

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 $\delta^{18}\text{O}_{\text{fluid}}$ values suggest that hydrothermal activity in the Almadén basin was favoured by interaction of basaltic rocks with seawater. The observed $\delta^{13}\text{C}$ values (-3.6‰ to -9.0‰), together with the lack of correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, 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 $^{87}\text{Sr}/^{88}\text{Sr}$ 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 máficas. Las características geoquímicas de estas rocas sugieren que se derivaron a partir de magmas de intraplaca de origen mantélico, que dieron lugar a basaltos (*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 $\delta^{18}\text{O}_{\text{fluido}}$ 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 $\delta^{13}\text{C}$ (-3.6‰ a -9.0‰) observados en carbonatos, y la ausencia de correlación entre $\delta^{18}\text{O}$ y $\delta^{13}\text{C}$, sugieren diversas fuentes para el origen de éstos, i.e., aparte del agua de mar, tanto carbono mantélico 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‰; cinabrio), 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 gigantes 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 mantélica que dio origen al magmatismo alcalino. Es posible que la combinación de una actividad metasomática mantélica, 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.

Palabras clave: Mercurio, Almadén, magmas máficos alcalinos, isótopos de O-C-S, circulación hidrotermal.

P. Higuera, R. Oyarzun, J. Munhá and D. Morata: The Almaden mercury metallogenic cluster (Ciudad Real, Spain): alkaline magmatism leading to mineralization processes at an intraplate tectonic setting. *Rev. Soc. Geol. España*, 13 (1): 105-119

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 Higuera (1995), Hernández *et al.* (1999), and Higuera *et al.* (1999a, b).

According to recent works on the geology of the district (Hernández *et al.*, 1999; Higuera *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) (Higuera *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; Higuera *et al.*, 1999a) consists of the following mineral assemblages: 1) quartz-chlorite-albite-carbonates (\pm ankerite, \pm siderite, \pm magnesite, \pm calcite) (mainly found in the alkaline basaltic rocks), and 2) chlorite \pm prehnite \pm pumpellyite \pm epidote \pm actinolite (restricted to the isolated bodies of tholeiitic diabases). The regional alteration is locally overprinted by a muscovite/illite-kaolinite-pyrophyllite

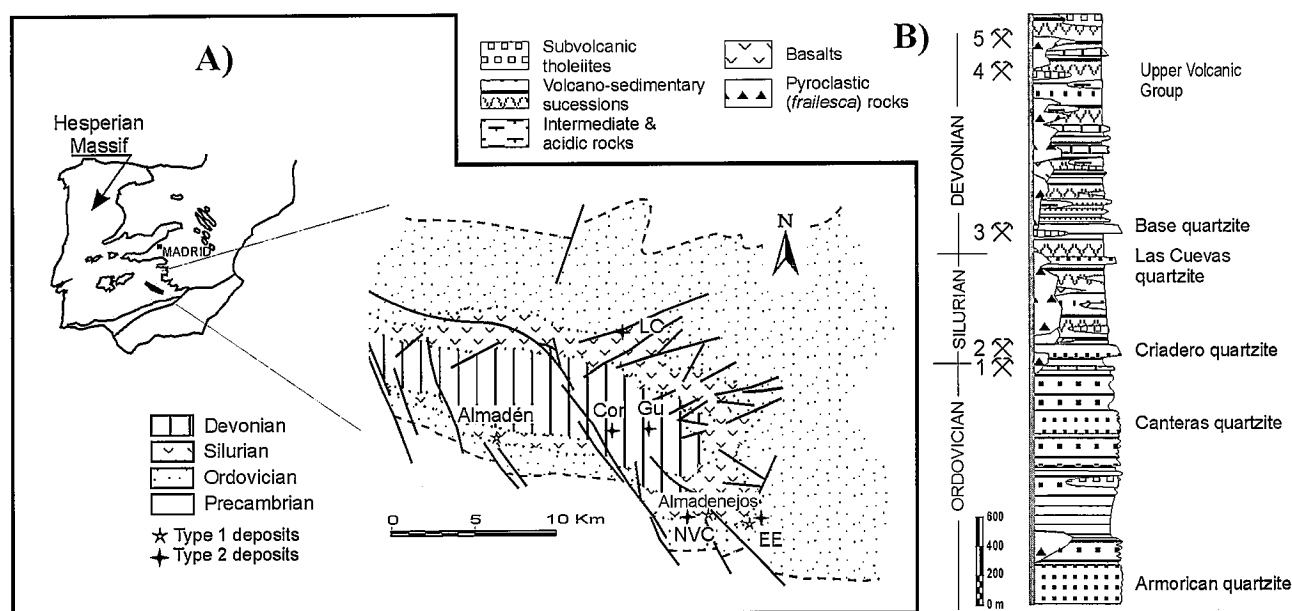


Figure 1.- Geologic sketch of the Almadén realm. A): Location and geologic setting of the Almadén syncline, with indication of types of Hg deposits. COR: Corchuelo; EE: El Entredicho; Gu: Guadalperal; LC: Las Cuevas; NVC: Nueva y Vieja Concepción. B): Stratigraphic sequence of the Almadén syncline, with location of the main sedimentary events, magmatic rocks, and mercury mineralizations: 1.- Location of Type 1 mineralizations (Almadén, El Entredicho, Vieja Concepción) and some Type 2 mineralizations (Pilar de la Legua, Nueva Concepción); 2, 3, 4 and 5.- Location of other Type 2 deposits: Las Cuevas (2), El Burcio-Las Tres Hermanas (3), Corchuelo (4) and Guadalperal (5).

te assemblage, which is typically associated with the late, type 2 ore deposits (e.g., Las Cuevas). The pattern is clearly depicted by the CO₂ distribution in the district, which shows a deep low at Las Cuevas, roughly outlining the destruction of the pervasive carbonatization related to the regional alteration (Hernández *et al.*, 1999).

