THE ALMADEN MERCURY METALLOGENIC CLUSTER (CIUDAD REAL, SPAIN): ALKALINE MAGMATISM LEADING TO MINERALIZATION PROCESSES AT AN INTRAPlate TECTONIC SETTING

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Abstract: The Silurian to Devonian Almadén mercury deposits are directly or indirectly related to mafic rocks. The geochemical characteristics of these rocks suggest mantle-derived intraplate magmas, that yielded basalts (s.l.) and olivine diabases of alkaline affinity, and quartz-diabases of transitional to tholeiitic affinity. These rocks may have been generated from a volatile- and incompatible element-rich asthenospheric source of EM-I type. O, C, and S isotopic data provide new insights into the genesis of the Almadén mineralization. Close correspondence between estimated and observed δ18Ofluid values suggest that hydrothermal activity in the Almadén basin was favoured by interaction of basaltic rocks with seawater. The observed δ18O values (-3.6‰ to -9.0‰), together with the lack of correlation between δ18O and δ13C, favour multiple carbon sources for the hydrothermal carbonates associated with the Almadén deposits, i.e., besides seawater, both mantle and organic sedimentary carbon sources were contributors to these carbonates. This is supported by sulphur isotopic data (-1.6‰ to +9.0‰; cinnabar), which may reflect variable source compositions. Leaching of spilitic sulphur by geothermal waters provides an indirect mechanism for incorporating variable proportions of magmatic and seawater sulphur into the mineralizing fluids, explaining the different isotopic compositions of Hg sulphides. Ar-Ar, Rb/Sr, and 87Sr/86Sr data suggest that hydrothermal activity in the Almadén basin was long-lasting, spanning both the Silurian and Devonian. The huge, unique Almadén Hg deposits would have required exceptional conditions for their genesis. It is proposed that a world-class geochemical anomaly such as Almadén should ultimately reflect the characteristics of the mantle source for the alkali basaltic magmas; indeed, mantle metasomatic activity and the initial low degrees of partial melting inherent to the genesis of the Almadén mafic magmas could have converged to provide an efficient mechanism for Hg pre-enrichment of the basaltic rocks.

Key words: Mercury, Almadén, alkaline mafic magmas, O-C-S isotopic data, hydrothermal circulation.

Resumen: Los yacimientos mercurio de Almadén (Silúrico-Devónico) se encuentran directa o indirectamente relacionados con rocas maficas. Las características geoquímicas de estas rocas sugieren que se derivaron a partir de magmas de intraplaca de origen mantelicio, que dieron lugar a basalts (s.l.) y basaltos olivínicos de afinidad alcalina, y cuarzodiabases de afinidad transicional a toleítica. Estas rocas pueden haber sido generadas a partir de una fuente astenosférica rica en volátiles y elementos incompatibles, de tipo EM-I. Datos isotópicos para O, C, y S permiten desarrollar una nueva visión acerca del origen de las mineralizaciones de Almadén. La estrecha correspondencia entre los valores observados y estimados de δ18Ofluid sugieren que la actividad hidrotermal en la cuenca de Almadén se vio favorecida por la interacción entre el agua de mar y los basaltos. Los valores observados de δ18O (-3.6‰ a -9.0‰) observados en carbonatos, y la ausencia de correlación entre δ18O y δ13C, sugieren diversas fuentes para el origen de éstos, i.e., aparte del agua de mar, tanto carbono mantelicio como orgánico habrían contribuido a la formación de los carbonatos. Esta idea se sustenta además en los datos de isotópicos de azufre (-1.6‰ a +9.0‰; cinnabario), los cuales parecen indicar diferentes fuentes. En este sentido la lixiviación de azufre por las soluciones hidrotermales, a partir de los basaltos espilitizados, puede constituir un mecanismo adecuado para la incorporación de proporciones variables entre azufre magmático y de agua de mar. Los gigantescos y singulares depósitos de mercurio de Almadén deben de haber requerido condiciones excepcionales para su génesis. Sugerimos que una anomalía geoquímica cortical tan excepcional como lo es el conjunto de Almadén, debería de alguna manera reflejar las características de la fuente mantelicia que dio origen al magmatismo alcalino. Es posible que la combinación de una actividad metasomática mantelica, y los bajos valores de fusión parcial requeridos para la génesis de los magmas máficos de Almadén, podrían haber constituido un eficiente mecanismo para una preconcentración del mercurio en las rocas basálticas.
The Almadén mercury mining district is located in the Almadén syncline, in central Spain (Fig. 1). The district is the largest geochemical anomaly on the Earth’s crust, having produced one third of the total world mercury consumption, thus we may regard Almadén as a huge Hg metallogenic cluster. In a way, Almadén has been to mercury what the Witwatersrand to gold. The district comprises several deposits; the main ones being Almadén, El Entredicho, Nueva and Vieja Concepción, and Las Cuevas. Classic works on the geology of these mineral deposits include those of Croizant (1965), Lauret (1974), Saupé (1967, 1973, 1990, among others), Arnold et al. (1971), Saupé and Arnold (1992), Saupé et al. (1977), Eichmann et al. (1977), and Hernández (1984). More recent, and updated contributions to the understanding of Almadén include those from Higueras (1995), Hernández et al. (1999), and Higueras et al. (1999a, b).

