Intraplate mafic magmatism, degasification, and deposition of mercury: The giant Almadén mercury deposit (Spain) revisited

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A B S T R A C T

The giant Almadén mercury deposit (Spain) is hosted by the Lower Silurian Criadero Quartzite; in turn this ore-bearing rock unit is cross-cut by the so-called Frailesca unit, a diatreme body of basaltic composition. The geochemical characteristics of the Silurian to Devonian Almadén District volcanic units indicate that these rocks originated from an enriched, evolving mantle source that ultimately yielded basanites–nephelinites to rhyolites, through olivine-basalts, pyroxene-basalts, trachybasalts, trachytes, very scarce rhyolites, and quartz-diorabes. The Silurian intraplate alkaline volcanism developed in submarine conditions which triggered widespread hydrothermal activity resulting in Hg ore formation and pervasive alteration to carbonates. The δ18O, δ13C, and δ34S isotopic signatures for carbonates and pyrite suggest different sources for carbon and sulfur, including magmatic and organic for the former and magmatic and sea water for the latter. The most important and efficient natural source of mercury on Earth is by far the volcanic activity, which liberates mercury via quiescent degassing and catastrophic (Plinian) events when eruptions can overwhelm the atmospheric budget of Hg. Thus, we suggest that CO2 degassing and coeval distillation of mercury from the volcanic rocks fed the huge hydrothermal system that led to massive deposition of mercury at Almadén. Build up of Hg0 in magmatic chambers during waning rifting in the Late Ordovician, followed by renewed volcanism in the Early Silurian, would have resulted in massive degasification of the accumulated mercury. Part of this mercury went into the Criadero Quartzite leading to formation of the huge Almadén deposit and others (e.g., El Entredicho) along the same stratigraphic level. Progressive depletion of the deep seated magmatic Hg stock would have resulted in a drastic reduction in ore deposit size after the Lower Silurian when smaller deposits formed (e.g., Las Cuevas).

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1. Introduction

The Almadén district (Fig. 1) is the largest mercury geochemical cluster on Earth, having produced one third of the total world mercury production. Almadén has been to mercury what the Witwatersrand is to gold, with the difference that contrary to gold, mercury deposits are rare indeed. For example, only two mercury deposits of relative economic importance (Huancavelica, Perú; and Punitaqui, Chile) are present in the Andean chain, which is peculiar for one of the richest metallic provinces of the world. Furthermore, neither Huancavelica nor Punitaqui is ‘one-metal-only’ deposits such as Almadén. The district comprises several deposits; the main ones being Almadén, El Entredicho, Nueva and Vieja Concepción, and Las Cuevas (Fig. 1). Classic works on the geology of these mineral deposits include those of Saupé (1990), Higueras (1995), Hernández et al. (1999), Higueras et al. (1999a), and Palero and Lorenzo (2009), among others. The mining history of the Almadén district (Hernández et al., 1999) began some 2000 years ago, when Romans started to use cinnabar as a vermilion red pigment, but it was not until the Arabs invaded this realm that the locality acquired the etymological roots of its present name: Al-maaden (meaning “the mine”). However, the ‘modern’ history of Almadén and mercury begins in 1555, when the Spaniard Bartolomé de Medina (1497–1550) discovered the use of mercury in silver processing (Higueras et al., 2012). Thus, from the middle of the 16th Century Almadén had a major strategic importance for the colonization of America, becoming one of the largest early mining and metallurgical centers in Europe. Total production during the 16th and 17th Centuries is estimated at 17,250 t of mercury. Peak production was reached in 1941 with 82,000 flasks of mercury, a flask (or frasco as originally named in Spanish) being the standard weight unit for this metal, which is equivalent to 34.5 kg Hg. Mercury was in the past one of the leading export products of Spain, with price peaking at US$ 571/flask in 1965. Concerns about its environmental impact arose from the Minamata incident in Japan, which led to

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a sharp decrease in the world prices to US$ 121/flask in 1976. A recovery in the late 1970s was due to the development of new small batteries for electronic devices. A final blow for Almadén came in the 2000’s when the European Union (EU) banned all the use and sale of mercury, and made illegal the export of raw mercury and mercury compounds. Thus, at present all mercury products are to be regarded as ‘toxic residues’ and dealt with following EU directives. As a result all mining and metallurgical activities ceased in 2003, and the mine and installations have become a theme park for visitors.