One of the most remarkable facts about type 1 mineralization is its simple mineralogy: cinnabar, and minor pyrite. This mineralization is directly or indirectly related to the mafic magmatism and its alteration stages (Hernández *et al.*, 1999; Higuera *et al.*, 1999a). In fact, magmatic rocks are present in all the stratabound deposits, and a spatial relationship can be defined between them and the mineralization (Higuera, 1993, 1994; Hernández *et al.*, 1999). At the deposit scale, the higher Hg grades in the *Criadero quartzite* are zoned around the magmatic rocks.

Despite the numerous relationships between magmatism and Hg mineralization, relatively few petrological or geochemical studies have been carried out upon the magmatic rocks. The petrological and geochemical characteristics of the Almadén mafic magmatism are items reviewed in this paper. Using a trace element ratio systematic, the evolution of magmatism is characterized and a primary mantle source for the magmatism and mercury is proposed. Finally a link between the magmatism, geologic setting, and mineralizing processes is established.

Geologic setting

The Almadén syncline is located in the southern part of the Central Iberian Zone (Iberian Hercynian Massif; Dallmeyer and Martínez García, 1990). The Central Iberian Zone is characterized by Paleozoic synclines overlying pre-Ordovician anticlines, 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-Fametician) (Fig. 1b), and at a regional scale, they comprise four main quartzite horizons of Arenigian (*Armorican quartzite*), Caradocian (*Canteras quartzite*), Early Silurian (*Criadero quartzite*) and Siegenian (*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 volcanoclastic and porphyric rocks (lavas) 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).

The Central Iberian Zone is affected by an 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; Higuera *et al.*, 1995), and has been dated at 335 ± 15 Ma (Rb-Sr dating) in Ordovician shales (Nägler *et al.*, 1992).

Magmatism in the Almadén region

General purpose and limitations

We are aware of the many uncertainties derived from postmagmatic alteration processes. Gains and losses in the contents of chemical elements are to be expected within a zone that has been subjected to regional alteration, as 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

Magmatic rocks described in the Almadén syncline (Higuera, 1995) include the following petrographic types:

1) **Pyroclastic rocks** of variable composition. The most abundant are lapilli tuffs of basaltic composition (the so-called *frailasca* 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; diopsidic 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 phenocrysts in intermediate rocks; and K-feldspar and quartz in phenocrysts 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.