According to recent works on the geology of the district (Hernández et al., 1999; Higueras et al., 1999a), the mercury mineralization can be grouped into two main types: stratabound (type 1) and discordant (type 2). Type 1 deposits are the largest and include those of Almadén and El Entredicho (Fig. 1). This type of mineralization is hosted by the Criadero quartzite, i.e., it is restricted to a single stratigraphic horizon at the base of the Silurian. Type 2 deposits are fully discordant and hosted or related to diatremes (the so-called frailesca rocks of basaltic composition), although the mineralization can be hosted by other lithologies, including sedimentary and volcanic (lava) rocks. An example of the latter is provided by the Las Cuevas deposit, which is hosted by an extremely folded and sheared rock sequence of late Silurian age comprising a unit of frailesca, lavas, shales and quartzites. Its two main orebodies are 25-30 m wide, have an irregular shape, extend vertically for about 100-150 m and are hosted by frailesca rocks and metasedimentary units (metapelites and quartzites) (Higueras et al., 1999a). Type 2 deposits have in common their wide dispersion through the stratigraphic column (Fig. 1). They can be found in the Lower Silurian (Nueva Concepción), Upper Silurian (Las Cuevas), Lower Devonian (El Burcio) or Upper Devonian (Guadalperal and Corchuelo).

The whole sequence of Silurian to Devonian magmatic rocks is pervasively altered. This regional alteration (Hernández et al., 1999; Higueras et al., 1999a) consists of the following mineral assemblages: 1) quartz-chlorite-albite-carbonates (±ankerite, ±siderite, ±magnesite, ±calcite) (mainly found in the alkaline basic rocks), and 2) chlorite ± prehnite ± pumpellyite ± epidote ± actinolite (restricted to the isolated bodies of tholeiitic diabases). The regional alteration is locally overprinted by a muscovite/illite-kaolinite-pyrophyllite.
The magmatic rocks include subvolcanic bodies, found shown in figure 1, the stratabound mercury mineralization quartzite hosted by different lithologies at several horizons throughout the sedimentary sequence, and volcaniclastic radocian playing frequent magmatic units, which quartzite horizons of Arenigian cline sequence is anomalous within the regional setting, described in the previous sections. However, before this study was initiated we were also aware that unless these rocks were geochemically studied, no indication about their petrogenesis was going to be obtained. Thus, taking all this into account, what follows in the next sections is to be regarded for what it is, i.e., an attempt to characterize the magmatism of Almadén, in order to make suggestions and proposals regarding its source. We believe that this is a key step towards a better understanding of the Almadén mercury mineralization.

Petrographic classification

Magnetic rocks described in the Almadén syncline (Higueras, 1995) include the following petrographic types:

1) Pyroclastic rocks of variable composition. The most abundant are lapilli tuffs of basaltic composition (the so-called frailesca rocks), composed of completely altered olivine-basalt clasts, and sedimentary clasts. Outcrops of these rocks are subcircular, showing a cross-cutting relationships with the host rocks (diatreme-type morphologies).

2) Porphyric rocks, ranging in composition from basanites/nephelinites to rhyolites, through olivine-basalts, pyroxenitic-basalts (pyroxene cumulates), trachybasalts, trachytes, and very scarce rhyolites. Basanites/nephelinites and olivine basalts are the main petrographic types, while the intermediate and felsic members are less abundant. Minerals in these rocks comprise olivine phenocrysts; diopside pyroxene as phenocrysts and matrix; analcite as phenocrysts and matrix; plagioclase (microlites in the less differentiated, phenocrysts and matrix in intermediate and felsic varieties); biotite phenocrystals in intermediate rocks; and K-feldspar and quartz in phenocrystals and matrix of the felsic rocks. Late magmatic kaersutitic amphibole and Ti-rich biotite are also conspicuous in the mafic types. Textures are porphyric, with a crystalline matrix, and often vesicular. These rocks outcrop as horizons of variable thickness interbedded with the detrital sequences, and in places can be recognised as sub-concordant sills.

The Central Iberian Zone is affected by a Hercynian tectono-metamorphic event, which resulted in the present structural shaping of the zone. Typical features are gentle anticlines and synclines, an incipient schistosity, and a metamorphism of variable intensity. In the Almadén district the metamorphism reaches low-grade conditions (Saupé et al., 1977; Higueras et al., 1995), and has been dated at 335 ± 15 Ma (Rb-Sr dating) in Ordovician shales (Nágl et al., 1999).

