Abstract—Seventy-four new S isotope analyses of ore minerals and country rocks are given for the Hg deposit of Almadén. The spread of the cinnabar $\delta^{34}S$ is narrow within each of the three orebodies, but the $\delta^{34}S$ average values differ sufficiently between them (mean $\delta^{34}S$: San Nicolás = 0.2 ± 1.1%, San Francisco = 8.1 ± 0.7%, San Pedro = 5.9 ± 1.0%) to indicate three different mineralization episodes and possibly processes. The unweighted mean for all cinnabar samples is 5.6% and the S source is considered to be the host-rocks, either the Footwall Shales ($\delta^{34}S = 5.5\%$) or the spilites ($\delta^{34}S = 5.1 \pm 1.3\%$). For geometric and chronologic reasons, the former seem the best potential source. However, the high $\delta^{34}S$ values of the San Francisco cinnabar cannot be explained without addition of heavy S from reduction of seawater sulphate. Orderly distributions of the $\delta^{34}S$ values are observed in all three orebodies: (1) their increase from the stratigraphic bottom to the top in the San Pedro orebody is explained by a Rayleigh process, and (2) the maxima in the centres of the San Francisco and San Nicolás orebodies are explained by mixing of the S transporting hydrothermal fluids with seawater within the sediments. Associated pyrite and cinnabar were deposited under isotopic disequilibrium, probably because the low solubility of cinnabar caused rapid precipitation of cinnabar. The different morphological pyrite types have their own isotopic $\delta^{34}S$ signatures. The spilites are notably enriched in S ($n = 3$; average S content $= 0.56\%$) compared to normal basalts (1000 ppm) and have an average $\delta^{34}S = 5.1 \pm 1.3\%$. The linear relationship between the $\delta^{34}S$ and the S content of the spilites is interpreted as a mixing line between mantle S and a constant S source, probably an infinite open reservoir. An incomplete basalt-seawater reaction at nearly constant temperature is the best explanation for this relation. The S (predominantly pyrite) of the black shales ($n = 3$; $\delta^{34}S$ from -6.7% to 14.4%) is interpreted as resulting from bacterial seawater sulphate reduction under variable euxinic conditions. The stratabound pyrite ($n = 16$) found in the sediments near, but independent of the Hg ores, also has a wide range of $\delta^{34}S$ between 1.5-0% and 16.4%, with a mode of about 8%; the pyrite rims of the diagenetic dolomite nodules ($n = 2$; $\delta^{34}S = -14.7 \pm 0.35\%$) in the Hanging Wall Shales display the most negative values found at Almadén.

INTRODUCTION

ALMADÉN (FIG. 1) is the largest Hg deposit in the world, accounting for one-third (250 000 t) of the recorded production of this metal. Limited data was available until now on the S isotopes from the ores of this deposit (OZEROVA et al., 1973b; CALVO and GULEMANY, 1975; ARNOLD and SAUPÉ, 1985; RYTUBA et al., 1989) and from Hg deposits in general (ÖZEROVA et al., 1973a,b; BOCTOR et al., 1987). The following sulphur isotope data permit an attempt to understand the genesis of this deposit. The different potential sulphur sources (mantle, contemporary seawater, spilites and shales enclosing the deposit) of the sulphates and sulphides in the deposit were evaluated and the possible roles of metamorphism, remobilization and isotopic disequilibrium in ore deposition are discussed, as well as the coexistence of diagenetic and hydrothermal pyrites. The study of the spilites also gives insight into basalt/seawater reactions on a shallow epicontinental platform (in the following, spilite is taken in its compositional acception of a basalt converted to a low-temperature mineral assemblage as given by the AGI Glossary, without genetic connotation and not implying addition of Na).

The Almadén mine, most Hg mines and occurrences of the district, and by far the largest part of the metal are located in the same quartzite horizon ("Criadero Quartzite"; criadero meaning ore deposit). La Nueva Concepcion mine worked ore in this horizon and also ore from a volcanic pipe. The other types of Hg deposits of the district (HERNANDEZ SORBRINO, 1985; ORTEGA GIRONES and HERNANDEZ SORBRINO, 1992; SAUPÉ, 1973, 1990) are not dealt with in this paper.

GEOLOGICAL SETTING

Geology of the Almadén Area

The stratigraphic sequence comprises two successive sedimentary series. Upper Precambrian flyschoid alternations of greywackes and slates were folded and metamorphosed to greenschist facies before sedimentation of the second series. They are nonconformably overlain by a Middle Palaeozoic elastic assemblage of orthoquartzites, rhythmic sandstone-shale alternations and black shales. The fourth of the five major quartzite horizons, counting from bottom upwards, the Lower Silurian "Criadero Quartzite" is the main host to the mineralization, the four other being barren. It is of Llandoverian (lowermost Silurian) age. Like the four others, the Criadero Quartzite is a blanket-quartzite and was deposited on an epicontinental marine platform. The Palaeozoic rocks underwent only strong diagenesis or anchimetamorphism (SAUPÉ, 1973; SAN MIGUEL ARRIBAS and PAULITSCHE, 1974; SAUPÉ et al., 1991). During the Hercynian orogenesis, these rocks were folded in two episodes.

Abundant flows and some sills of submarine volcanic rocks (basalts and diabases) formed during three epochs: Llandoilo (Lower
than a magmatic one, because no ascension channel has so far been
determined, but a phmatomagmatic explosion seems more probable
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sheet silicates) and of clasts (predominantly altered basalts, shales
cation can sometimes be observed; they form a gently sloped bowl.