Mining has ceased, but many of the uncertainties that surround the genesis of the giant mercury ore deposit of Almadén and others in the district still remain. We here argue that these unique mercury deposits required unusual geologic conditions, involving: 1) the existence of high porosity detrital rocks (the Criadero Quartzite and sister units); 2) coeval explosive volcanism under submarine conditions; and last but not least 3) a persistent enriched mantle source that ultimately led to the formation of the Almadén magmatic rocks. As we argue in this work, Almadén could be one of the few cases in which mafic intra-plate volcanism has yielded economic mineralization of any type. We are not here presenting ‘new’ data on Almadén, but reviewing the geologic, petrologic and geochemical evidence to generate a conceptual model for the full district. This model involves aspects that were either neglected or its full importance inadequately recognized in the past: 1) the role of the intra-plate mafic magmatism as a potential deep source of mercury; 2) the unparalleled efficiency of volcanism for degasification and even formation of Hg deposits; and last but not least 3) the post Lower Silurian persistent hydrothermal activity (up to Devonian time) that led to the formation of minor, however relevant deposits of mercury.

2. Geology and ore deposits

The Almadén district is located within the so-called Central Iberian Zone of the Iberian Variscan Massif (e.g., Dallmeyer and Martínez García, 1990). This realm is characterized by gentle anticlines and synclines, slaty cleavage in the metapelites, and a metamorphism of variable intensity. In the Almadén district the metamorphism reaches low-grade conditions, and has been dated at 335±15 Ma (Rb/Sr) in Ordovician shales (Nägler et al., 1992). The Paleozoic successions in this tectonic domain range in age from Lower Ordovician to Upper Devonian, and comprise five main quartzite units of Arenigian (Armorican Quartzite), Caradocian (Canteras Quartzite), Early Silurian (Criadero Quartzite), Upper Silurian (Las Cuevas Quartzite), and Siegenian (Base Quartzite) ages (Fig. 1). Slates and volcanic rocks complete a sequence of over 4000 m thick. Key for the understanding of the mercury deposits is the anomalous character of the Almadén syncline, which is the only tectonic unit in the Central Iberian Zone hosting significant intercalations of magmatic rocks.

As shown in Fig. 1, the Almadén mercury deposit is hosted by the Early Silurian Criadero Quartzite, which can be divided into four members at the Almadén mine (Palero and Lorenzo, 2009): 1) the Lower Quartzite, hosting the 3–8 m thick San Pedro mineralized bed; 2) a barren 10–15 m detrital sequence. 3) the Upper Quartzite, hosting the 2.5–5 m thick San Francisco and San Nicolás mineralized beds; and 4) a thin horizon of barren slates. The sequence is overlain by volcanic and sedimentary rocks and cross-cut by the Frailesca diatreme (Saupé, 1990) whereas the cinnabar mineralization occurs as impregnations within the high porosity quartzite rocks (Palero and Lorenzo, 2009). The metallic mineral paragenesis is extremely
Almadén geologic history because given that the upper mantle cannot be investigated by direct sampling, it follows that peridotite xenoliths hosted in basaltic rocks provide a powerful insight to define its main petrological features (e.g., Gasperini et al., 2006).

The distribution of the different volcanic rock types in the stratigraphic column shows some remarkable features (Fig. 1). For example, only the Frailesca type rocks crop out in the Ordovician sequence, whereas in the Silurian and Lower Devonian both Frailesca type rocks and basaltic lavas are very common. On the other hand, the Upper Devonian is characterized by the common presence of trachytes, whereas the uppermost Devonian (Upper Frasnian) comprises the full spectra of magmatic rocks, thus revealing a complex magmatic evolution throughout time in the Palaeozoic basin hosting the Almadén district. All sedimentation and mafic magmatism ended in late Devonian time with the onset of the Variscan compressions in central Iberia (e.g., Doblas et al., 1994).

3. Whole-rock geochemistry and magmatic source

Thirty-four samples comprising the different rock types with the least possible alteration were selected for whole-rock analyses (Table 1) (Higueras, 1995). High Ni and Cr contents for basanites, olivine basalts, olivine diabases and pyroxene basalt, as well as their high [mg] (MgO/(MgO+FeO)) numbers suggest that they were derived from primitive, mantle-derived magmas. Most of the magmatic rocks plot in the alkali basalts and basanite/nepheline fields and correspond to an intraplute setting (Fig. 2). The primitive mantle normalized spider diagrams show the major differences found between these rocks.