Geologic setting

The Almadén syncline is located in the southern part of the Central Iberian Zone (Iberian Hercynian Massif; Dullmeyer and Martínez García, 1990). The Central Iberian Zone is characterized by Paleozoic synclines overlying pre-Ordovician antinclus, and one of these structures is the Almadén syncline (Fig. 1a). The Paleozoic successions in the Central Iberian Zone range in age from Lower Ordovician (Tremadocian) to Upper Devonian (Frasnian-Fametian) (Fig. 1b). At a regional scale, they comprise four main quartzite horizons of Arenigian (Armorican quartzite), Carboniferous (Canarios quartzite), Early Silurian (Criadero quartzite) and Siemenian (Base quartzite) age. These horizons represent late episodes of regressive megasequences deposited under epicontinental marine conditions. The total thickness of the sequence is over 4000 m. The Almadén syncline sequence is anomalous within the regional setting, displaying frequent magmatic units, which are not present in other areas of Paleozoic age in the Central Iberian Zone. The magmatic rocks include subvolcanic bodies, found throughout the sedimentary sequence, and volcaniclastic and porphyric rocks (lava) of variable composition. As shown in figure 1, the stratabound mercury mineralization (type 1) is restricted to the Early Silurian quartzite (Criadero quartzite), while the discordant mineralization (type 2) is hosted by different lithologies at several horizons throughout the Silurian-Devonian stratigraphic column (Hernández et al., 1999).
3) **Subvolcanic mafic rocks** with doleritic textures, which allows their classification as diabases. Major minerals are augitic pyroxene and calcic plagioclase. Minor minerals are olivine as small phenocrysts in olivine diabases, and alkaline feldspar and quartz (interstitial or in graphic intergrowths) in quartz-diabases. Olivine diabases are fine grained and outcrop as sills of metric scale thickness, almost indistinguishable from the porphyric varieties, while the quartz-diabases are medium grained and outcrop as small stocks, and sills up to 5 m thick.

4) **Ultramafic rocks**, present as clasts in the pyroclastic rocks, and as xenoliths in the least differentiated basalts. They are almost completely altered, although it is possible to identify that they are formed by 50-80% olivine, pyroxene, and minor spinel, usually unaltered, which allows their classification as spinel lherzolites.

The distribution of the different volcanic rock types in the stratigraphic record shows some remarkable features. In the Ordovician sequence, only the *frailesca* rocks are present. *Frailesca* diatremes, and basanite/nephelinite horizons, often with ultramafic xenoliths (El Entredicho and Vieja Concepción mines) are common in the *Criadero* quartzite. In the Silurian and lower Devonian sequences, *frailesca* and basaltic horizons are very common, with occasional intermediate

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**Figure 2.** Pyroxene composition of the mafic rocks from the Almadén syncline. (a) Wo-En-Fe diagram (after Morimoto et al., 1988). (b) Le Bas (1962) diagram. (c) Leterrier et al. (1982) diagram. Black squares = quartz-diabases; white squares = olivine diabases; circles = basalts (s.l.).
composition members. In the Upper Devonian, intermediate rocks (trachytes) are quite common, together with pyroclastic and basaltic horizons. In the highest part of the Paleozoic succession (Upper Volcanic Group, Upper Frasnian) in the syncline, the full spectra of volcanic rocks (pyroclasts and olivine basalts to rhyolites) appear within the stratigraphic record.

**Metallogeny**

Chemical analyses of the primary metal minerals in the mafic rocks have been performed on two CAMEBAX SX-50 electron microprobes, from the Universities of Granada and Oviedo (Spain), with working conditions of 20 KV and 20 nA, and 15 KV and 15 nA, respectively. Analysed samples were the least altered from each type, in order to avoid interference by possible secondary processes.

Pyroxene composition is considered to be an excellent petrologic indicator, even in paleovolian rocks affected by secondary processes (Nisbet and Pearce, 1977; Leterrier et al., 1982, among others). The studied minerals demonstrated the differences between the magmatic affinity of the subvolcanic quartz-diabases and the rest of the mafic rocks. In the former the pyroxene is of augitic composition, whereas in the latter (basalts and olivine diabases) it is of diopsidic composition (Fig. 2a). These observations, together with the plot of pyroxene composition in the Le Bas (1962) diagram, confirm the tholeiitic affinity of the quartz-diabase (basalts and olivine diabases) it is of diopsidic magmatic affinity of the subvolcanic quartz-diabases (Fig. 2b) and Leterrier et al. (1982) (Fig. 2c) diagrams, confirm the tholeiitic affinity of the quartz-diabases, and the alkali affinity of the rest (Higuera and Morata, 1994). Plagioclase composition is variable from AAlfa.60 in basaltic rocks to AAlfa.65 in the dolerite varieties, showing limited albitionization processes in samples with prehnite-pumpellyite associations (Higuera et al., 1995). Spinel is present as the only unaltered mineral in ultramafic xenoliths in basalts, and as small phenocrysts in basalites. The composition of spinels in the xenoliths is quite variable, with #Mg (=100Mg/Mg+Fe2+ in atomic proportions) ranging from 50 to 75, and #Cr (=100Cr/Cr+Al in atomic proportions) ranging from 20 to 70 (Fig 3a). These values match those of spinels from harzburgitic xenoliths in alkaline basalts. Also, their high Mg and Cr contents are characteristic of spinels from kimberlitic xenoliths (Haggerty, 1991). Spinel phenocrysts in the basanites (Fig. 3b) display compositions typical of alkaline basalts (Leblanc, 1992). Late magmatic amphiboles and biotites are Ti-rich varieties, with high Mg/Fe ratios (Higuera, 1995). According to the Leake (1978) classification, the amphibole is of kaersutite composition. The biotite composition is close to the boundary annite-phlogopite (Deer et al., 1992).