The type of the explosion responsible for the Frailesca remains to be
explained. Stippled pattern: Pre-Mesozoic formations.

is a lapilli tuff, consisting of a tine-grained matrix (carbonates and
the Criadero Quartzite soon after its deposition. The rock generally
and quartzite being very subordinate). Graded bedding or stratifi-
maximum thickness amounts to 60 m and its horizontal diameter is
of the Almadén mine it forms a conformable lens within the Criadero
plored depth of 600 m (Fig. 2). Among the volcanoclastic breccias,
with vesicular basalts, they suggest limited water depths. Vertical
dykes of strongly altered rocks intersect the stratigraphic sequence
according to C and O isotope data (weighted means: $^{13}$C = -6.1
$^{18}$O = 15.3 ± 1.6‰/SMOW) (EICHMANN et al., 1977). Limestones and dolostones are very subordinate in the region.
However, derivation of the CO$_2$ from the organic matter, abundant
in the shales, cannot be ruled out (SAUPÉ, 1990). Indeed, the dia-
genesis of the organic matter in shales can produce $^{13}$C values
formerly considered to be typical for the mantle (IRWIN et al., 1977).
The $^{18}$O of the spilite carbonate is largely controlled by seawater,
and the reaction temperature is estimated to be between 200 and
130°C (SAUPÉ, 1990), using the data of NORTHROP and CLAYTON
(1966). Volcanoclastic rocks are present in the sequence. Together
with vesicular basalts, they suggest limited water depths. Vertical
dykes of strongly altered rocks intersect the stratigraphic sequence
and are known in the Almadén mine. SAUPÉ (1990) suggested that
the origin of these rocks was (1) feeder channels of the spilites or (2)
independent later intrusions, preferring the latter. They were provi-
sionally termed "lamprophyres" because of higher K and P contents.

Geology of the Almadén Ore Deposit

At Almadén, the entire stratigraphic sequence was folded to the
vertical and this attitude does not change substantially over the ex-
plored depth of 600 m (Fig. 2). Among the volcanoclastic breccias,
the "Frailesca" is the best known (for a full treatment of this rock
see ALMELA and FEBREL, 1960, and SAUPÉ, 1990). In the upper part
of the Almadén mine it forms a conformable lens within the Criadero
Quartzite, both having been tilted to the vertical during folding. Its
maximum thickness amounts to 60 m and its horizontal diameter is
approximately 300 m. The Frailesca fills a crater blown out through
the Criadero Quartzite soon after its deposition. The rock generally
is a lapilli tuff, consisting of a fine-grained matrix (carbonates and
sheet silicates) and of clasts (predominantly altered basalts, shales
and quartzite being very subordinate). Graded bedding or strati-
fication can sometimes be observed; they form a gently sloped bowl.
The type of the explosion responsible for the Frailesca remains to be
determined, but a phreatomagmatic explosion seems more probable
than a magmatic one, because no ascension channel has so far been
discovered at Almadén. The Frailesca contains no ore, except in a
fracture zone of limited volume. However, the nearby deposit of Las
Cuevas, slightly younger than Almadén, is in a hydrothermal conduit
consisting of a silica cemented breccia containing pyrite, cinnabar,
and native Hg. A similar hydrothermal conduit was found by drilling
underneath the El Entredicho openpit, another productive mine in
the Almadén district (A. Hernandez, written commun., 1988).

The ore minerals impregnate the Criadero Quartzite roughly fol-
lowing stratification. They form three irregular, flattened, crescent-
shaped orebodies surrounding the lower part of the Frailesca lens.
All three have similar dimensions. The largest dimensions are 600
m along the vertical and 450 m along the horizontal, with a maximum
individual thickness of up to 10 m. Two are in the upper, black
quartzite member of the Criadero Quartzite (from top to bottom
San Nicolás and San Francisco) and one in the stratigraphically lower,
white quartzite member of the Criadero Quartzite (San Pedro y San
Diego, in short called San Pedro, Figs. 3 and 4). If restored to their
original horizontal position, the three orebodies would have had their
centres aligned along one vertical line. The Frailesca lens is decentred
by approximately 300 m with respect to this reference line. Thus,
before folding and erosion the Frailesca lens was surrounded by the
sandey sediments. This situation was obscured by subsequent folding
and scissor faulting.

Inclusions of cinnabar in the quartzite between rounded quartz
grains and diagenetic quartz growth rings were observed in a few
thin sections from San Pedro (SAUPÉ, 1967). Cinnabar inclusions
were described from the intersection between spherules of framoidal
pyrite grains. Similarly, they were seen in these pyrite grains between
the framoidal core and the compact diagenetic euhedral outer growth
rings (MAUCHER and SAUPÉ, 1967; ARNOLD et al., 1971). In samples
from private collections, mechanically reworked cinnabar fragments
that induced early gravity deformation in unconsolidated cinnabar
and are evidence for an early arrival of this cinnabar (SAUPÉ, 1973).
Similar samples were found, although not in situ, in the sixth level

![Fig. 1. Geologic sketch map of Spain showing the location of the Almadén district. Stippled pattern: Pre-Mesozoic formations.](image1)

![Fig. 2. Vertical geological section through the Almadén mine (Re-
production of Fig. 12 in SAUPÉ, 1990; with kind permission from Economic Geology, 1990, Vol 85, pp 482-510).](image2)
Sulfur isotope geochemistry of the Hg ores of Almadén, Spain

SAN NICOLAS
SAN Fm
NLSCO
3,465-
ALQ2h ALO=3-j@
Intsmmdlate
Shale
SAN Pmo
Y SAN DIEGO
b
EG421-
At 1 km: 18 ->
1
5m
iii,-
white balYal
qusmlts

FIG. 3. Stratigraphic profile and position of the samples from the Almadén mine. Cross-hatching and italicized small capitals: ore-bodies; italics: profiles; plain lettering: sample designation.