### Table 1

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[mg] 0.68 0.62 0.66 0.54 0.62 0.57
Alkaline porphyritic rocks (basanites/nephelinites, olivine basalts and trachybasalts) show similar patterns. Major differences between the alkaline and the transition to tholeiitic rocks are related to the presence of a positive Nb anomaly, higher TiO₂ and HFSE contents, and higher LREE/HREE ratios for the alkaline rocks (Fig. 3A). All these geochemical characteristics are indicative of continental intraplate magmas that eventually yielded basalts (s.l.) and olivine diabases of alkaline affinity, and quartz-diabases of transitional to tholeiitic affinity (Higueras, 1995). Other conspicuous feature of the Almadén mafic magmatism is its high content in CO₂. Most of the mafic volcanic rocks display high concentrations of CO₂ ranging from 8 to 15%, while in and around the mercury deposits, these figures can be as high as 20 and 30% in basalts and ultramafic xenoliths respectively (Higueras, 1995). The isotopic composition of these carbonates at about −6‰ (Eichmann et al., 1977; Rytuba et al., 1989) suggests a primary and probably a mantle origin for this component. The recent work of Helo et al. (2011) for Mid Ocean Ridge basalts provides some useful insights into this matter. These authors indicate that given its low solubility, CO₂ is the only magmatic volatile phase that undergoes significant exsolution as the basaltic magmas ascend to the sea floor; there CO₂ may trigger explosive eruptions and widespread pyroclastic deposits. These findings would further explain the explosive nature of volcanism at Almadén as shown by the numerous Frailesca rock units and pyroclastic rocks along the stratigraphic column.

The geochemical and mineralogical data suggest that the Almadén mafic magmas had an upper mantle origin, and were then extruded and/or emplaced in a continental intraplate setting, evolving from alkaline basaltic lavas and olivine diabases to quartz-diabases of transitional tholeiitic affinity. The K/P and Nb/U ratios, coupled to the absence of a negative Nb anomaly, rule out a crustal component in the generation of the Almadén mafic magmas (Cox and Hawkesworth, 1984; Hart et al., 1989; Hoffman et al., 1986). The Zr/Nb (3.45–6.08) and Zr/Y (5.74–11.29) ratios are similar to those of mafic rocks originating from enriched mantle sources. La/Nb ratios lower than 1 for the Almadén mafic rocks suggest that they may have been derived from an asthenospheric source (Fitton et al., 1988). Other trace element ratios, such as Th/La (0.09 to 0.13), Th/Nb (0.06 to 0.08), and Ba/Nb (3.86 to 21.66), are similar to those of enriched mantle sources (Wilson, 1993). Besides, this interpretation is further supported by Hf-isotope signatures suggesting the involvement of enriched mantle components for the origin of the Variscan gabbros from the Central Iberian Zone (Villaseca et al., 2011).

**Fig. 2.** A: Whole rock trace-element plot of Winchester and Floyd (1977) for the classification of volcanic rocks. Boundaries between tholeiitic-transitional-alkaline after Pearce (1982). B: Whole rock trace-element plot of Meschede (1986) for the tectonic setting of volcanic rocks.

**Fig. 3.** A: Primitive mantle normalized spider diagrams for subvolcanic rocks (above), and lavas (below); normalization values after Taylor and McLennan (1985). B: Chondrite normalized spider diagrams for mafic rocks of the Almadén syncline.
from other sectors of the Gondwanan margin show equivalent signatures (Brendan Murphy et al., 2008). Evolution from basanite dominant mafic members in the Silurian to trachybasaltic, trachytic and even rhyolitic magmas in the Upper Devonian is a conspicuous indicator of the geochemical evolution of the Almadén magmas. The LREE/HREE ratios show evidence of a decreasing evolution from the Silurian rocks, through Devonian to the intrusive quartz-diorabes (Fig. 3B). According to White and McKenzie (1995), this pattern is indicative of decrease in the depth of generation, which could be from about 100 km for the Silurian rocks to 60 km for the tholeiitic quartz-diabases. These estimated depths are in agreement with the presence of spinel lherzolites as xenoliths in the Silurian basaltic lavas.

4. Discussion and conclusions

4.1. Hydrothermal processes

Eichmann et al. (1977), and Saupé and Arnold (1992) reported the results of extensive research on the carbon, oxygen and sulfur isotope geochemistry of the country rocks and ores from the Almadén Hg deposits. Eichmann et al. (1977) proposed a primary mantle source for the carbonate constituents in the metavolcanics, whereas Saupé and Arnold (1992) suggested that the Ordovician shales were the main source of carbon and sulfur.