**Whole-rock geochemistry**

Thirty four samples represent different of the same lithologies, with the least possible alteration, were selected for whole-rock analyses. The analyses were performed in the analytical services laboratory of the University of Granada (Spain) and XRAL-Assay Laboratory of Ontario (Canada), using different analytical methods for major, trace and rare earth elements (Higuera et al., 1995).

Table I shows the mean values for the different rock types. High Ni and Cr contents for basalites, olivine basalts, olivine diabases and pyroxene basalt, as well as their high [mg] values (=MgO/MgO+FeO) suggest a

**Table I** - Average chemical analysis of selected basic rocks present in the Almadén syncline.
mantle-derived origin for the magmas, and indicate that they were derived from primitive liquids. Due to the mobility of some chemical elements during secondary alteration processes, only relatively immobile elements were used for the geochemical characterisation of the magmatism. The plot of data for the porphyric and subvolcanic rocks onto the Nb/Y vs Zr/TiO$_2$ diagram (Fig. 4) gives their classification in terms of their geochemical affinity (Winchester and Floyd, 1977). Most of the magmatic rocks plot in the alkaline basalts and basanite/nephelinites fields. Only the quartz-diabases display values of the Nb/Y ratio that allow their classification as transitional to tholeiitic basalts. The primitive mantle normalized spiderdiagrams (Fig. 5) shows the major differences found between these rocks. Alkaline porphyric rocks (basanites/nephelinites, olivine basalts and trachybasalts) show similar patterns. Also, these porphyric rocks have strong similarities to the olivine diabase pattern. Major differences between the alkaline and the transition to tholeiitic rocks are related to the presence of a positive Nb anomaly, higher TiO$_2$ and HFSE contents, and higher LREE/HREE ratios for the alkaline rocks. The absence of a negative Nb anomaly in the quartz-diabases is also remarkable. The use of the Meschede (1986) 2Nb : Zr/4 : Y diagram (Fig. 6) shows that the alkaline rocks plot in the field proposed for the within-plate alkaline basalts. 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.

**Petrogenetic model for the Almadén magmas: suggestions and proposals**

**Origin of magmas**

The data indicates that the Almadén mafic magmas may have had a mantle origin, and were then extruded and/or emplaced in a continental intraplate setting, and evolved from alkaline basaltic lavas and olivine diabases to quartz-diabases of transitional tholeiitic affinity. The K/P and Nb/U ratios (Hoffman et al., 1986; Hart et al., 1989), coupled with the absence of a negative Nb anomaly (Cox and Hawkesworth, 1984), rule out a crustal component in the generation of the Almadén mafic magmas. 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 an enriched mantle source (EM-I type) (Wilson, 1993). On the other hand, the Zr/Sc ratio in primary magmas can be considered as an indicator of the relative homogeneity of the magma source areas. The plot on figure 7 shows that this ratio has a wide dispersion. This fact can be interpreted as indicative of a very heterogeneous source. However, as we have previously shown, the mantle source for this magmatism could be rather homogeneous. Thus, an alternative explanation for the Zr/Sc ratio is that the generation of these rocks from an homogeneous source but under very different partial melting ratios.

Another interesting feature of the Almadén mafic magmatism is its high content in CO$_2$. Most of the mafic volcanic rocks display CO$_2$ values ranging from 8 to 15%, while in and around the mercury deposits, these values may be as high as 20 and 30% in basalts and ultramafic xenoliths respectively (Higueras, 1995). Although the values could be of secondary origin, the high explosivity of the volcanism recorded by the frailesca abundance throughout the stratigraphic record, together with the isotopic composition of this carbonates (around -6‰; Eichmann et al., 1977; Rytuba et al., 1988), suggest a primary and possibly a mantle origin for this component.

**Evolution of magmas**

Petrographic 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 chondrite normalized REE signature of the mafic rocks in relation to their age is shown on figure 8. The LREE/HREE ratios (indicated by the discrete slope of the diagrams) display clear evidence of a decreasing evolution from the Silurian samples, through Devonian, to the intrusive quartz-diabases. 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 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. This fact, together with the homogeneous asthenos-
pheric origin of the magmas, as indicated by the elemental ratios, suggests an upwelling of the source, rather than a source area migrating through the upper mantle.