In the San Pedro orebody, the grade of the ore increases stratigraphically upwards, in direction of its hanging wall ("Intermediate Shales"; Figs. 3 and 4). The uppermost bed of the lower quartzite member, separated from the underneath San Pedro orebody by a very thin clayey interlayer, is white and barren (Fig. 3). Such a figure can be explained by a cinnabar impregnation of sands on the sea bottom before the following sand layer (now the white barren quartzite) was deposited (SAUPÉ 1967). It is not compatible with impounding in the sense of MAC Kay (1946) because the clayey interlayer is too thin to have acted as a barrier (SAUPÉ, 1990). These observations led to the conclusion that some cinnabar was deposited at a sediment/seawater interface to explain the abrupt upper limit of the ore of San Pedro. With continuing sedimentation, more cinnabar impregnated the still porous sands of the following layers during a second episode, this time a few meters below the sediment/seawater interface, forming in turn San Francisco and San Nicolas where the ore grades are highest in the centers. A last episode would have produced the other massive ore from the collections and from San Nicolas. Cinnabar is the major ore mineral with subordinate amounts of pyrite. Metallic Hg was abundant a few decades ago, whereas rare metacinnabar is found only in fissures, as fillings or as euhedral crystals and formed later than the cinnabar on this evidence. Microinclusions of chalcopyrite, sphalerite, and galena occur in pyrite crystals found in the barren black sandstone at the base of the Intermediate Shales. This pyrite is independent from the Hg ores and is thought to be diagenetic. The gangue is quartzite, not vein quartz. Euhedral dolomite and barite crystals, subordinate in amount, are found in open fractures formed during the Hercynian orogeny and thus are unrelated to the main cinnabar deposition. They contain minute cinnabar inclusions resulting from late remobilization.

Figures 3 and 4 show the stratigraphic profiles and positions of the orebodies reported on the geological map of the seventeenth level of the Almadén mine.

The concept of an early arrival of the Hg leads to two possible sources of the metal (SAUPÉ, 1973): (1) it may have been remobilized from the Palaeozoic black shales, which have higher background values than the Precambrian shales (2 ppm vs. 0.6 ppm average; whether or not these are really primary values is not yet satisfactorily resolved); (2) Hg may also have directly originated from the mantle, ascending together with the lavas or in a gas phase. Indeed, Devonian lavas host showings of cinnabar at Chillon and Guadalperal. The cinnabar of these two occurrences may have been an original constituent of the magma or may have been remobilized when the Criadero Quartzite was intersected by the ascending magma.

SAMPLES

The S isotope composition was determined for thirty-one cinnabar samples (not including eight repeat analyses of the same sample), one metacinnabar, thirty pyrites, four barites, and total S extractions from three black shales immediately surrounding the ore deposit and from five volcanic rocks (Tables 1 to 4). Among the latter, only three spilites were analyzed because of the difficulty of extracting a sufficient amount of S for mass spectrometry. One is an ordinary sample from surface (EG 254), another is from the footwall sill in the Almadén deposit (EG 421), and the last is from the volcanic pipe of La Nueva Concepción mine (EG 389). A Silurian dolerite (EG 9) and a typical Frailesca sample (EG 67) were also analyzed. Special attention was paid to coexisting pyrite and cinnabar, but only a few such pairs were found. Pyrite samples not directly related to the Hg ores and total S samples were included to investigate possible S sources.

The stratigraphic positions are reported for the mine samples in Figs. 3 and 4. The reported sampling profiles in the mine are all on the seventeenth level (Figs. 4 and 5) that is located within a plane that, before folding, was a vertical section through the ore deposit. This plane is off centre with respect to the Frailesca lens and the geometric centres of the orebodies.

ANALYTICAL PROCEDURES

Mass Spectrometry (MS)

Sample preparation of cinnabar was tedious because of its interlocking with quartz grains (estimated average size of the quartz grains: 100 µm) at a small scale. After grinding the samples to about 50 µm,
The sulphur isotope composition of a synthetic and a natural cinnabar standard

<table>
<thead>
<tr>
<th>Anal. Weight</th>
<th>Yield</th>
<th>$\delta^{34}S$</th>
<th>2σ10</th>
</tr>
</thead>
<tbody>
<tr>
<td>n°</td>
<td>mg</td>
<td>%</td>
<td>%O</td>
</tr>
</tbody>
</table>

**Synthetic standard**

Hg$_2$S (ProLabo batch 25458)

<table>
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<th>Yield</th>
<th>$\delta^{34}S$</th>
<th>2σ10</th>
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<td></td>
<td></td>
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<tr>
<td>1516</td>
<td>11.5</td>
<td>107</td>
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<tr>
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<td>10.6</td>
<td>108</td>
<td>2.1</td>
</tr>
<tr>
<td>1522</td>
<td>13.3</td>
<td>106</td>
<td>3.5</td>
</tr>
<tr>
<td>1524</td>
<td>16.8</td>
<td>108</td>
<td>1.5</td>
</tr>
<tr>
<td>1527</td>
<td>13.7</td>
<td>103</td>
<td>2.7</td>
</tr>
<tr>
<td>1535</td>
<td>14.3</td>
<td>100</td>
<td>1.8</td>
</tr>
<tr>
<td>1537</td>
<td>19.1</td>
<td>106</td>
<td>1.5</td>
</tr>
<tr>
<td>1538</td>
<td>17.6</td>
<td>109</td>
<td>1.9</td>
</tr>
</tbody>
</table>