On the basis of the most frequent mineral assemblages in the Almadén volcanic rocks (albite–chlorite–carbonate–quartz ± epidote–pyrite ± titianum–iron oxides), the dominant conditions for the regional alteration can be estimated at 200–300 °C; pH from near to neutrality to alkaline, and fO2 close to the magnetite–pyrite stability boundary (Ellis, 1979; Hemley et al., 1971; Ohmoto and Goldhaber, 1997). These temperatures are in agreement with those measured for equivalent mineral assemblages in presently active geothermal fields, such as those of Reykjanes in Iceland (Yardley, 1989), in the range of 100–300 °C. Besides, the albite–chlorite–carbonate–quartz alteration assemblage is also typical of the Canadian type Archean lode gold deposits (e.g., Dubé and Gosselin, 2007) in both their mafic and ultramafic rock units. Specific thermal data for carbonate alteration (plus quartz, chlorite, albite) in this type of deposits is provided by the comprehensive work of Kishida and Kerrich (1987) on oxygen isotope temperatures for gold mineralization at the Kerr-Addison mine, which indicates that temperatures are consistently in the range of 200–300 °C.

Oxygen isotope compositions reported by Eichmann et al. (1977) range from +12.8‰ to +19.9‰ (versus SMOW) for carbonates in mafic lavas and from +14.0‰ to +18.9‰ for carbonates in mineralized veins and the Frailesca rocks. The study of the δ18O values for hydrothermal fluids in the Almadén case is difficult because the variable carbonate mineralogy (Eichmann et al., 1977), and by the well known susceptibility of carbonates to oxygen isotopic re-equilibration at low temperatures (O’Neill, 1987). Carbonates in active geothermal systems may achieve isotopic equilibrium with fluids down to temperatures as low as 150 °C. Below this temperature the solute species H2CO3 is depleted in 13C as low as 150 °C. Below this temperature the solute species H2CO3 is depleted in 13C as low as 150 °C. Depending on the pertinent carbonate–fluid equilibrium, the δ18O and δ13C values for the Almadén hydrothermal fluids are estimated to have ranged either from +0.6‰ to +7.7‰ if coexisting with calcite/ankerite (Mumin et al., 1996), or from −1.0‰ to +6.0‰ if coexisting with dolomite (Mathews and Katz, 1977). The range of estimated δ18Ofluid values is a characteristic of both modern and fossil submarine hydrothermal systems (Bowers and Taylor, 1985; Munhá et al., 1988), where geothermal waters of marine origin (δ18Oseawater = 0 ± 1‰; Knauth and Lowe, 1978; Shepard, 1986) commonly undergo positive oxygen isotope shifts to higher δ18O values, due to oxygen isotope exchange reactions with 18O-rich host rocks. Close correspondence between estimated and observed δ18Ofluid values strongly supports the hypothesis that hydrothermal activity in the Almadén basin was favored by the interaction of basaltic rocks with seawater.

The carbon isotope compositions of Almadén hydrothermal carbonates (Eichmann et al., 1977) range from −3.6‰ to −9.0‰ (vs. PDB) (−9.0‰ < δ13C(mafic metavolcanics) < −3.6‰; −8.6‰ < δ13C(mineralized veins/fragmental volcanics) < −3.9‰), which is similar to δ13C values measured on aqueous CO2 and calcite from modern, sub-marine hydrothermal systems (e.g., Bowers and Taylor, 1985; Stakes and O’Neill, 1982). Exclusive derivation of CO2 from organic matter in the Ordovician black shales (δ13Corganic ~ −30‰; Eichmann et al., 1977) as suggested by Saupé and Arnold (1992) seems unlikely. Low temperature maturation of organic matter yields δ13Corg ≈ −21‰ (Eichmann et al., 1977) which is much lighter than that inferred for equilibrium with hydrothermal carbonates. On the other hand, the hydrolysis of reduced carbon would imply δ13Corg ≈ −26‰, requiring almost invariant highly reduced conditions of carbonate deposition (e.g., Ohmoto, 1972). As discussed above, this is quite unlikely for the Almadén hydrothermal system. At a specified (T, pH, fO2) range of conditions, the observed δ13C values, together with the lack of correlation between δ18O and δ13C, favor multiple carbon sources for the hydrothermal carbonates in the Almadén deposits. Considering the CO2-rich mantle source, the undersaturated character of the magmas that gave rise to the Almadén mafic volcanics (Higueros, 1995), and the analogy with modern, submarine hydrothermal systems, it seems hard to escape the conciliatory hypothesis that, besides seawater (δ18Cwater ~ −2‰; Saltzman, 2002) both mantle (δ13Cmanto ~ −5‰; e.g., Deines, 2002) and organic sedimentary carbon sources (δ13Corganic ~ −30‰; Eichmann et al., 1977) were contributors to the hydrothermal carbonates in Almadén.