The high incompatible element composition of the magmas displays temporal variations that can be regarded as an indicator of the evolution of the magmas. In the following figures, the temporal evolution of this signature is analysed. A question to consider is the probable effect of fractional crystallisation that could have affected the magmas after their formation. In order to avoid this factor, and to characterize primary variations in the magmas, the original analytical values have been recalculated considering the necessary removed olivine to pass from an initial common value of 350 ppm Ni to the observed value (Allegre and Minster, 1978). Only these recalculated values have been used in the following plots.

On figure 9, elements with slightly different degrees of incompatibility, $P_2O_5$ vs $TiO_2$ and $Nb$ vs $Y$ are plotted. A progressive decrease in the slope of the correlation lines, and an increase in the intercept at the origin (probably indicative of a progressive depletion in the source of the less incompatible elements) is evident from this plot. Similar incompatible elements ($La$ vs $Ce$, $Th$ and $Nb$) are plotted on figure 10, showing relatively good correlation, and with an intercept at the origin equal to 0. Absolute values are progressively lower, but the ratios, expressed in the plots are constant and can be extrapolated to the source ratios. Figure 11 plots $La$ vs ratios of $La$/incompatible elements ($TiO_2$, $P_2O_5$, $Zr$, $Nd$, $Sm$, $Tb$, $Eu$ and $Y$), and shows correlation lines with intercept at the origin proportional to the respective ratios in the mantle source (Minster and Allegre, 1978).

Assuming a chondrite normalized value of 2 times for the HREE (Y and Yb), which is common in most mantle types (McDonough and Frey, 1989), it is possible to calculate the values for the other elements in the mantle source for the Almadén magmatism. Table II and figure 12 display the resulting values. These are characteristic of an enriched mantle and are in agreement with: 1) the source established previously using trace element ratios; and 2) the presence of spinel lherzolites as xenoliths in the basaltic lavas. From the cal-
culated mantle composition, and following formulations of Minster and Allègre (1978), it is also possible to estimate the partial melting degrees needed to generate each of the magmas in the district. The results suggest that the Silurian mafic rocks represent liquids formed by the lowest partial melting rates (1.6-6%), while increasingly higher values can be estimated for the Devonian mafic rocks (4-9%), and the subvolcanic tholeiites (10-17.5%).

All these characteristics are consistent with a plume-related origin for the Almadén magmas at a continental intraplate tectonic setting (Higueras et al., 1999b). Based on the geological record of the zone, we envisage an aborted rift type environment in which, after an initial pulse of extension and magmatism (Lower Silurian), the area underwent a progressive decrease in tectonic activity while volcanism persisted well into the Devonian.

The origin of mercury: bases for the understanding of Almadén

Eichmann et al. (1977), and Saupé and Arnold (1992) reported the results of extensive research on the carbon, oxygen and sulphur isotope geochemistry of the country rocks and ores at the Almadén Hg deposits. Eichman 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 sulphur in the Hg mineralization.

Meaningful interpretation of stable isotope data requires information on the physical and chemical conditions (temperature, $f_{O_2}$, pH) of mineral deposition (Ohmoto, 1972). On the basis of the most frequent spilitic mineral assemblages in the Almadén metavolcanics (albite-chlorite-carbonate-quartz±epidote-pyrite±titanium-iron oxides), the dominant conditions for the regional alteration can be estimated at 200-300°C, pH near neutrality, and $f_{O_2}$ close to the magnetite-pyrite stability boundary (Hemley, 1959; Hemley et al., 1971; Ellis, 1979; Ohmoto and Rye, 1979). Extensive development of pyrophyllite-kaolinite alteration assemblages associated with type 2 mineralization (Higueras, 1995; Higueras et al., 1995b; Higueras et al., 1999a), as well as the presence of graphite intimately mixed with the sulphides, suggest Hg sulphide deposition at 250-300°C from felsic and relatively reduced brines (Burt, 1976; Rose and Burt, 1979; Hemley et al., 1980).

Oxygen isotope compositions reported by Eichmann et al. (1977) range from +12.8‰ to +19.9‰ (vs SMOW) for carbonates in mafic metavolcanics (spilites) and from +14.0‰ to +18.9‰ for carbonates in mineralized veins and frailesca rocks. The calculation of $\delta^{18}O$ values for hydrothermal fluids in the Almadén case is complicated due to variable carbonate mineralogy (Eichmann et al., 1977), and by the well known susceptibility of carbonates to oxygen isotope re-equilibration at low temperatures (O’Neil, 1987). Carbonates in active geothermal systems may achieve isotopic equilibrium with fluids down to temperatures as low as 150°C (Clayton et al., 1968). Thus we can use this value as a reference in our $\delta^{18}O_{fluid}$ estimates. Depending on the pertinent carbonate-fluid equilibrium, the $\delta^{18}O$ values for the Almadén hydrothermal fluids are estimated to have ranged either from +0.6‰ to +7.7‰ if co-existing with calcite/ankerite (O’Neil et al., 1969; Mu-

![Figure 8](image_url)  
**Figure 8.** Chondrite normalized spiderdiagrams for basic rocks of the Almadén syncline. Symbols, as in figure 7.