$x = 2.1$

st. dev. 0.6

**Natural standard**: AL17-40/4 III

(1000°C)

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<th>Yield</th>
<th>$\delta^{34}S$</th>
<th>2σ10</th>
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<tbody>
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<td>1523</td>
<td>15.1</td>
<td>108</td>
<td>6.9</td>
</tr>
<tr>
<td>1525</td>
<td>18.7</td>
<td>98</td>
<td>6.2</td>
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</table>

(1100°C)

<table>
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<th>Yield</th>
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<th>2σ10</th>
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</tr>
<tr>
<td>1530</td>
<td>14.7</td>
<td>100</td>
<td>6.5</td>
</tr>
<tr>
<td>1532</td>
<td>13.8</td>
<td>95</td>
<td>6.2</td>
</tr>
<tr>
<td>1533</td>
<td>19.7</td>
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<td>6.1</td>
</tr>
<tr>
<td>1534</td>
<td>15.0</td>
<td>105</td>
<td>6.6</td>
</tr>
</tbody>
</table>

$x = 6.5$

st. dev. 0.3

cinnabar was handpicked. If not in larger crystals or blebs, pyrite is fortunately scanty in most ore samples and its absence was carefully checked in the analyzed cinnabar fractions. The isotopic analyses were routinely carried out with a double collector "VG 602 D" mass spectrometer. Analytical reproducibility is approximately 0.3% (Table 1), whereas the instrumental reproducibility is usually better than 0.05%. Sulphide S was converted to gaseous SO$_2$ by reacting the sample (10 mg pyrite or 30 mg of cinnabar) with excess CuO at 1050°C following the procedure of HOLT and ENGELKEMIER (1970). The laboratory standard (commercial Cu$_2$O) and a synthetic (commercial HgS). The natural standard (Table 1) was from a variety of morphological types, and the spread of their $\delta^{34}S$ is much larger than for cinnabar. Each sulphide morphology exhibits a distinctive range of $\delta^{34}S$ values. In the Almadén deposit itself, the following morphological pyrite types were studied, listed in a stratigraphically ascending order (Table 3).

1) Intimately mixed pyrite and cinnabar in the uppermost layer of the San Pedro orebody have only slightly different $\delta^{34}S$ values, the pyrite S being heavier than cinnabar S as theoretically expected (OHMOTO and RYE, 1979).

2) Pyrite (sample 22) from a 1 to 2 cm thick pyrite layer on top of the San Pedro orebody and separated from it by a white barren quartzite bed has a $\delta^{34}S$ of 16.4%.

3) Disseminated pyrite forming seams parallel to the bedding of the black barren quartzite between the San Pedro and the San Francisco orebodies (samples AL 0-2 and AL 0-3) have $\delta^{34}S$ values near 0%. Pyrite from another seam (sample 7) has $\delta^{34}S$ of about 9%. A pyrite (sample 18) at approximately the same stratigraphic position and collected from a barren dark quartzite 1 km east of the mine has a $\delta^{34}S$ of 7.8%. YIELD OF THE SULPHUR ISOTOPIC DISTRIBUTIONS<br>RESULTS<br>The analytical results for minerals and rocks are given in Tables 2 to 4 and Figs. 5 to 8. The most striking overall features are a small spread for the $\delta^{34}S$ values for cinnabar within each orebody (Table 2) and notable qualitative and quantitative differences between the three orebodies (Table 5). In the San Pedro orebody, the $\delta^{34}S$ increases stratigraphically upwards (Fig. 5a). In the topmost and richest ore layer of San Pedro the $\delta^{34}S$ decreases laterally from the centre outwards. Profile IV (east of San Pedro—Fig. 5a) (av. $\delta^{34}S$ = 6.1%) and profile VI (west of San Pedro) (av. $\delta^{34}S$ = 5.2%) are situated on both sides of profile I (centre of San Pedro) (av. $\delta^{34}S$ = 6.4%). The distributions of the $\delta^{34}S$ in the two upper orebodies, San Francisco (profile III—perpendicular to stratification; Fig. 5b) and San Nicolas (profile II—perpendicular to stratification; Fig. 5c) follow symmetric patterns. The $\delta^{34}S$ values are highest toward the centres of the lenses and decrease towards the stratigraphic top and bottom (the lateral variation of the $\delta^{34}S$ was not investigated in these two orebodies). Thus, both $\delta^{34}S$ distribution patterns reproduce the distribution patterns of the ore grades as they can be observed on stope faces. Unfortunately this $\delta^{34}S$ vs. grade relation could not be quantified, because initially the sampling was not devised to include Hg analyses.

Three barite samples have a very small dispersion and an average $\delta^{34}S$ of 8.5%, but the fourth lies significantly apart ($\delta^{34}S$ = 14.9%; Table 4).

Pyrite is rare in the Precambrian clastic formations of Almadén (alternations of greywackes and schists) and one individual cm-sized crystal has a $\delta^{34}S$ = -8.0% (Table 5). The sulphide $\delta^{34}S$ (Table 3) of the three black shales surrounding the Almadén deposit (Figs. 2, 3, and 4) show a wide spread resulting from the important palaeogeographic changes evidenced by lithological changes. The pyrite samples collected near the ore (although in some cases genetically unrelated to it) come from a variety of morphological types, and the spread of their $\delta^{34}S$ is much larger than for cinnabar. Each sulphide morphology exhibits a distinctive range of $\delta^{34}S$ values. In the Almadén deposit itself, the following morphological pyrite types were studied, listed in a stratigraphically ascending order (Table 3).