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

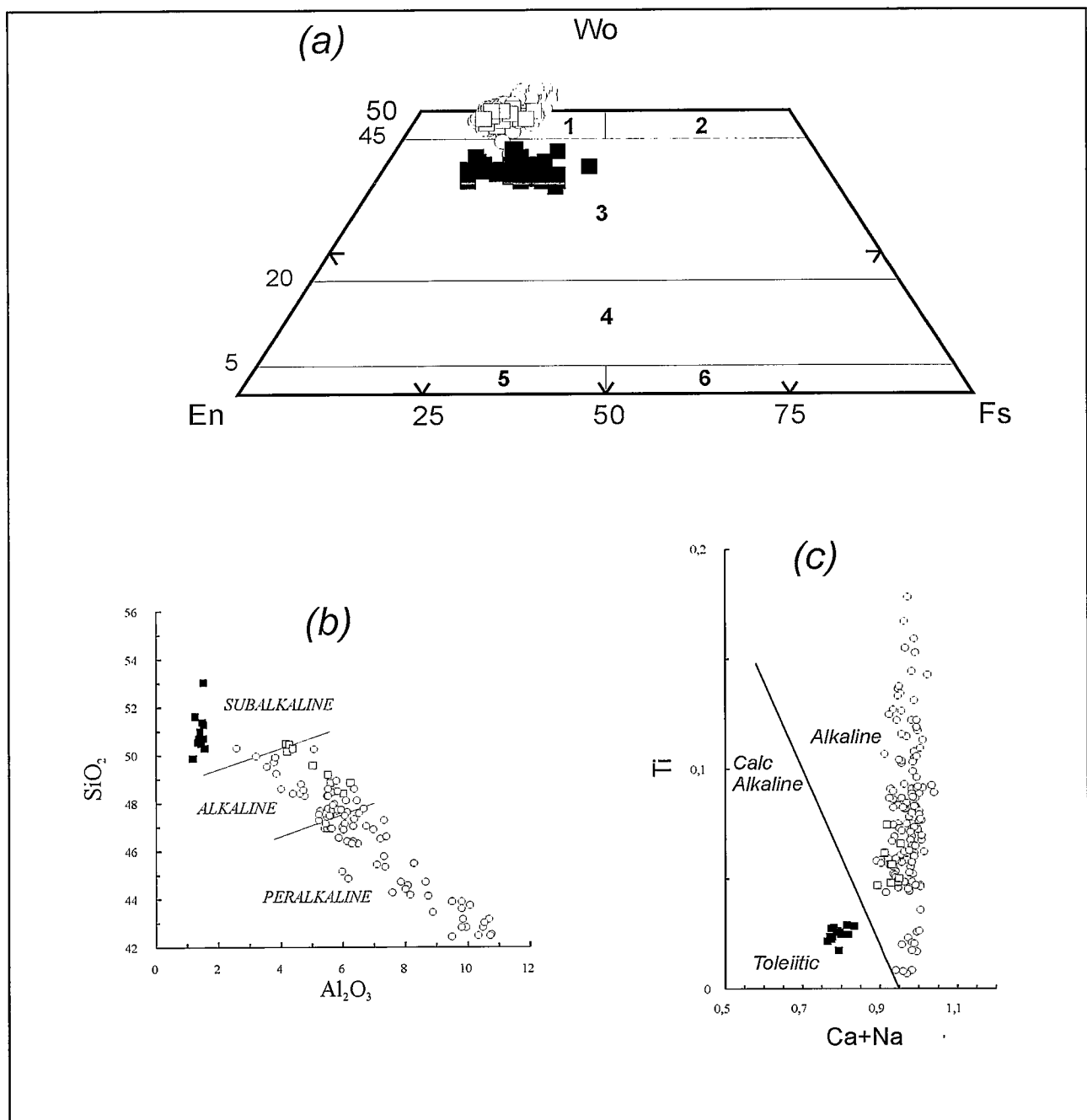


Figure 2.- Pyroxene composition of the mafic rocks from the Almadén syncline. (a) Wo-En-Fs diagram (after Morimoto et al., 1988). (b) Le Bas (1962) diagram. (c) Leterrier et al. (1982) diagram. Black squares = quartz-diabases; white squares = olivine diabases; circles = basalts (s.l.).

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.

Mineral chemistry

Chemical analyses of the main primary 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 paleovolcanic 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) (Fig. 2b) and Leterrier *et al.* (1982) (Fig. 2c) diagrams, confirm the tholeiitic affinity of the quartz-diabases, and the alkaline affinity of the rest (Higueras and Morata, 1994). Plagioclase composition is variable

Rock Type	Basanites	Oliv. bas.	Pirox. bas.	Trachybas.	Oliv. diab.	Qdiab.
N. of analysis	8	6	4	3	8	5
SiO ₂	38,01	44,44	39,18	49,32	43,57	50,65
Al ₂ O ₃	9,84	14,22	12,12	14,69	13,70	14,29
Fe ₂ O ₃	1,78	1,39	1,85	1,47	1,66	1,50
FeO	10,67	9,98	11,11	7,80	10,13	8,00
MnO	0,19	0,16	0,25	0,14	0,17	0,19
MgO	12,70	9,07	11,86	5,21	9,38	5,99
CaO	11,11	6,83	10,16	6,84	7,52	8,22
K ₂ O	0,79	0,80	0,61	1,02	0,67	0,54
Na ₂ O	1,31	1,64	1,60	3,89	1,88	3,16
TiO ₂	2,86	2,58	2,98	2,29	2,35	1,80
P ₂ O ₅	0,65	0,37	0,71	0,43	0,44	0,20
LOI	9,02	7,81	6,90	5,43	7,39	3,78
SUM	100,10	100,16	100,56	98,95	99,87	99,06
CO ₂	6,01	3,24	3,48	3,24	3,39	0,93
H ₂ O ⁺	3,04	4,09	3,29	2,18	3,92	2,93
Cr	340,00	443,67	n.a.	146,00	414,25	185,50
Ni	263,63	196,17	257,50	91,33	147,63	61,60
Co	63,00	51,00	53,50	33,00	44,57	39,50
Sc	18,42	25,40	20,50	n.a.	23,65	20,80
V	217,00	193,00	239,50	136,00	213,57	158,00
Cu	58,58	46,43	62,00	27,00	58,49	57,60
Pb	6,38	11,17	7,00	4,67	5,25	4,40
Zn	107,67	89,53	93,50	158,00	88,60	80,50
Rb	33,33	2,50	24,00	n.a.	23,00	14,00
Ba	1478,50	437,00	715,00	198,00	1144,43	305,00
Sr	939,63	469,50	738,00	n.a.	612,33	409,00
Nb	68,25	47,17	66,00	51,33	54,50	17,40
Zr	235,13	198,00	287,50	312,33	197,50	97,60
Y	23,63	23,67	27,00	27,67	19,63	17,00
Th	5,46	3,00	4,50	4,15	3,45	1,65
U	1,88	1,10	1,40	1,40	1,33	0,40
La	61,08	31,40	51,45	35,85	35,25	12,50
Lu	0,24	0,23	0,27	0,28	0,23	0,19
[mg]	0,68	0,62	0,66	0,54	0,62	0,57
(La/Lu) _n	26,39	14,17	20,36	13,70	15,96	7,01
Nb/Y	2,89	1,99	2,44	1,86	2,78	1,02
La/Nb	0,89	0,87	0,78	0,70	0,65	0,72

Notes: Major elements in percent by weight. Trace elements in parts per million by weight. LOI: loss on ignition. [mg] = MgO/(MgO+FeO). Rock type abbreviations: Oliv. bas.: Olivine basalts; Pirox. bas.: Pyroxenitic basalts; Trachybas.: Trachybasalts; Oliv. diab.: Olivine diabases; Qdiab.: Quartzdiabases.

Table I.- Average chemical analysis of selected basic rocks present in the Almadén syncline.