Besides, this is the least one might expect in a submarine hydrothermal system triggered by volcanic activity, and the same can be said for sulfur on what multiple sources is concerned. The sulfur isotopic compositions reported by Ryutuba et al. (1989), Saupé and Arnold (1992), Jébrak et al. (1997) and Higueros et al. (1999b) for the Almadén ore minerals and country rocks show a wide range of variation. Cinnabar displays a wide overall range of δ34S values, from −1.6‰ to +9.0‰. Particularly significant to the discussion is the positive correlation between sulfur contents and δ34S values (+1.0‰ ± +6.8‰), reported by Saupé and Arnold (1992) for the Almadén volcanic rocks. Although the linear δ34S–S relationship suggests an external source of constant composition (and, consequently, constant physical/chemical conditions of basalt/seawater interaction), probably this was not the case. Within the hydrothermal system, water–rock interactions should have proceeded under a wide range of temperatures, pH, fO2, and water/rock ratios, reflecting the variable lithological permeabilities at different sites of the fluid convection cells. Thus, a much wider range of S contents (e.g., Higueros et al., 1999b; Saupé, 1990), δ34S enrichment/depletion and variable δ34S–S trends (e.g., Saupé and Arnold, 1992) must be expected for the Almadén basaltic. At the conditions specified above for Hg sulfide deposition, δ34S must have been close to δ34Sfluid (Ohmoto, 1972), thus, the range of cinnabar δ34S values could also reflect variable source compositions.

Leaching of sulfur from the volcanic rocks by geothermal waters provides an indirect mechanism for incorporating variable proportions of magmatic and seawater sulfur into the mineralizing fluids, contributing (along with fractionation and physical chemical varia-tions) to the variable isotopic compositions of Hg sulfides. Sulfate can be converted to sulfide by organic matter-mediated sulfate reduc-tion either by bacterial activity (bacterial sulfate reduction, Jannasch, 1989) or by an abiological reaction (thermochemoical sulfate reduction; Machel, 2001). Given that seawater sulfur is isotopically heavier (δ34S ~ +27‰; Kampfschite and Straus, 2004) than that of the country rocks, then reduction of seawater sulfate to sulfide would thus produce a heavier δ34S signature in the ore (e.g., Bickle et al.,
The leaching of sulfur from the volcanic rocks by geothermal waters provides an indirect mechanism for incorporating variable proportions of magmatic and seawater sulfur into the mineralizing fluids, explaining the variable isotopic compositions of Hg sulfides. On the other hand, lead isotopic data for cinnabar (Higueras et al., 2005) show that the bulk of the lead data defines a steep array trend on the $^{207}$Pb/$^{206}$Pb-$^{208}$Pb/$^{204}$Pb diagram and suggests a significant contribution of sedimentary Pb for the ores of the Almadén Hg deposits, although other minor contributions from a less radiogenic reservoir (e.g. magmatic) cannot be ruled out. A multiple source of lead is common in seafloor hydrothermal systems, including both magmatic and sedimentary reservoirs. The latter may be the major source of Pb, representing a large detrital input of upper crustal material (Halbach et al., 1997). In this respect, a major issue regarding mercury in hydrothermal systems is that its behavior departs from that of other metals to form sulfides (such as Pb). As indicated in the comprehensive work of Varekamp and Buseck (1984a), different from other metals (M) that will form M in the comprehensive work of Varekamp and Buseck (1984a), heavy sulfur (Hg) is the dominant species. Furthermore, as discussed by these authors, the contributions of Hg–Cl, Hg–S, Hg–CO$_2$, and Hg–OH are apparently unimportant for Hg transport in dilute systems. Hg deposition may then occur in response to mixing with either oxidizing or acidic water, turning Hg$^{2+}$ into Hg$_2^{2+}$:

\[ \text{HgS}_2^{2-} \rightarrow \text{Hg}_2\text{O}_2^{2+} + 1/2\text{S}_2\text{O}_3^{2-}. \]

Subsequent cinnabar deposition may follow if sulfur is available in the system, although this mineral is unstable in a vapor-dominated system (Varekamp and Buseck, 1984a):

\[ \text{HgS}_2^{2-} \rightarrow \text{Hg}_{2}\text{O}_2^{2+} + 1/2\text{S}_2\text{O}_3^{2-}. \]

Thus, given the highly volatile character of mercury, the path to ore deposition can be entirely different to that of lead (or even sulfur), and as such, it would be unwise to mix up the sources of one and the other. In very simple terms: the fact that two objects are found side by side does not necessarily imply that they ‘came together’ to that particular site. This is particularly relevant to the case of open hydrothermal systems, in which the solutions can be leaching metals from entirely different sources such as older sedimentary rocks and the volcanic units that actually triggered the system.