Secondary Ion Mass Spectrometry (SIMS)

The $\delta^{34}S$ values of coeval cinnabar and pyrite were determined in one polished section by SIMS on the Cameca "IMS 3F" ion probe at the CRPG by M. Chaussidon. Analytical reproducibility is usually better than 1.5%. SIMS permits the analysis of grains as small as 30 μ. The analytical procedure is reported by CHAUSSIDON and DEMANGE (1988).

Table 1. Sulphur isotope composition of a synthetic and a natural cinnabar standard
Table 2. Sulphur isotope composition of sulphides along profiles in the Almadén mine (level 17) (listed from top to bottom if the profile is perpendicular to stratification)

<table>
<thead>
<tr>
<th>Anal.</th>
<th>Sample</th>
<th>Mineral</th>
<th>Yield</th>
<th>δ</th>
<th>σ</th>
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<tbody>
<tr>
<td>n°</td>
<td>n°</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Profile I - San Pedro (perpendicular to stratification)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1594</td>
<td>AL17/40/4.1</td>
<td>Cinnabar</td>
<td>83</td>
<td>7.3</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>1587</td>
<td>AL17/40/7.1</td>
<td>Cinnabar</td>
<td>108</td>
<td>6.4</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>3477</td>
<td>AL17/40 (10)</td>
<td>Pyrite</td>
<td>99</td>
<td>7.7</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>3478</td>
<td>AL17/40-3a</td>
<td>Pyrite</td>
<td>88</td>
<td>7.3</td>
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<tr>
<td>3479</td>
<td>AL17/40-3b</td>
<td>Pyrite</td>
<td>90</td>
<td>6.9</td>
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<tr>
<td>3480</td>
<td>AL17/40-3c</td>
<td>Pyrite</td>
<td>92</td>
<td>8.3</td>
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Profile II - San Nicolas (perpendicular to stratification)

<table>
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<th>δ</th>
<th>σ</th>
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<tbody>
<tr>
<td>4011</td>
<td>II - 11</td>
<td>Cinnabar</td>
<td>108</td>
<td>0.1</td>
</tr>
<tr>
<td>3898</td>
<td>II - 7</td>
<td>Cinnabar</td>
<td>105</td>
<td>-0.3</td>
</tr>
<tr>
<td>3897</td>
<td>II - 5</td>
<td>Cinnabar</td>
<td>104</td>
<td>1.2</td>
</tr>
<tr>
<td>3896</td>
<td>II - 4</td>
<td>Cinnabar</td>
<td>107</td>
<td>0.8</td>
</tr>
<tr>
<td>3895</td>
<td>II - 3</td>
<td>Cinnabar</td>
<td>106</td>
<td>1.2</td>
</tr>
<tr>
<td>3894</td>
<td>II - 2</td>
<td>Cinnabar</td>
<td>104</td>
<td>-1.6</td>
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Profile III - San Francisco (perpendicular to stratification)

<table>
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<th>δ</th>
<th>σ</th>
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<tbody>
<tr>
<td>1579</td>
<td>III - 1</td>
<td>Cinnabar</td>
<td>90</td>
<td>7.4</td>
</tr>
<tr>
<td>1540</td>
<td>III - 2</td>
<td>Cinnabar</td>
<td>98</td>
<td>7.3</td>
</tr>
<tr>
<td>1542</td>
<td>III - 2/3</td>
<td>Cinnabar</td>
<td>102</td>
<td>7.3</td>
</tr>
<tr>
<td>1541</td>
<td>III - 3</td>
<td>Cinnabar</td>
<td>105</td>
<td>8.2</td>
</tr>
<tr>
<td>1544</td>
<td>III - 4</td>
<td>Cinnabar</td>
<td>104</td>
<td>8.1</td>
</tr>
<tr>
<td>1547</td>
<td>III - 5</td>
<td>Cinnabar</td>
<td>109</td>
<td>9.0</td>
</tr>
<tr>
<td>1548</td>
<td>III - 7</td>
<td>Cinnabar</td>
<td>95</td>
<td>8.4</td>
</tr>
<tr>
<td>1546</td>
<td>III - 7</td>
<td>Cinnabar</td>
<td>101</td>
<td>8.9</td>
</tr>
<tr>
<td>1552</td>
<td>III - 8</td>
<td>Cinnabar</td>
<td>108</td>
<td>8.1</td>
</tr>
<tr>
<td>1554</td>
<td>III - 9</td>
<td>Cinnabar</td>
<td>107</td>
<td>8.9</td>
</tr>
<tr>
<td>1511</td>
<td>III - 10</td>
<td>Cinnabar</td>
<td>100</td>
<td>7.0</td>
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</table>

Profile IV - San Pedro (E - perpendicular to stratification)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>Yield</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>3904</td>
<td>IV - 1</td>
<td>Cinnabar</td>
<td>103</td>
</tr>
<tr>
<td>3903</td>
<td>IV - 2</td>
<td>Cinnabar</td>
<td>103</td>
</tr>
<tr>
<td>3905</td>
<td>IV - 3</td>
<td>Cinnabar</td>
<td>108</td>
</tr>
<tr>
<td>3906</td>
<td>IV - 5</td>
<td>Cinnabar</td>
<td>100</td>
</tr>
<tr>
<td>3907</td>
<td>IV - 6</td>
<td>Cinnabar</td>
<td>105</td>
</tr>
<tr>
<td>3909</td>
<td>IV - 8</td>
<td>Cinnabar</td>
<td>100</td>
</tr>
</tbody>
</table>

Profile VI - San Pedro (W - parallel to stratification)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>Yield</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1582</td>
<td>VI - 1</td>
<td>Cinnabar</td>
<td>100</td>
</tr>
<tr>
<td>1574</td>
<td>VI - 2</td>
<td>Cinnabar</td>
<td>104</td>
</tr>
<tr>
<td>1581</td>
<td>VI - 3</td>
<td>Cinnabar</td>
<td>106</td>
</tr>
</tbody>
</table>

4) Three pyrite nodules (samples 3, 4, and 5) in the barren footwall quartzite of the San Francisco orebody have positive and widely variable values (five values between 8.6 and 9.9%; high values of 17.0 and 26.8% correspond to central parts of nodules; Fig. 6). Diagenetic quartz observed within one of these nodules has a fibrous facies.