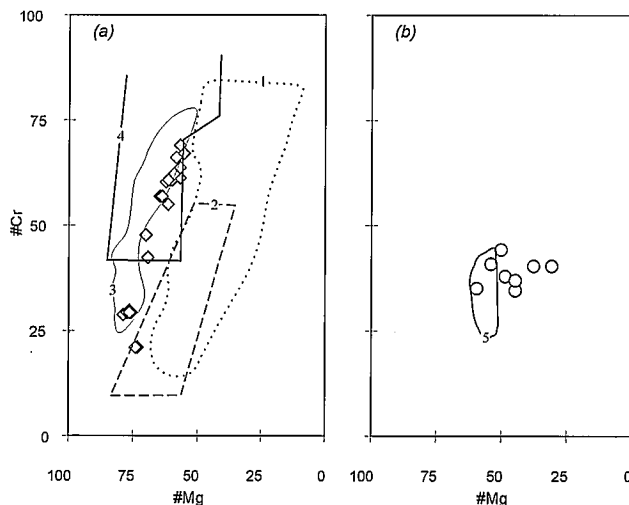


Figure 3.- Spinel composition for: (a) ultramafic and (b) mafic rocks of the Almadén syncline. #Mg=100Mg/(Mg+Fe²⁺) in atomic proportions; #Cr=100Cr/(Cr+Al) in atomic proportions. 1.- Field of spinels from ophiolitic complexes; 2.- Field of spinels from lherzolititic xenoliths in alkaline basalts; 3.- Field of spinels from harzburgitic xenoliths in alkaline basalts; 4.- Field of spinels from kimberlitic xenoliths; 5.- Field of spinels from alkaline basalts (Iceland). Fields 1, 2 and 5, from Leblanc (1985); Fields 3 and 4, from Haggerty (1991).

from An₄₅₋₆₀ in basaltic rocks to An₆₀₋₈₅ in the doleritic varieties, showing limited albitization processes in samples with prehnite-pumpellyite associations (Higueras *et al.*, 1995). Spinel is present as the only unaltered mineral in ultramafic xenoliths in basalts, and as small phenocrysts in basanites. 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, 1985). Late magmatic amphiboles and biotites are Ti-rich varieties, with high Mg/Fe ratios (Higueras, 1995). According to the Leake (1978) classification, the amphibole is of kaersutitic composition. The biotite composition is close to the boundary annite-phlogopite (Deer *et al.*, 1992).

Whole-rock geochemistry

Thirty four samples representative of the different 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 (Higueras 1995).

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

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 sub-volcanic rocks onto the Nb/Y vs Zr/TiO₂ 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 TiO₂ 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

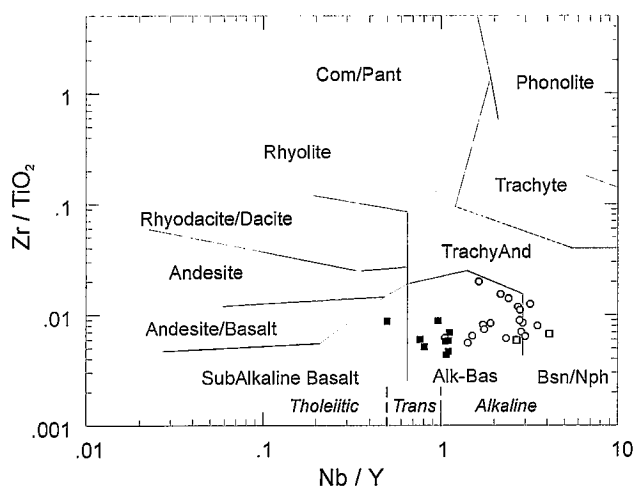


Figure 4.- Nb/Y vs Zr/TiO₂ diagram (Winchester and Floyd, 1977) for the classification of paleovolcanic rocks. Boundaries between tholeiitic-transitional-alkaline, from Pearce (1982). Symbols, as in figure 2.

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/Ni 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/Ni scattering would be the generation of these rocks from an homogeneous source but under very different partial melting ratios.

Other interesting feature of the Almadén mafic magmatism is its high content in CO₂. Most of the mafic volcanic rocks display CO₂ 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 (Higuera, 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-

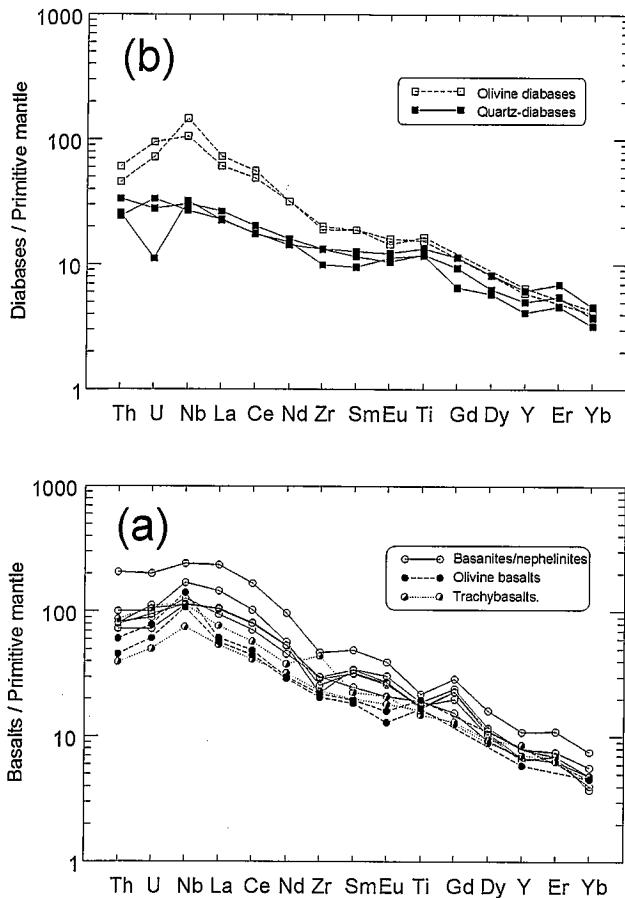


Figure 5.- Primitive mantle normalized spiderdiagrams for: (a) porphyric rocks, and (b) subvolcanic rocks. Normalization values, after Taylor and MacLennan (1985).

