales (with $C_{organic}$ up to 7.64 wt%; Saupé1990) were probably the source of hydrothermal organic complexes, which formed by alteration and remobilization of indigenous organic matter. Thus, a contribution of mercury from the black shale (which is likely to have been initially enriched in mercury by degassing of ascending magmas; Rytuba and

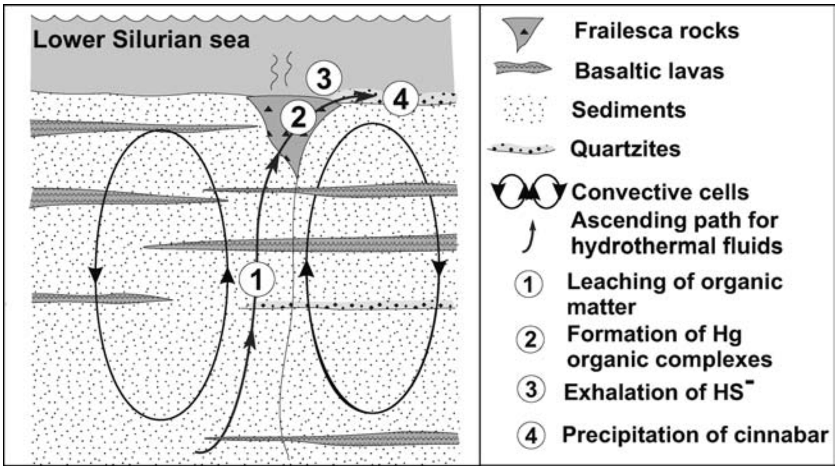


Fig. 4 Schematic "cartoon" illustrating mercury metallogenic processes at Almadén mining district (see text)

Heropoulos 1992; Volkov et al. 2002), may have been significant. However, this does not forcedly imply that these rocks were the exclusive source of mercury. Indeed, the available stable and radiogenic isotope data on hydrothermal paragenesis (Eichmann et al. 1977; Saupé and Arnold 1992; Higueras et al. 2000a, 2000b; Jébrak et al. 2002; this study) indicate that multiple (seawater, sedimentary, magmatic) sources were involved in the hydrothermal processes related to Hg mineralization. Thus, considering all the available geological and geochemical data, we may finally suggest that the huge deposits of Almadén formed due to a combination of different but related processes (Fig. 4): 1) a deep seated source of heat (plus mercury?) associated with the basaltic alkaline volcanism; 2) the development of widespread, convective hydrothermal activity; and 3) the leaching of organic matter, lead and probably mercury from the black shales and formation of Hg organic complexes. The latter would have enhanced metal solubility and promoted transport from and within the volcanic units.

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