5) The pyrite rim (samples 1 and 2) surrounding an early diagenetic dolomite nodule has the lightest sulphur found in Almadén (−14.7%), in contrast with the δ34S of the hosting black Hanging Wall Shale (14.4%). The soluble sulphate concentration of this shale is negligible and is not responsible for its heavy S.

The volcanic rocks of Almadén have the following S systematics. (1) The S concentration is high (2500 ppm on average, compared to about 1000 ppm in normal alkali olivine basalts), mainly as sulphide (pyrite is the only sulphide visible in polished sections of EG 389 and predominates over chalcopyrite in EG 67). (2) Soluble sulphates are subordinate, and even if all the Ba was present as barite, the sulphide/sulphate ratio would not be substantially changed. (3) The δ34S is positive, up to 6.8%, deviating from assumed mantle values around 1 to 2%. (4) The δ34S is positively correlated with the S concentration (Fig. 7).

Useful primary fluid inclusions could not be identified. Isolated fluid inclusions in the rounded quartz grains are meaningless because they were formed in much earlier events than the ore. The fluid inclusions in the diagenetic overgrowth could give a clue to the conditions of the diagenesis (and thus pro parte to the conditions during ore deposition), but they are too small to be studied. Grains and overgrowths are indifferently intersected by warped and healed cracks trapping numerous inclusions, also too small to be studied. They could only point to the conditions during a period of intense deformation which remobilized part of the cinnabar. Larger fluid inclusions were found in euhedral cinnabar crystals grown in open spaces during or after deformation, but they decrpatimated, possibly during sample preparation. This difficulty is general for cinnabar, and “Fluid Inclusion Research” reports little data on cinnabar-hosted fluid inclusions.

**DISCUSSION**

The main guidelines for discussion are: Did the S isotope composition of the Almadén ores remain unchanged since their deposition? Which of the two ultimate sources (mantle or Silurian seawater) provided this S? Did this happen directly or through intermediate reservoirs (black shales or spilites for example)? Are coeval cinnabar and pyrite in isotopic equilibrium and can they serve as geothermometers? Is the distribution of the δ34S values observed in the orebodies significant?

**Effects of Metamorphism and Remobilization**

During regional metamorphism isotopic exchange can take place, and many authors agree that the fractionation between sulphide pairs systematically varies with metamorphic grade. It is admitted that pyrite does not isotopically reequilibrate with the S concentration (Fig. 7) of the orebody, but they are too small to be studied. They could only point to the conditions during a period of intense deformation which remobilized part of the cinnabar. Larger fluid inclusions were found in euhedral cinnabar crystals grown in open spaces during or after deformation, but they decrpatimated, possibly during sample preparation. This difficulty is general for cinnabar, and “Fluid Inclusion Research” reports little data on cinnabar-hosted fluid inclusions.
Table 3. Sulphur isotope composition of various pyrites and rocks from the Almadén mine and area