![Figure 9](image_url)  
**Figure 9.** Diagrams $P_2O_5$ vs $TiO_2$ (a) and $Nb$ vs $Y$ (b) for the basic rocks of the Almadén syncline. Lines: correlation fits for the indicated sample groups, with equation expressed in the diagram. Symbols, as in figure 7.
min et al., 1996), or from -1.0%o to +6.0%o if coexisting with dolomite (Mathews and Katz, 1977). The range of estimated $\delta^{18}O_{\text{fluid}}$ values are characteristic of both modern and fossil submarine hydrothermal systems (Alt et al., 1985; Bowers and Taylor, 1985; Munhá et al., 1986), where geothermal waters of marine origin ($\delta^{18}O_{\text{seawater}} = 0 \pm 1%o$; Kaunath and Lowe, 1978; Shepard, 1986) commonly undergo positive oxygen isotope shifts to higher $\delta^{18}O$ values, due to oxygen isotope exchange reactions with $^{18}O$-rich host rocks. Close correspondence between estimated and observed $\delta^{18}O_{\text{fluid}}$ values strongly corroborates the hypothesis that hydrothermal activity in the Almadén basin was favoured by interaction of basaltic rocks with seawater.

The carbon isotope compositions of Almadén hydrothermal carbonates (Eichmann et al., 1977) range from -3.6%o to -9.0%o (vs PDB) (-9.0%o < $\delta^{13}C_{\text{mafic mafic}}$ < -3.6%o; -8.6%o < $\delta^{13}C_{\text{mineralized veins/fragmental volcanics}}$ < -3.9%o), which are similar to $\delta^{13}C$ values measured on aqueous CO2 and calcite from modern, submarine hydrothermal systems (e.g., Stakes and O’Neil, 1982; Alt et al., 1985; Bowers and Taylor, 1985). Exclusive derivation of CO2 from organic matter in the Ordovician black shales ($\delta^{13}C_{\text{organic}}$ » -30%o; Eichmann et al., 1977), as suggested by Saupé and Arnold (1992), seems unlikely. Low temperature maturation of organic matter yields $\delta^{13}C_{\text{CO2}} < \delta^{13}C_{\text{organic}}$ (e.g., Arnett and Matzgkeit, 1986), which is much lighter than that inferred for equilibrium with hydrothermal carbonates. On the other hand, hydrolysis of reduced carbon would imply $\delta^{13}C_{\text{HCO3}}$ - $\delta^{13}C_{\text{C}}$ > +21%o - +26%o, requiring almost invariant highly reduced conditions of carbonate deposition (e.g., Ohimoto, 1972). As discussed above, this is quite unlikely for the Almadén hydrothermal system. At a specified (T, pH, fO2) range of conditions, the observed $\delta^{13}C$ values, together with the lack of correlation between $\delta^{18}O$ and $\delta^{13}C$ (see Rye and Williams, 1981), favour 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 Al­maden mafic volcanics (Higueras, 1995), and the analogy with modern, submarine hydrothermal systems, it seems hard to escape the conciliatory hypothesis that, besides seawater, both mantle and organic sedimentary carbon sources were contributors to the hydrothermal carbonates.

The sulphur isotopic compositions reported by Ry­tuba et al. (1989), Saupé and Arnold (1992), Jébrak et al. (1997) and Higueras et al. (1999c) for Almadén ore minerals and country rocks show a very wide range of variation, which is indicative of different mineralization events, processes and sulphur sources. Cinnabar also displays a wide overall range of S₃⁴S values, from -1.6% to +9.0%. Particularly significant to the discussion is the positive correlation between sulphur contents and S₃⁴S values (+1.0% - +6.8%), reported by Saupé and Arnold (1992) for the Almadén spilites. Although the linear S₃⁴S - S relationship suggests an external source of constant composition (and, consequently, constant physical/chemical conditions of basal/ 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., Saupé, 1990; Higueras et al., 1999c), S₃⁴S enrichment/depletion and variable S₃⁴S-S trends (e.g., Saupé and Arnold, 1992) must be expected for the Almadén spilites. At the conditions specified above for Hg sulphide deposition, S₃⁴Sₛₛ must have been close to S₃⁴Sₙₑᵤₙₙ (Ohmoto, 1972). Thus, the range of cinnabar S₃⁴S values could also reflect variable source compositions. Leaching of spilitic sulphur by geothermal waters provides an indirect mechanism for incorporating variable proportions of magmatic and seawater sulphur into the mineralizing fluids, explaining the variable isotopic compositions of Hg sulphides.