4.2. On the origin of mercury

Derivation of the Almadén Hg from sediments (e.g., Ordovician black shales) has been advocated by Saupé (1990) and Saupé and Arnold (1992), who also refuted a mantle origin. Saupé in his classic work of 1990 stated that a positive mercury anomaly of the mantle below Almadén left unanswered a double question: why should such an anomaly be so limited in space (Almadén) and in time (Silurian)? We can answer both questions but let us first take into account a piece of the puzzle that perhaps has not received all the required attention: the clasts and xenoliths of spinel lherzolites that account a piece of the puzzle that perhaps has not received all the attention. The clasts and xenoliths of spinel lherzolites that account a piece of the puzzle that perhaps has not received all the attention. The fact that two objects are found side by side does not necessarily imply that they ‘came together’ to that particular site. This is particularly relevant to the case of open hydrothermal systems, in which the solutions can be leaching metals from entirely different sources such as older sedimentary rocks and the volcanic units that actually triggered the system.

4.2.1. On the origin of mercury

The huge, unique, Almadén Hg deposits should have required exceptional conditions for their genesis. We suggest that such a world-class geochemical anomaly should ultimately reflect the characteristics of the mantle source for the alkaline basaltic magmas; indeed, mantle metasomatic activity and the low degrees of partial melting inherent to the genesis of the Almadén magmatic rocks (Dromgoole and Pasteris, 2001). The dating results from ilite separates suggest that the later stages of Hg mineralization or remobilization occurred about 360 Ma, which is about 20 Ma younger than any mercury-hosting rocks in the district and coincides with the onset of regional deformation during the Hercynian orogeny. Cr-mica ages are variable and range from 365 Ma to 427 Ma.

However, the huge, unique, Almadén Hg deposits should have required exceptional conditions for their genesis. We suggest that such a world-class geochemical anomaly should ultimately reflect the characteristics of the mantle source for the alkaline basaltic magmas; indeed, mantle metasomatic activity and the low degrees of partial melting inherent to the genesis of the Almadén magmatic rocks (Dromgoole and Pasteris, 2001). The dating results from ilite separates suggest that the later stages of Hg mineralization or remobilization occurred about 360 Ma, which is about 20 Ma younger than any mercury-hosting rocks in the district and coincides with the onset of regional deformation during the Hercynian orogeny. Cr-mica ages are variable and range from 365 Ma to 427 Ma.
just about 1 Ma. This is a short time span that nevertheless resulted in the extrusion of about 2–3 millions of cubic kilometers of volcanic rocks (Renne et al., 1995). Thus, that volcanic activity (in general), and mantle derived intraplate volcanism (specifically) can transport and release mercury in great amounts should therefore be beyond dispute. For example during the first two weeks of September 1980 the daily Hg output from the Mt St Helens system (during a non-eruptive phase) ranged from 200 to 1700 kg (Varekamp and Buseck, 1981).

On the other hand, neither alkaline intraplate nor tholeiitic ocean ridge basalts appear to be particularly enriched in mercury, showing a range of 2 to 9 ppb Hg (Corderre and Steinhorsson, 1977). These authors argue that mercury is either distilled into a gas phase such as CO₂ before or during the eruption, or the magmas never contained mercury in excess of the observed low concentrations because the source area is continuously degassing, thus becoming Hg-depleted. This assertion is somehow supported by the fact that magmatic vapors are usually enriched in mercury, and a common component of these vapors is magmatic CO₂ (Varekamp and Buseck, 1984b). In this regard, mercury is not only efficiently transported and discharged to the atmosphere by the volcanism, because degasification can also lead to the formation of economic mineralization. This is the case of Mount Amiata in Italy, where Plio-Pleistocene volcanism is related to a deep seated magmatic source with crustal and mantle components (Wilson, 1989). There the CO₂-rich geothermal activity triggered by this volcanism resulted in Hg-(Sb–Au) ore deposit formation (e.g., Morteani et al., 2011).

At this point we should take into consideration the widespread, pervasive alteration to carbonates in the Almadén rocks. As explained above, the volcanic rocks have CO₂ concentrations ranging from 0.93 to 6.01% (Table 1), whereas in and around the mercury deposits these figures may be as high as 20–30% (Higuera, 1995), thus suggesting massive magma degasification. In this regard, as indicated by Varekamp and Buseck (1984b), key for the fate of mercury in a hydro-thermal system are the conditions at which a CO₂-rich phase is formed, that is, confining pressure, CO₂ content of the fluid, and pH of the fluid. If any of these parameters is modified, distillation of mercury from the hot solution will follow. In this respect, an excellent example of the relationships and co-evolution of the CO₂ phase and mercury may be provided by cinnabar grains visible in the center of the lava flows that filled vesicles in the volcanic rocks of Almadén (Saupé, 1990).