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 (Allègre 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

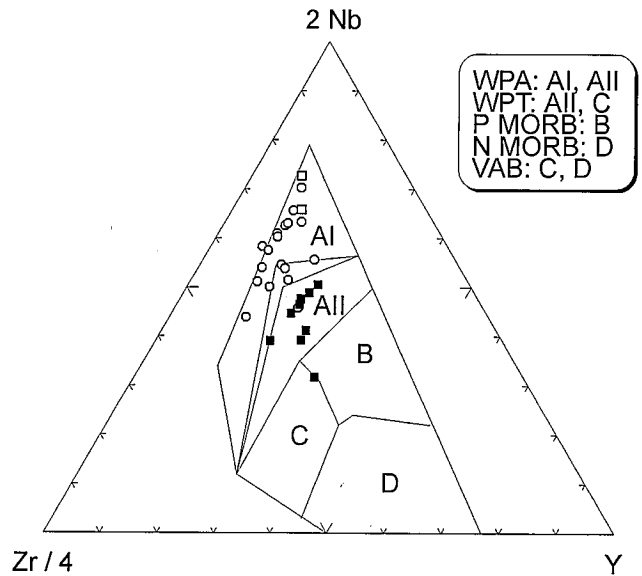


Figure 6.- $2Nb:Zr/4:Y$ diagram (after Meschede, 1986) for the discrimination of the tectonic setting of paleovolcanic rocks. Symbols as in figure 2. WPA: alkaline within plate basalts. WPT: tholeiitic within plate basalts. MORB: mid-ocean ridge basalts. VAB: volcanic arc basalts.

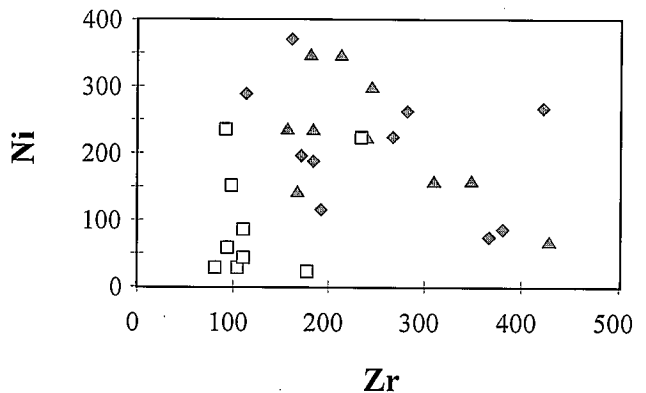


Figure 7.- Zr/Ni diagram for basic rocks of the Almadén syncline. Triangles: Silurian rocks; Diamonds: Devonian; Squares: quartz-diabases.

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 Allègre, 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 (Higuera *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, fO_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 fO_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 (Higuera, 1995; Higuera *et al.*, 1995b; Higuera *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 *frailasca* 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 coexisting with calcite/ankerite (O’Neil *et al.*, 1969; Mu-

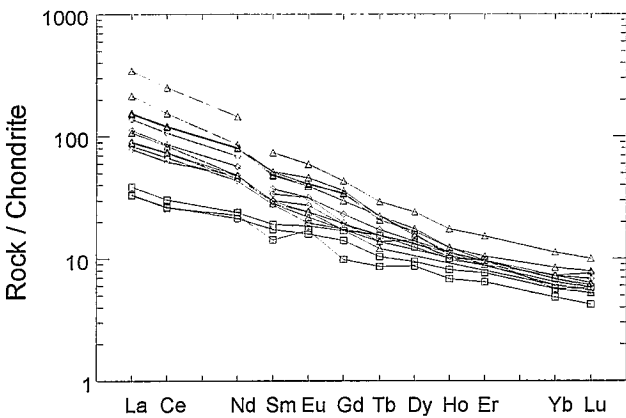


Figure 8.- Chondrite normalized spiderdiagrams for basic rocks of the Almadén syncline. Symbols, as in figure 7.

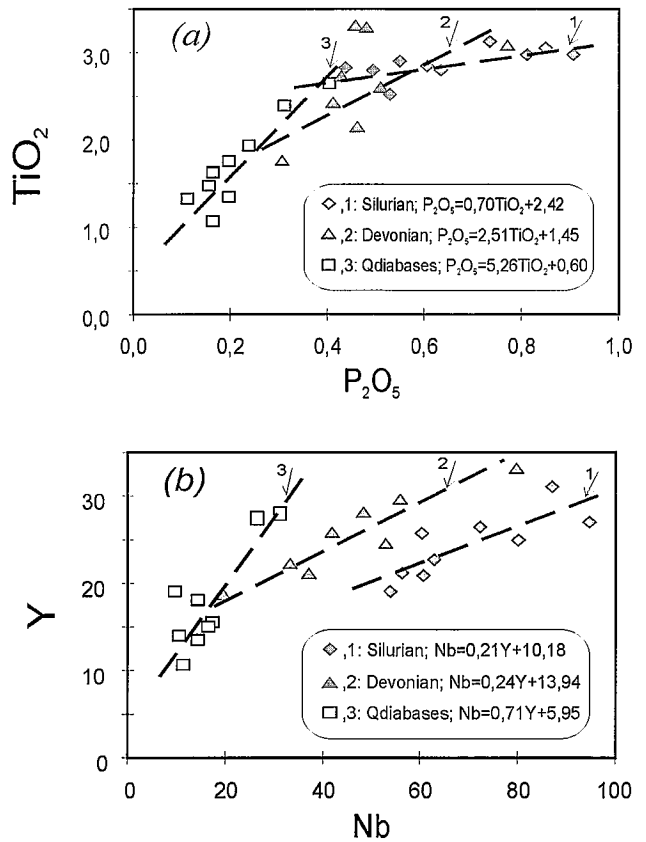


Figure 9.- Diagrams P2O5 vs TiO2 (a) and Nb vs Y (b) for the basic rocks of the Almadén syncline. Lines: correlation fits for the indicated sample groups, with equation expressed in the diagram. Symbols, as in figure 7.

