Palaeozoic magmatic-related hydrothermal activity in the Almadén syncline, Spain: a long-lasting Silurian to Devonian process?

P. Higueras, R. Oyarzun, J. Munáñ and D. Morata

Almadén (central Spain) is the most remarkable mercury-mining district in the world, having produced one-third of the total world output of this element. The mercury orebodies are hosted by sedimentary and volcanic rocks belonging to a Lower Palaeozoic sequence that unconformably overlies the pre-Ordovician basement of the Central Zone of the Iberian Variscan Chain. Fig. 1). The Almadén rocks and mineralization pose an intriguing problem because in addition to the classic Lower Silurian strata-bound mineralization (e.g. Almadén and El Entredicho) other deposits are found higher in the stratigraphic sequence in both Silurian and Devonian rocks (Fig. 1). Furthermore, throughout the stratigraphic column the volcanic rocks are perversively transformed to albite-chlorite-carbonate-rich splitties, i.e. the effects of the so-called regional alteration.

A preliminary investigation of strontium isotopic compositions in different hydrothermal alteration assemblages has been carried out in conjunction with re-evaluation of the already available isotopic and stratigraphic data in the hope of providing new insights into the genetic environment in which the alteration and mineralization processes took place. It is suggested that the persistent submarine magmatic activity in the Almadén basin may have sustained long-lasting submarine hydrothermal activity through most of the Silurian and Devonian, i.e. a time-span of about 70 m.y.

Geology, mineralization and alteration processes

The Almadén volcanic-sedimentary rocks range from Lower Ordovician to Upper Devonian in age. They comprise several sequences of black shale and sandstone/quartzite units with frequent intercalations of submarine mafic alkaline volcanic rocks (Fig. 1). Geophysical data and surface mapping show that the mafic volcanism within the Almadén syncline was far more important than elsewhere in the region. The magnetic record is almost continuous and evolved from early, widespread basaltic-nephelinitic and alkali-olivine basaltic volcanism, mostly into the Silurian–Devonian part of the section, to late transitional/thetaitic intrusive dolerites, which are scattered throughout the whole sequence. These rocks are perversively transformed to albite-chlorite-carbonate-rich splitties. The whole sequence was folded, weakly metamorphosed and intruded by felsic plutonic rocks during the Variscan deformation.

The mercury deposits are classified into two main types on the basis of their structural setting, host rocks and hydrothermal alteration. Type 1 deposits are the largest and include those of Almadén and El Entredicho (Fig. 1). These are hosted by the Criadero quartzite and are restricted to this single stratigraphic unit at the base of the Silurian. The associated hydrothermal alteration is typified by the extensive development of Ca–Mg–Fe carbonates, chlorite and microcrystalline quartz as well as Cr-rich mica (fuchsite) in ultramatic xenoliths—a mineral assemblage defined as the regional alteration. The effects of the regional alteration can be traced in the mafic volcanic rocks along the whole Silurian–Devonian section of the Almadén stratigraphic

![Fig. 1. (a) Geological map and (b) stratigraphic column of Almadén syncline showing locations of selected Hg deposit and samples (modified after Higueras).](image-url)
Type 2 deposits display a typical alteration mineral assemblage known as the local alteration (muscovite/illite–kaolinite–pyrophyllite), which at ore deposit scale overprints the regional low-grade alteration assemblage.

Isotopic data and interpretation

Hail et al. 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 m.y., whereas Cr-mica ages are much more variable and range from 365 to 427 m.y. (see, for example, Fig. 8 of Hall et al.1) This age range was initially interpreted by Hall et al.1 as reflecting two episodes of Hg mineralization, the oldest Cr-mica ages being associated with Lower Silurian, stratiform-type cabinar deposits and the younger ages representing partial or total argon loss contemporaneous with a later episode of mineralization, which was attributed to Hg remobilization caused by the Variscan metamorphism.1 Although this is a valuable working hypothesis, the available geological data make an evaluation of alternative explanations worthwhile.