Based on the data from Varekamp and Buseck (1981) for mercury output from quiescent degassing of the St Helens system, we may assume that the generation of 1000 kg Hg/day would be a conservative figure for a scenario such as Almadén where volcanism was explosive. Given that Almadén had reserves in excess of 250,000 t Hg, it follows that it would have taken some 700 years to in
timate fi
gure 4) and only 200 kg Hg/day went to the sea (Fig. 4), which is a key for our model for as early discussed for other metals, magmas that lose their volatile species will not form large ore deposits (or any at all) (e.g., Oyarzun et al., 2001; Oyarzun et al., 2003; Pasteris, 1996). As tectonic conditions evolved in the south (Azor et al., 1994) magmatism restarted but this time with a much larger Hg volatile fraction, a prerequisite for large deposition of mercury in the Lower Silurian. We propose that the deep seated magmas did not become Hg-depleted in a single (catastrophic) episode, but nonetheless no large deposits formed after the Lower Silurian (Fig. 1). On one hand a large stock of Hg was lost in this episode, on the other, persistent volcanism must have led to a more continuous Hg degasification thus no large stocks were ever built up again after the Lower Silurian. This model somehow resembles that of Sibson (1990) for fluid pressure and earthquake ruptures along a fault zone (fluid-activated valve), only that in this case we are dealing with deep seated magmas that progressively accumulated Hg\textsubscript{0} instead of fluids. However the outcome is relatively similar, with sudden outbursts that in the Almadén case resulted in magma degasification and ore deposit formation. That is what we call our “decreasing sawtooth wave model” (Fig. 4).

There is an additional matter to deal with, and that concerns the huge amount of mercury deposited at the Almadén deposit compared to other mineralized sites in the world. In this regard, most mercury deposits are very small and belong to the hot-spring type (Rytuba, 2004a,b), which from a geologic and thermodynamic perspective are shallow seated “open systems” (and as such, ready to outgas mercury), with many examples from Chile (e.g., Andacollo: Cu–Au–Hg) (Oyarzun et al., 1996), Spain (e.g., Azogue Valley: Hg) (Viladevall et al., 1999), California (USA) (e.g., McLaughlin: Au–Hg) (Smith et al., 2008), and elsewhere. In this respect, we should bear in mind these two facts: 1. Almadén is a “submarine” deposit, and as such it formed near to the sea floor under strong hydrostatic pressure conditions from Ordovician time onwards, but it is only at the base of the Silurian that huge Hg deposition took place (Fig. 1). No mercury deposits formed in the Ordovician, and those above the Lower Silurian are either small or insignificant (Fig. 1). So what makes the Lower Silurian so different? This period can be regarded as a transitional time span, between the scattered barren explosive volcanism (Ordovician) and the lava eruptions that began soon after the Criadero Quartzite was deposited. Thus, a connection between mercury deposition and volcanism goes beyond the mere existence of the latter, and poses additional doubts on a mercury source located at the Ordovician black shales. After all, if the ‘recycling’ case (Saupé, 1990) is based on mercury mobilization via explosive volcanic activity from sedimentary beds, why then no deposits formed precisely at the Ordovician where the putative Hg source was located? On the other hand, if we take into account that the Almadén syncline magmatism evolved in time, there is no reason to preclude a similar (although reversed) path for the metallogenic activity. In fact, as stated above, after Almadén and coeval deposits were formed, mercury deposition became less important in size (Fig. 1).