Derivation of the Almadén Hg from sediments (Or­­do­vician black shales) has been advocated by Saupé (1990) and Saupé and Arnold (1992), who also refuted a mantle origin. However, except for a possible contribution to the carbon budget, the isotope data reviewed here do not require any significant involvement of the sedimentary reservoir in the hydrothermal processes related to Hg mineralization. Recent work indicates a close relationship between the mercury deposits and the lower Palaeozoic alkali basaltic volcanism in the Al­madén basin (Hernández et al., 1999; Higueras et al., 1999b). Interestingly, this relationship also appears to hold true for other areas outside Almadén, in the Pa­­la­eeozoic of Iberia (Maucher, 1976). Clearly, 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 alkali basaltic magmas; indeed, mantle metasomatic activity and the lowdegrees of partial melting inherent to the genesis of the Almadén mafic magmas (Higueras and Munhá, 1993) could have converged to provide an efficient mechanism for Hg pre-enrichment in the basaltic rocks (Dromgoole and Pasteris, 1987).

Several mercury deposits around the world have shown some unexplained connections with mantle metasomatism (Fedorchuk, 1974). The Almadén synclinorium and its eastern extension is the only place where ultramafic rocks (xenoliths) have been observed. This, together with geological and geochemical data for the Almadén volcanic rocks, suggest rifting processes and mantle plume activity during the early Palaeozoic (Higueras and Munhá, 1993; Higueras et al., 1999b). The composition of the Cr-spinel (picotite) in the ultramafic xenoliths of the El Entredicho mine is similar to that of spinel in the ultrama­fic rocks related to the Californian mercury deposits (Ortega and Hernández, 1992). Russian authors have also noted the possible connection of mercury with several types of ultramafic rocks (Fedorchuk, 1974). However, the mercury content of the mantle and the likelihood of magmatic concentration remain poorly known. The geochemical behaviour of Hg is rather si­milar to that of Sb and Ag, and could be introduced into the surface by the degassing of an intrusion (Verekamp and Buseck, 1984; Rytuba and Heropoulos, 1992). Alternately, a spatial association might not be directly significant for an origin of the mercury, but could indicate favourable geographical conditions for the transport of Hg, such as the abundance of CO₂ and/or CH₄, produced either during the volcanic process or during retrograde alteration (Morency et al., 1986).

\[\begin{array}{c|c|c}
\text{ppm} & \text{C.N.} \\
\hline
Y & 4.00 & 2 \\
Yb & 0.42 & 2 \\
Th & 0.22 & 5.14 \\
Nb & 2.92 & 7.30 \\
La & 2.16 & 6.86 \\
Ce & 4.32 & 5.31 \\
Nd & 2.70 & 4.52 \\
Sm & 0.67 & 3.50 \\
Eu & 0.23 & 3.18 \\
Ti & 4760 & 7.28 \\
P & 236 & 5.13 \\
Gd & 0.65 & 2.51 \\
Tb & 0.12 & 2.42 \\
\end{array}\]

\(\text{Table II.- Absolute (ppm) and chondrite normalized (C.N.) values for the calculated upper mantle source for the Almadén magmatism.}\)
Age constraints for hydrothermal processes

Hall et al. (1997) reported a detailed 40Ar/39Ar study on illite and Cr-rich micas that are intimately associated with mercury mineralization in both Devonian and Silurian host rocks. Illite Ar retention ages cluster around 360 Ma, whereas Cr-mica ages are much more variable and range from 365 to 427 Ma (Fig. 13). This age range was interpreted by Hall et al. (1997) as reflecting two episodes of Hg mineralization; the oldest Cr-mica ages would correspond to Lower Silurian, strataform-type cinnabar deposits, whereas the younger ages would represent partial/total argon loss contemporaneous with a later episode of mineralization, attributed by Hall et al. (1997) to Hg remobilization caused by the Variscan metamorphism. Although this is a valuable working hypothesis, the available geological data make it worthwhile to evaluate alternative explanations as discussed below.

Rb and Sr were analysed from drill core samples using standard cation exchange chromatography techniques (Janousek et al., 1995). The Rb analyses were performed on a VG MM30 thermal ionization mass spectrometer, whereas Sr was analysed on a VG 54E thermal ionisation mass spectrometer (Table III). The 87Sr/86Sr ratio was corrected for mass fractionation using 86Sr/88Sr = 0.1194. Repeat analysis of NBS 987 Sr standard gave 87Sr/86Sr = 0.71023 ± 4 (2 s.d.). Following Hall et al. (1997), we have selected our samples as to be representative of the two main styles of hydrothermal alteration associated with Hg mineralization at Almadén. Three samples (S.CS-1/C-10, S.VC-1/C-21, S.VC-4/C-10) correspond to variably carbonated mafic metavolcanics, whereas the fourth sample (S.NC-1/C-15) displays the argillite type (pyrophyllite ± kaolinite ± illite) alteration, as described by Higueras et al. (1999a).