The samples for the present work were selected to be representative of the two main styles of hydrothermal alteration associated with Hg mineralization at Almaden, as distinguished by Hall et al.1 Three samples (S.C.S.-I/C-10, S.V.C.-I/C-21, S.V.C.-4/C-10) correspond to variably carbonized mafic metavolcanics, whereas the fourth sample (S.N.C.-I/C-15) displays the argilitic-type (pyrophyllite ± kaolinite ± illite) alteration described by Higuera et al.4 B and Sr (this work) were separated from drill-core samples by the use of standard cation-exchange chromatography techniques.7 The Sr analyses were performed on a VG MM30 thermal ionization mass spectrometer, whereas its Sr was analysed on a VG 54E thermal ionization mass spectrometer (Table 1). The 87Sr/86Sr ratio was corrected for mass fractionation by use of 86Sr/88Sr = 0.1194. 87Sr/86Sr = 0.71023 ± 4 (2 s.d.)

Table 1 Results of analytical work. Location of samples: S.V.C.-I/C-21 and S.V.C.-4/C-10 from La Vieja Concepción mine, Almaden; S.C.S.-I/C-10 from Cerro de los Santos mineral showing; S.N.C.-I/C-15 from La Nueva Concepción mine, Almaden. All samples from diamond drill-holes

<table>
<thead>
<tr>
<th>Sample</th>
<th>87Sr/86Sr</th>
<th>87Rb/86Sr</th>
<th>Alteration</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.V.C.-I/C-21</td>
<td>0.053</td>
<td>0.152</td>
<td>0.706993</td>
</tr>
<tr>
<td>S.C.S.-I/C-10</td>
<td>0.018</td>
<td>0.052</td>
<td>0.708262</td>
</tr>
<tr>
<td>S.V.C.-4/C-10</td>
<td>0.036</td>
<td>0.017</td>
<td>0.707641</td>
</tr>
<tr>
<td>Average</td>
<td>0.012</td>
<td>0.035</td>
<td>0.707951</td>
</tr>
<tr>
<td>S.N.C.-I/C-15</td>
<td>0.416</td>
<td>1.200</td>
<td>0.714654</td>
</tr>
</tbody>
</table>

The measured Sr isotope ratios (87Sr/86Sr) in the carbonized rocks range from 0.706993 to 0.708262 and show no positive correlation with the 87Rb/86Sr values (Fig. 2); the higher 87Sr/86Sr values (0.707641-0.708262) correspond to the two samples with lower 87Rb/86Sr ratios (0.017-0.052), suggesting that carbonization involved leaching of Rb and/or introduction of Sr from an external source. Given the low overall 87Rb/86Sr ratios of 0.017-0.152 (Table 1), it is evident that the radiogenic Sr component in the carbonized samples cannot have been derived by in-situ decay of 87Rb to develop the lowest observed 87Sr/86Sr value from a typical alkali-basalt protolith (87Sr/86Sr_initial = 0.704, 87Rb/86Sr = 0.152). For that to be the case an elapsed time in excess of 1300 m.y. 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 the radiogenic Sr is the hydrothermal fluid itself.

Because of their dominant hydrothermal mineral assemblages and very low 87Rb/86Sr ratios samples S.C.S.-I/C-10 and S.V.C.-4/C-10 should have initial 87Sr/86Sr values almost identical to those acquired at the time of hydrothermal carbonate-rich alteration; therefore, the mean 87Sr/86Sr value (0.707051 ± 0.000311) was used here together with the isotopic data for sample S.N.C.-I/C-15 (Fig. 3; Table 1) to obtain a model age for the mineralizing event.3 The age obtained (365 ± 17 m.y.) agrees with the clustering of Ar retention ages at 360-365 m.y. determined by Hall et al.1 for hydrothermal illites and Cr-micas. This calculated age is also close to the upper bound of the Rb-Sr isochron age range (320-350 m.y.) reported by Nügler and co-workers9 for the enclosing sedimentary rocks. It is suggested here that these overlapping age ranges reflect a high heat flux related to intense hydrothermal activity contemporaneous with the waning stages of magmatism in the Almaden basin (Upper Devonian).