We suggest that the passage from minor and scattered emplacements of Fraillesca rocks in the Ordovician to a more consolidated volcanism (explosive and lava type) in the Silurian as the deep seated magma source evolved, marks a ‘before and after’ scenario in the Almadén syncline. Furthermore, we propose that this change may relate to major tectonic changes in the Iberian Massif, resulting in the isolation of the southern neighboring tectonic terrane (Ossa Morena), an event also marked by an abrupt change in magmatism during the late Ordovician – early Silurian transition (Simancas et al., 2004). In this regard, a profound change in the rheological conditions at the crustal and/or continental lithospheric scale was bound to have far reaching consequences on the magmatic activity. Some clues may be provided by the southern Ossa Morena, where after a stage of lower Paleozoic rifting, subduction took place in Silurian times resulting in crustal thickening, gravitational instability, and extensional shearing (Azor et al., 1994). This may have resulted further north in increasingly overpressurized magmas and therefore in the accumulation of volatile species in the deep magma chambers (Fig. 4). This is a key for our model for as early discussed for other metals, magmas that lose their volatile species will not form large ore deposits (or any at all) (e.g., Oyarzun et al., 2001; Oyarzun et al., 2003; Pasteris, 1996). As tectonic conditions evolved in the south (Azor et al., 1994) magmatism restarted but this time with a much larger Hg volatile fraction, a prerequisite for large deposition of mercury in the Lower Silurian. We propose that the deep seated magmas did not become Hg-depleted in a single (catastrophic) episode, but nonetheless no large deposits formed after the Lower Silurian (Fig. 1). On one hand a large stock of Hg was lost in this episode, on the other, persistent volcanism must have led to a more continuous Hg degasification thus no large stocks were ever built up again after the Lower Silurian. This model somehow resembles that of Sibson (1990) for fluid pressure and earthquake ruptures along a fault zone (fluid-activated valve), only that in this case we are dealing with deep seated magmas that progressively accumulated Hg\textsubscript{0} instead of fluids. However the outcome is relatively similar, with sudden outbursts that in the Almadén case resulted in magma degasification and ore deposit formation. That is what we call our “decreasing sawtooth wave model” (Fig. 4).

Thus, a volcanogenic origin for mercury, followed by distillation from a hot solution and transport, is not only plausible from the geothermal point of view (in a CO₂-rich system such as that of Almadén) but additionally answers the question of why mercury was deposited in the Criadero Quartzite. This unit hosts an early (pre-cinnabar) framboidal pyrite and as shown by Corderre and Steinhorsson (1977), pyrite-rich horizons in geothermal fields may act as geochemical traps for mercury inducing precipitation.

4.3. The search for a conceptual model

At a larger scale a final question concerns the role of the Almadén Fraillesca unit. As shown above, Fraillesca type rocks were emplaced
provided by the water column. 2. The Criadero Quartzite (CQ) must have had some degree of consolidation before mercury was introduced (otherwise mercury would have escaped), but it is unlikely that the unit had undergone complete diagenesis, because in that case most of its effective porosity would have been lost. In this respect, we suggest that mercury was introduced into the CQ unit during or soon after deposition of the upper (hanging wall) shales (US) (Fig. 1, 4). Even if part of the mercury was lost to sea from the Frailesca diatreme, the pressure exerted by the water column during or soon after deposition of the upper (hanging wall) shales would have played a role impeding a large release of mercury from the Frailesca diatreme, and the retention process is enhanced by the hydrostatic pressure exerted by the water column.

**Fig. 4.** The build up and degasification, followed by the precipitation of Hg conceptual model for Almadén and younger deposits. The model also depicts the emplacement and degasification of the Almadén Frailesca diatreme at the sea bottom, and the decrease in magmatic Hg build up from Silurian to Devonian time.

4.4. Final remarks

As shown by Müller (2002), alkaline rocks have gained much attention among petrologists worldwide, mainly due to their distinct geochemistry, and many geoscientists still consider them as petrological curiosities with an obscure petrogenesis. We could not agree more, their petrogenesis is complex, and the genesis of the mafic volcanic complexes found in intraplate settings is bound to generate bitter discussions. This is quite understandable because the mantle isotopic signatures, degrees of partial melting, participation of the lithosphere (versus) asthenosphere, and mantle metasomatism are not simple matters, therefore they are subjected to multiple interpretations. However, if for Almadén we stick to the basics, a direct relationship to the mantle (whatever the components are involved at the source) is beyond dispute. On the other hand, ore deposition in relation to the alkaline magmatism does not result in a very long list of names, at least regarding Cu–Au mineral deposits (Sillitoe, 2002). The Sillitoe’s list is even narrower if only volcanic complexes are taken into account. Furthermore, if we only consider the “mantle-derived” “mafic intraplate volcanism”, either at oceanic (e.g., Canary Islands, Galapagos, Easter Island, and Hawaii) or continental settings (French Massif Central, Höggar and Tihesti in northern Africa) not a single significant ore deposit (of any kind) is found. That is what makes Almadén so unique, and why we should keep studying this formidable district. In this regard we would like to see our contribution as ‘one step further’ (hopefully more than ‘a single one’) towards a better understanding of this Nature’s wonder. Finally, whatever the shortcomings that (most probably) our model may have, we believe that it nonetheless certainly explains: 1) why such a huge amount of mercury was deposited in the Lower Silurian; and 2) why the younger Hg deposits were progressively smaller as volcanism (and therefore degasification) became more important.

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