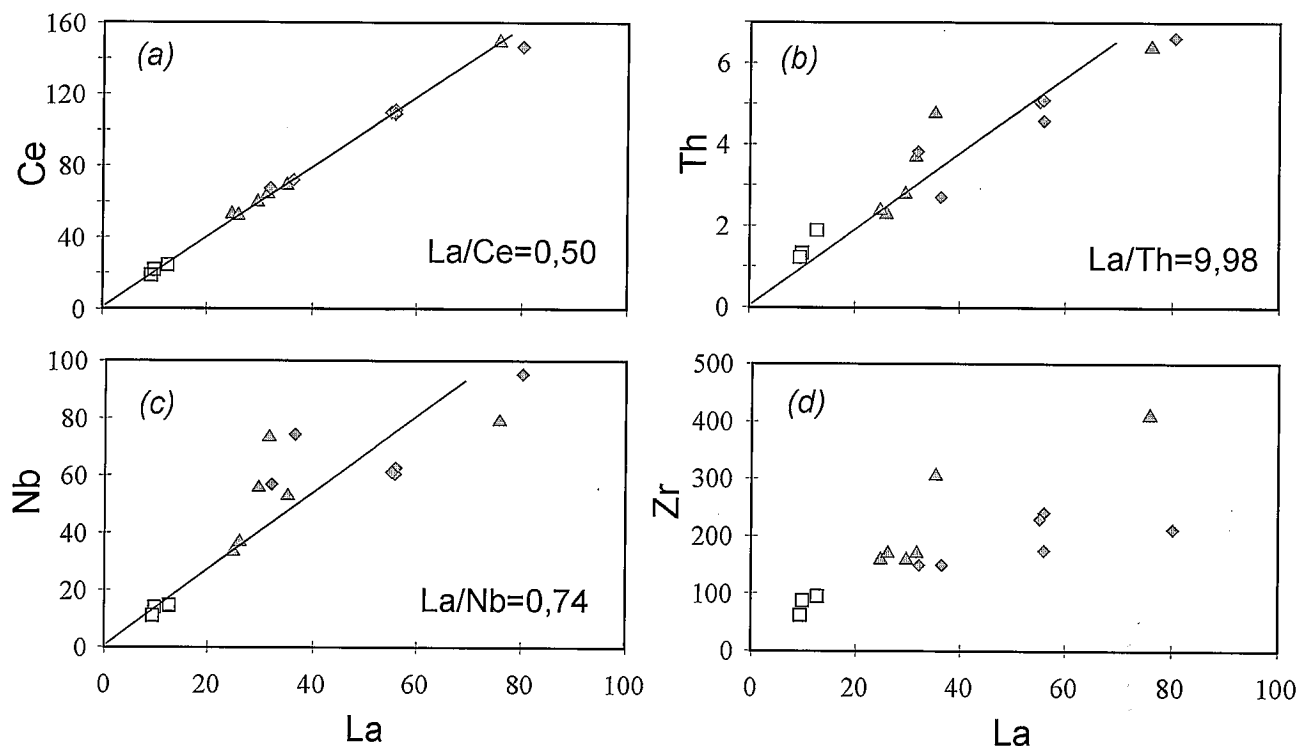


Figure 10.- Diagrams of La vs highly incompatible elements: (a).- La vs Ce; (b).- La vs Th; (c).- La vs Nb; (d).- La vs Zr. Average ratio is indicated in the diagrams, except for La/Zr. Symbols, as in figure 7.

min *et al.*, 1996), or from -1.0‰ to +6.0‰ if coexisting with dolomite (Mathews and Katz, 1977). The range of estimated $\delta^{18}\text{O}_{\text{fluid}}$ 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 ($\delta^{18}\text{O}_{\text{seawater}} = 0 \pm 1\text{‰}$; Knauth and Lowe, 1978; Shepard, 1986) commonly undergo positive oxygen isotope shifts to higher $\delta^{18}\text{O}$ values, due to oxygen isotope exchange reactions with ^{18}O -rich host rocks. Close correspondence between estimated and observed $\delta^{18}\text{O}_{\text{fluid}}$ 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‰ to -9.0‰ (vs PDB) ($-9.0\text{‰} < \delta^{13}\text{C}_{\text{mafic meta-volcanics}} < -3.6\text{‰}$; $-8.6\text{‰} < \delta^{13}\text{C}_{\text{mineralized veins/fragmental volcanics}} < -3.9\text{‰}$), which are similar to $\delta^{13}\text{C}$ values measured on aqueous CO_2 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 CO_2 from organic matter in the Ordovician black shales ($\delta^{13}\text{C}_{\text{organic}} \gg -30\text{‰}$; Eichmann *et al.*, 1977), as suggested by Saupé and Arnold (1992), seems unlikely. Low temperature maturation of organic matter yields $\delta^{13}\text{C}_{\text{CO}_2} \gg \delta^{13}\text{C}_{\text{organic-C}}$ (e.g., Arneeth and Matzigkeit, 1986), which is much lighter than that inferred for equilibrium with hydrothermal carbonates. On the other hand, hydrolysis of reduced carbon would imply $\delta^{13}\text{C}_{\text{H}_2\text{CO}_3} - \delta^{13}\text{C}_{\text{CS}_2} \gg +21\text{‰} - +26\text{‰}$, requiring almost invariant highly reduced conditions of carbonate deposition (e.g., Ohmoto, 1972). As discus-

sed above, this is quite unlikely for the Almadén hydrothermal system. At a specified (T, pH, $f\text{O}_2$) range of conditions, the observed $\delta^{13}\text{C}$ values, together with the lack of correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (see Rye and Williams, 1981), favour multiple carbon sources for the