<table>
<thead>
<tr>
<th>Anal. Sample</th>
<th>Mineral</th>
<th>Yield</th>
<th>δ</th>
<th>2σ10</th>
</tr>
</thead>
<tbody>
<tr>
<td>o</td>
<td>n</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1598 1</td>
<td>Crust surrounding a dolomite nodule of hanging wall shale</td>
<td>Pyrite</td>
<td>100</td>
<td>-14.3</td>
</tr>
<tr>
<td>1609 2</td>
<td>Pyrite nodule 1 (id. 2)</td>
<td>Pyrite</td>
<td>91</td>
<td>26.8</td>
</tr>
<tr>
<td>3462 3-c</td>
<td>Pyrite nodule 2 in the orebody</td>
<td>Pyrite</td>
<td>95</td>
<td>17.0</td>
</tr>
<tr>
<td>3463 4-a</td>
<td>San Francisco footwall quartzite of the Pyrite</td>
<td>Pyrite</td>
<td>96</td>
<td>9.9</td>
</tr>
<tr>
<td>3469 4-c</td>
<td>Pyrite nodule (id. 2)</td>
<td>Pyrite</td>
<td>79</td>
<td>8.9</td>
</tr>
<tr>
<td>3470 5.1</td>
<td>Pyrite nodule (id. 2)</td>
<td>Pyrite</td>
<td>91</td>
<td>-8.0</td>
</tr>
<tr>
<td>3474 5.9</td>
<td>Barren Criadero quartzite</td>
<td>Pyrite</td>
<td>39</td>
<td>7.8</td>
</tr>
<tr>
<td>1631 AL0-2</td>
<td>Bedded dissemination</td>
<td>Pyrite</td>
<td>103</td>
<td>0.8</td>
</tr>
<tr>
<td>1633 Al1-1</td>
<td>Bedded dissemination</td>
<td>Pyrite</td>
<td>109</td>
<td>-0.1</td>
</tr>
<tr>
<td>1637 7</td>
<td>Isolated pyrite crystals in seams</td>
<td>Pyrite</td>
<td>90</td>
<td>9.6</td>
</tr>
<tr>
<td>3468 7</td>
<td>Layer on top barren quartzite</td>
<td>Pyrite</td>
<td>95</td>
<td>8.8</td>
</tr>
<tr>
<td>3475 22</td>
<td>Barren Criadero quartzite</td>
<td>Pyrite</td>
<td>71</td>
<td>16.4</td>
</tr>
<tr>
<td>3473 18</td>
<td>Precambrian</td>
<td>Pyrite</td>
<td>39</td>
<td>7.8</td>
</tr>
<tr>
<td>1593 19</td>
<td>Precambrian</td>
<td>Pyrite</td>
<td>103</td>
<td>-8.0</td>
</tr>
<tr>
<td>4104 4003</td>
<td>Footwall  Black shale</td>
<td>Total S</td>
<td>101</td>
<td>5.5</td>
</tr>
<tr>
<td>4105 4005</td>
<td>Intermed. Black shale</td>
<td>Total S</td>
<td>99</td>
<td>-6.7</td>
</tr>
<tr>
<td>4106 4006</td>
<td>Hang. wall  Black shale</td>
<td>Total S</td>
<td>95</td>
<td>14.4</td>
</tr>
<tr>
<td>3625 4005</td>
<td>Spilite (N. Concepcion)</td>
<td>Total S</td>
<td>101</td>
<td>6.8</td>
</tr>
<tr>
<td>3626 4005</td>
<td>Spilite (Ordovician)</td>
<td>Total S</td>
<td>98</td>
<td>5.3</td>
</tr>
<tr>
<td>3629 4005</td>
<td>Spilite (Footwall Almadén mine)</td>
<td>Total S</td>
<td>98</td>
<td>3.1</td>
</tr>
<tr>
<td>3628 4005</td>
<td>Frailesca (Almadén mine)</td>
<td>Total S</td>
<td>100</td>
<td>1.9</td>
</tr>
<tr>
<td>3467 4005</td>
<td>Dolerite (Silurian)</td>
<td>Pyrite</td>
<td>10</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Table 4. Sulphur isotope composition of various barites and mercury sulphides from the Almadén mine

<table>
<thead>
<tr>
<th>Anal. Sample</th>
<th>Mineral</th>
<th>Yield</th>
<th>δ</th>
<th>2σ10</th>
</tr>
</thead>
<tbody>
<tr>
<td>o</td>
<td>n</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4014 TV 1 (mine run)</td>
<td>Barite</td>
<td>102</td>
<td>8.3</td>
<td>0.06</td>
</tr>
<tr>
<td>4015 TV 2 (mine run)</td>
<td>Barite</td>
<td>104</td>
<td>8.5</td>
<td>0.02</td>
</tr>
<tr>
<td>4017 AL17-5</td>
<td>Darmic</td>
<td>102</td>
<td>8.8</td>
<td>0.07</td>
</tr>
<tr>
<td>4393 AL17-54</td>
<td>Barite</td>
<td>98</td>
<td>14.9</td>
<td>0.05</td>
</tr>
<tr>
<td>4012 Late cinnabar</td>
<td>102</td>
<td>5.0</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>4013 Metacinnabar</td>
<td>103</td>
<td>-14.1</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

Almadén folding and deformation was accompanied by a local remobilization of cinnabar into small cracks of the host rock. It has not been possible to sample separately the cinnabar from the veinlets and from the impregnations. Because the samples analyzed are a mixture of both types in variable proportions, and because the two orderly δ34S distributions in the ore lenses were not obliterated, it is possible to conclude that cinnabar did not isotopically reequilibrate during metamorphism.

Late cinnabar (δ34S = 5.0%, Table 4) maintains the S isotope composition of the first cinnabar generation (mean δ34S = 5.6%). To the contrary, at Almadén metacinnabar δ34S (= -14.1%, Table 4) strongly differs from that of cinnabar (mean δ34S = 5.6%). Because the polymorphic transformation metacinnabar to cinnabar should not affect the S isotopic composition, the metacinnabar and cinnabar of Almadén do not result from a polymorphic transformation. The cinnabar must have been dissolved and precipitated as metacinnabar above the inversion temperature (about 345°C).
Sulfur isotope geochemistry of the Hg ores of Almadén, Spain

POTTER and BARNES, 1978). At New Idria, California, the $\delta^{34}S$ for metacinnabar (0.0 to 3.2%) and for cinnabar (1.3 to 4.4%) overlap (BOCTOR et al., 1987).

**Source of the S in the Country Rocks of the Almadén Ore Deposit (Spilites, Black Shales, and Quartzites)**

Because the S of the ore minerals may be derived from the spilites or from the black shales, these two possible sources will be discussed first.

**Estimate of the total S concentration and the $\delta^{34}S$ of the upper mantle**

An evaluation of the S geochemistry in the spilites can be attained reviewing the total S concentration and $\delta^{34}S$ of basalts in general (SCHNEIDER, 1970) of unaltered ocean-floor basalts (MOORE and FABBI, 1971; JOHNSON, 1972; MOORE and SCHILLING, 1973; KANEHIRA et al., 1973; GRINENKO et al., 1975; MOTTI et al., 1979; ARNOLD and SHEPPARD, 1981; SAKAI et al., 1984; UEDA and SAKAI, 1984; VON GEHLEN, 1988), of the upper mantle (CHAUSSIDON, 1988; CHAUSSIDON et al., 1989), and of ultramafic rocks and carbonatites (MITCHELL and KROUSE, 1975; GRINENKO et al., 1987).