In the samples analysed there are neither primary relict minerals nor any secondary Sr-rich phase, other than the hydrothermal carbonates. In this case the measured 87Sr/86Sr ratios in the most intensely carbonized samples may be considered as a valid approximation of the initial isotopic composition of the hydrothermal fluid.6 The data indicate that the hydrothermal fluid should have had an initial 87Sr/86Sr ratio close to 0.708 (Table 1). This ratio is significantly lower than that of regional sedimentary rocks (87Sr/86Sr_initial = 0.716 ± 0.003),7 which precludes extensive, mass-exchange interaction between the Ordovician sediments and the Almaden mineralizing solutions. However, the estimated 87Sr/86Sr value is close enough to the 87Sr/86Sr ratio of contemporaneous sea water (0.7078-0.7085)10 to allow identification of the main radiogenic Sr component in the hydrothermal fluid as characteristic of a sea water-dominant solution.
Fig. 3 Schematic model (not to scale) of evolution of hydrothermal system in Almadén sequence from initial stage in early Silurian through intermediate stage in late Silurian to final, mature stage in late Devonian. Note persistent magmatic activity (alkaline lavas and frailesca-type diatremes, see also Fig. 1), which ends with emplacement of subvolcanic bodies of tholeiitic affinities in late Devonian time. 1. Frailesca rocks (diatremes); 2. basaltic lavas; 3. quartzites; 4. sediments; 5. diabases; 6. convection cells.
Discussion and proposal of working hypothesis

Despite the small number of analysed samples, the new strontium geochronological data confirm the clustering of ages at 360–365 m.y. for the Almadén Hg deposits. Although further analytical work will be needed, the preliminary $^{87}\text{Sr}/^{86}\text{Sr}$ results presented here suggest that the hypothesis of hydrothermal activity related to the thermally driven convective flow of seawater could also explain the general features of stratification and ore formation in the Almadén mining district. An alternative explanation for the Hall et al.² data ($^{40}\text{Ar}/^{39}\text{Ar}$ range, 426.9 ± 2.8 to 364.3 ± 3.0 m.y.; Fig. 2) would be the heterogeneous, partial isotopic resetting (and recrystallization) of the rocks due to a high heat flow, reflecting the magmatic events that took place throughout most of the Silurian and Devonian times (Figs. 1 and 3). 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 m.y.)³ also suggests successive recrystallization and resetting events. Textural evidence from the mineral samples, including superimposition 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 different cold input zones to hot discharge zones would have resulted in the observed variable overprinting. An excellent example of the latter is provided by Las Cuevas (type 2), where the local alteration overprints the regional alteration assemblage.⁴

The Variscan regional metamorphism postdates the Hg mineralization events. Furthermore, the Variscan deformation and plutonic activity, which could have provided the mechanical and thermal energy sources for orogenic metamorphism in Almadén, is about 30–60 m.y. younger than the youngest ages reported by Hall et al.¹

The isotopic data, together with (1) the lack of orogenic activity and the persistence of magmatism throughout most of the Silurian and Devonian and (2) the large-scale effects of the regional alteration throughout the stratigraphic column, suggest that the Almadén marine basin may have been the site of long-lasting hydrothermal processes (Fig. 3), some of them leading to mercury deposition. Although pauses are not ruled out, if the hypothesis presented here is correct, the Almadén basin could be regarded as one of the world’s longest-lived hydrothermal centres. In this respect it is worth mentioning the similarities between the Almadén submarine hydrothermal activity and associated regional alteration and equivalent facies found in modern analogues, such as the Icelandic geothermal fields⁵—in particular, the Reykjanes field, where fluid circulation is dominated by seawater.¹¹

Acknowledgement

The authors are grateful to Dr. Finlay Stuart (Scottish Universities Research and Reactor Centre, United Kingdom) for his help during the Rb/Sr determinations. The work was carried out with the financial support of the ‘Ayudas a la Investigación (Financiación Interna)’ programme of the University of Castilla-La Mancha (PH) and JNICT through research project TECTIBER-PRAAX/2/2.1/CTA:553/4 (JM).

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