Measured isotope (87Sr/86Sr) ratios in the carbonatized rocks range from 0.706993 to 0.708262 and show no positive correlation with the 87Rb/86Sr values; higher 87Sr/86Sr values (0.707641 - 0.708262) correspond to the two samples with lower 87Rb/86Sr ratios (0.017 - 0.052), suggesting that the carbonatization involved leaching of Rb and/or introduction of Sr from an external source. Given the low overall 87Rb/86Sr ratios of 0.017 to 0.152 (Table III), it is evident that the radiogenic Sr component in the carbonatized samples cannot have been derived by in situ decay of 87Rb, to develop the lowest observed 87Sr/86Sr value from a typical alkalibasalt protolith (with 87Sr/86Sr ini = 0.704, 87Rb/86Sr = 0.152). If that were the case, an elapsed time in excess of 1.3 Ga would be required. Thus, the observed large radiogenic Sr component must have been inherited from a high 87Sr/86Sr reservoir elsewhere; a logical source for radiogenic Sr is the hydrothermal fluid itself.

Because of their dominant hydrothermal mineral assemblages and very low 87Rb/86Sr ratios, samples S.CS-1/C-10 and S.VC-4/C-10 should have actual 87Sr/86Sr values almost identical to those acquired at the time of hydrothermal carbonate-rich alteration; therefore, we have used the average of their 87Sr/86Sr values (0.707951 ± 0.000311), together with the isotopic data for sample S.NC-1/C-15 (Fig. 14), to obtain a model age for the mineralizing event (e.g. Ruiz et al., 1984). The age obtained (365 ± 17 Ma) confirms the clustering of Ar retention ages at 360 - 365 Ma determined by Hall et al. (1997) for hydrothermal illites and Cr-micas. This calculated age is also close to the upper bound of the Rb-Sr errorchron age range (320 - 350 Ma) reported by Nagler et al. (1992) for the enclosing sedimentary rocks. We suggest that these overlapping age ranges reflect high-heat flux related to intense hydrothermal activity contemporaneous with the vanishing stages of magmatism in the Almadén basin (Upper Devonian).

In the analysed samples there are neither primary relic minerals nor any secondary Sr-rich phase, other than the hydrothermal carbonates. In this case the measured 87Sr/86Sr ratios in the most intensively carbonatized samples may be considered as a valid approximation to the initial isotopic composition of the hydrothermal fluid (Kontak and Kerrich, 1997). The data indicate that the hydrothermal fluid should have had an initial 87Sr/86Sr ratio close to 0.708 (Table III). This ratio is...
significantly lower than that of regional sedimentary rocks (87Sr/86Srinit = 0.716 ± 0.003; Nigler et al., 1992), precluding extensive, mass-exchange interaction between Ordovician sediments and the Almadén mineralizing solutions. However, the estimated 87Sr/86Sr value is close enough to the 87Sr/86Sr ratio of contemporaneous seawater (0.7078 - 0.7085; Veizer and Compston, 1974) to allow identification of the main radiogenic Sr component in the hydrothermal fluid as characteristic of a seawater-dominant solution.

The 87Sr/86Sr results presented here suggest that the hypothesis of hydrothermal activity related to thermally driven convection of seawater is also applicable to explain the general features of spilitization and ore formation in the Almadén mining district. An alternative explanation for the Hall et al. (1997) data (40Ar/39Ar range: 426.9±2.8 to 364.3±3.0 Ma) would be a heterogeneous partial isotopic resetting (and recrystallization) due to high heat flux, reflecting the magmatic events that took place throughout most of the Silurian and Devonian. The wide range of ages obtained from single samples (e.g., EE11, 40Ar/39Ar range: 426.9±2.8 to 374.3±1.0; Hall et al., 1997) further suggests these successive recrystallization/resetting episodes. Textural evidence from the mineral samples, including superposition of alteration events at the scale of single crystals or mineral aggregates, supports this interpretation. Dissipation of magmatic heat in a submarine environment (by convective circulation of seawater) could also provide the necessary framework to explain the chronological relationships of the hydrothermal assemblages in the Almadén Hg deposits. Thus, the seawater flow from cold input zones to hot discharge zones would have resulted in the observed overprinted alteration patterns throughout the Silurian and Devonian.

Conclusions

Magmatism in the Almadén syncline expands from Ordovician to Devonian-Carboniferous time, evolving from discrete explosive alkaline volcanic types (frailescas), through alkaline volcanics with limited degree of secondary differentiation processes, to postdepositional tholeiitic mafic subvolcanic activity. The magmas may have been derived from a volatile- and incompatible element-rich asthenospheric source of EM-I type, by partial melting processes, with rates possibly varying from 1.6-6% during the Silurian, to 4-9% in Devonian, and to 10 to 17.5% for the subvolcanic transitional to tholeiites rocks. The increase in the partial melting ratios with time are in agreement with the decrease in the melting depth after the decrease in the LREE/HREE ratio. This fact is a consequence of a mantle plume driven asthenospheric uplift related to an extensional episode during incipient rifting.

The geologic, mineralogic and isotope data suggest that long-lasting submarine magmatic activity in the Almadén basin may have triggered persistent submarine hydrothermal activity throughout most of the Silurian and Devonian, i.e., a time-span of about 70 Ma, and suggest a magmatic origin for mercury. Submarine geothermal activity would then have established the necessary links between early and late sulphide deposition, isotopic multiple source signatures, and an original mantle source of Hg in the Almadén deposits.

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