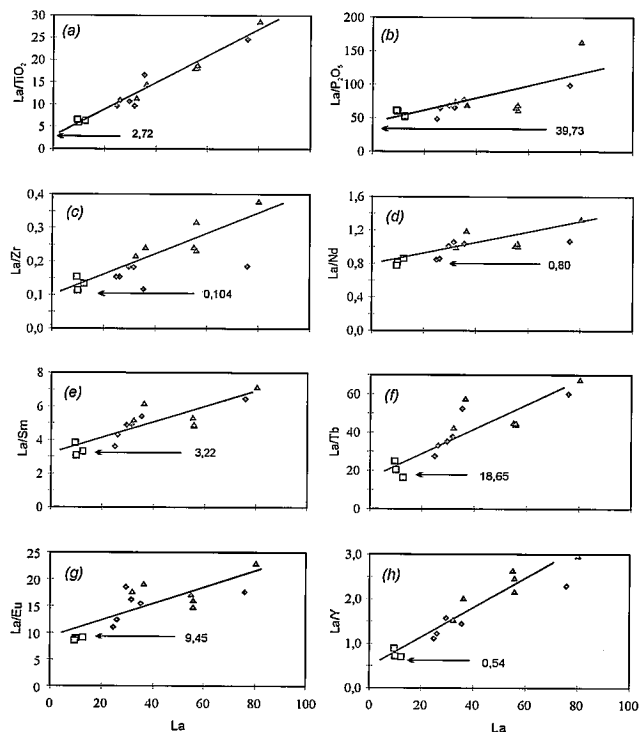


Figure 11.- Diagrams of La vs La/i (i = highly incompatible elements): (a).- La vs La/TiO₂; (b).- La vs La/P₂O₅; (c).- La vs La/Zr; (d).- La vs La/Nd; (e).- La vs La/Sm; (f).- La vs La/Tb; (g).- La vs La/Eu; (h).- La vs La/Y. Regression fit lines and ordinate in the origin are shown in every diagram. Symbols, as in figure 7.

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 (Higuera, 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 Higuera *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 $\delta^{34}\text{S}$ values, from -1.6‰ to +9.0‰. Particularly significant to the discussion is the positive correlation between sulphur contents and $\delta^{34}\text{S}$ values (+1.0‰ - +6.8‰), reported by Saupé and Arnold (1992) for the Almadén spilites. Although the linear $\delta^{34}\text{S}$ - 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, $f\text{O}_2$, 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; Higuera *et al.*, 1999c), $\delta^{34}\text{S}$ enrichment/depletion and variable $\delta^{34}\text{S}$ -S trends (e.g., Saupé and Arnold, 1992) must be expected for the Almadén spilites. At the conditions specified above for Hg sulphide deposition, $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ must have been close to $\delta^{34}\text{S}_{\text{S-fluid}}$ (Ohmoto, 1972). Thus, the range of cinnabar $\delta^{34}\text{S}$ 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; Higuera *et al.*, 1999b). Interestingly, this relationship also appears to hold true for other areas outside Almadén, in the Palaeozoic 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

	ppm	C.N.
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

Table II.- Absolute (ppm) and chondrite normalized (C.N.) values for the calculated upper mantle source for the Almadén magmatism.

for the alkali basaltic magmas; indeed, mantle metasomatic activity and the low degrees of partial melting inherent to the genesis of the Almadén mafic magmas (Higuera 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 (Higuera and Munhá, 1993; Higuera *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). Alternatively, a spatial association might not be directly significant for an origin of the mercury, but could indicate favourable geochemical 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).

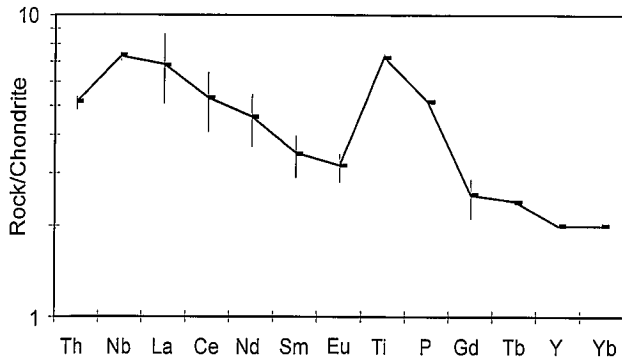


Figure 12.- Chondrite normalized interpretative composition for the upper mantle calculated for the Almadén region, on the basis of information from figures 10 and 11, and assuming a chondrite normalized value of 2 for Y and Yb. Error bars derived from the calculations of the element ratios are shown.

Age constraints for hydrothermal processes

Hall *et al.* (1997) reported a detailed $^{40}\text{Ar}/^{39}\text{Ar}$ 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, stratiform-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 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was corrected for mass fractionation using $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Repeat analysis of NBS 987 Sr standard gave $^{87}\text{Sr}/^{86}\text{Sr} = 0.71023 \pm 4$ (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 carbonatised mafic metavolcanics, whereas the fourth sample (S.NC-1/C-15) displays the argillic type (pyrophyllite \pm kaolinite \pm illite) alteration, as described by Higuera *et al.* (1999a).

Measured isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) ratios in the carbonatised rocks range from 0.706993 to 0.708262 and show no positive correlation with the $^{87}\text{Rb}/^{86}\text{Sr}$ values; hig-

SAMPLE	Rb/Sr	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Alteration
S.VC-1/C-21	0.053	0.152	0.706993	Weakly carbonated
S.CS-1/C-10	0.018	0.052	0.708262	Hardly carbonated
S.VC-4/C-10	0.006	0.017	0.707641	Hardly carbonated
average	0.012	0.035	0.707951	
S.NC-1/C-15	0.446	1.290	0.714654	Argillic

Table III.- Results of the Rb/Sr analytical work. Location of the samples: S.VC-1/C-21 and S.VC-4/C-10, from La Vieja Concepción mine, Almadenejos. S.CS-1/C-10, from Cerro de los Santos mineral showing; S.NC-1/C-15, from La Nueva Concepción mine, Almadenejos. All samples, from DDHs.

her $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.707641 - 0.708262) correspond to the two samples with lower $^{87}\text{Rb}/^{86}\text{Sr}$ 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 $^{87}\text{Rb}/^{86}\text{Sr}$ ratios of 0.017 to 0.152 (Table III), it is evident that the radiogenic Sr component in the carbonatised samples cannot have been derived by in situ decay of ^{87}Rb , to develop the lowest observed $^{87}\text{Sr}/^{86}\text{Sr}$ value from a typical alkali-basalt protolith (with $^{87}\text{Sr}/^{86}\text{Sr}_{\text{ini}} = 0.704$, $^{87}\text{Rb}/^{86}\text{Sr} = 0.152$). 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 $^{87}\text{Sr}/^{86}\text{Sr}$ reservoir elsewhere; a logical source for radiogenic Sr is the hydrothermal fluid itself.

Because of their dominant hydrothermal mineral assemblages and very low $^{87}\text{Rb}/^{86}\text{Sr}$ ratios, samples S.CS-1/C-10 and S.VC-4/C-10 should have actual $^{87}\text{Sr}/^{86}\text{Sr}$ values almost identical to those acquired at the time of hydrothermal carbonate-rich alteration; therefore, we have used the average of their $^{87}\text{Sr}/^{86}\text{Sr}$ 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 Nägler *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 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the most intensively carbonatised 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 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio close to 0.708 (Table III). This ratio is

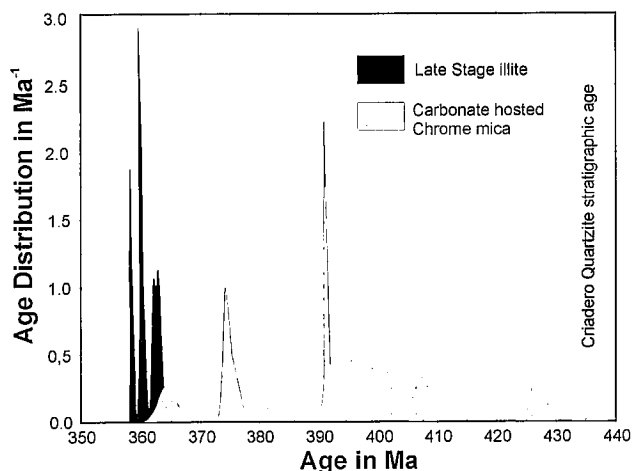


Figure 13.- Almadén $^{40}\text{Ar}/^{39}\text{Ar}$ dating results (after Hall *et al.*, 1997). Illite age clusters at 360 Ma, while fuchsite scatters from 360 to 430 Ma.

significantly lower than that of regional sedimentary rocks ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{ini}} = 0.716 \pm 0.003$; Nägler *et al.*, 1992), precluding extensive, mass-exchange interaction between Ordovician sediments and the Almadén mineralizing solutions. However, the estimated $^{87}\text{Sr}/^{86}\text{Sr}$ value is close enough to the $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 ($^{40}\text{Ar}/^{39}\text{Ar}$ 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, $^{40}\text{Ar}/^{39}\text{Ar}$ range: 426.9 ± 2.8 to 374.3 ± 1.0 ; Hall *et al.*, 1997) (Fig. 13) 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

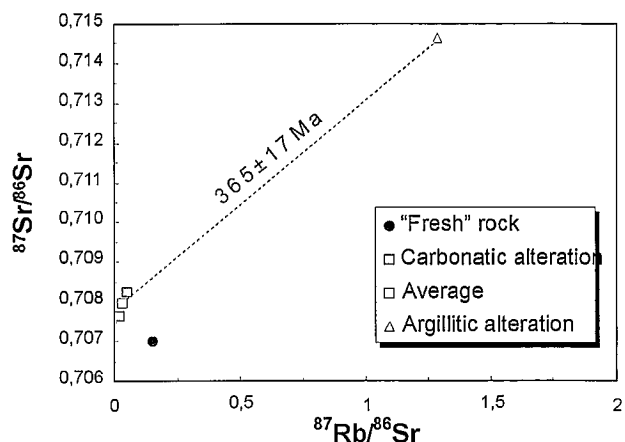


Figure 14.- $^{87}\text{Rb}/^{86}\text{Sr}$ vs $^{87}\text{Sr}/^{86}\text{Sr}$ isochron plot for the analysed samples. "Average" is for the two samples with more intense carbonatic alteration, and the 365 ± 17 Ma errorchron is between average and argillitic altered sample (see text for details). "Fresh" rock in the legend refers to the least carbonatised sample (see Table III).

from discrete explosive alkaline volcanic types (*frailesca*), 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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