The wide petrographical and geotectonic range of the material analyzed does not result in a great variability. From this short review we take for the upper mantle a S concentration of 1000 ppm essentially present as sulphides or dissolved in the basaltic glasses, within the range of 850 ± 150 ppm given by NIELSEN (1978), and a $\delta^{34}S$ of 1%.

**A "dynamic system": DSDP hole 504 B**

The data reported above are somewhat "static" because they were aimed at characterizing the undifferentiated mantle. The DSDP hole 504 B was drilled at approximately 1°N, between the Ecuador and the Panama Fracture Zones. It offers the first "dynamic" insight into the evolution of the S geochemistry within a 1288 m deep section of hydrothermally altered oceanic crust. The volcanic pile intersected by hole 504 B is made up of three different units: the dyke zone at the bottom, the transition zone, and the pillow zone at the top. The reaction between the basalts of this pile and the convectively circulating seawater led to (1) a redistribution of magmatic S within the pile, (2) a fixation of part of the seawater S, and (3) the loss of some magmatic S to the seawater. The combined result of these processes is an increase in both the total S concentration and the $\delta^{34}S$ in the upper oceanic crust (ALT et al., 1989).

**Application to the spilites of Almadén**

The system intersected by hole 504 B (ALT et al., 1989) differs in various aspects from the situation studied here. At Almadén, the flows are normally a few, exceptionally a few tens of m thick; they are separated by shales, tuffs, or sandstones. Thus, the geometry and the duration of the hydrothermal circulation were different from those in a thick basaltic pile, and deep descending convective circulations do not seem to have occurred at Almadén. The deviation of the $\delta^{34}S$ of basic volcanic rocks of Almadén (Table 5) from the mantle values can be explained by one or several of the following processes (FAURE, 1986): (1) contamination by

---

**Table 5. Average $\delta^{34}S$ features for the cinnabar of the three orebodies**

<table>
<thead>
<tr>
<th>Orebody</th>
<th>Average $\delta^{34}S$</th>
<th>Sample number</th>
<th>$\sigma_{0.1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>San Nicolas</td>
<td>0.2</td>
<td>6</td>
<td>1.1</td>
</tr>
<tr>
<td>San Francisco</td>
<td>8.1</td>
<td>11</td>
<td>0.71</td>
</tr>
<tr>
<td>San Pedro</td>
<td>5.9</td>
<td>13</td>
<td>0.99</td>
</tr>
</tbody>
</table>

---

**Fig. 6. Isotopic analyses of pyrite from a diagenetic pyrite nodule (the dotted line is a visible discontinuity within the nodule).**
country rocks, (2) alteration by seawater, and (3) outgassing of \( \text{SO}_2 \). The positive \( \delta^{34}\text{S} \) vs. wt% S correlation (Fig. 7) together with the S enrichment in the basalts at Almadén can only be explained by introduction of extraneous S of constant isotopic composition, and thus process (3) is not the dominant process.

An experimental fractionation of the S isotopes (e.g., during the chemical extraction from whole rocks) cannot explain the linear array of the \( \delta^{34}\text{S} \) vs. S% in Fig. 7 for two reasons. (1) The isotope analysis on the dolerite was obtained on a pyrite separate, not on a total S extract. (2) No linear correlation was observed in two other sample sets, prepared and analyzed at the CRAG by the same procedures \([a]\) the shales of this study \((n = 3)\) and \(b\) a set of BIF samples \((n = 16)\); \cite{Arnold1990}.

From the regression line of Fig. 7 it appears that for 0.1% S the \( \delta^{34}\text{S} \) would be of 0.6%, typical values for oceanic basalts. Taking the above estimated average S concentration for the upper mantle of 1000 ppm and the average concentration of the Almadén spilites of 2500 ppm \(^1\) at \( \delta^{34}\text{S} = 5.1\%\), some 1500 ppm S were added to the rock. Let \( x \) be the original \( \delta^{34}\text{S} \) of the basaltic magma of Almadén and \( y \) the \( \delta^{34}\text{S} \) of the additional S. From isotopic and the mass balance considerations we can write

\[
(1000x + 1500y)/2500 = 5.1.
\]

For \( x = 0.6 \), as derived from Fig. 7, \( y = 8.1\% \), surprisingly the most frequent \( \delta^{34}\text{S} \) value for pyrite independent from mineralization.

\cite{Ueda1984} have shown that \( \delta^{34}\text{S} \) values for basalts may reach 7%, but always in S-depleted basalts, which is not the case for Almadén. A S enrichment can be the result of a reduction of seawater sulphate circulating within basalts by oxidation of the Fe\(^{2+}\) of olivine and pyroxene as proposed by \cite{Ohmoto1979} and \cite{Mottl1979}. The corresponding transformation of S\(^{6+}\) to S\(^{2-}\) requires the oxidation of 8 Fe\(^{2+}\) to Fe\(^{3+}\), i.e., 14 g Fe for 1 g of S. As an average alkali basalt contains 6.2% Fe\(^{2+}\) (8% FeO), this amount of Fe allows the reduction of a maximum of 0.44 g S/100 g of basalt. A complete reaction would lead to the formation of 0.83 g of pyrite/100 g of rock, but is excluded because the S isotope and the mass balances cannot be satisfied at the same time: if \( y = 28 \) in the above reaction, the right member would be 17.0%, far from the observed 5.1%.

From the mass balance only, the 0.44 g of reduced S would be sufficient to account for the increase of 1500 ppm S. The low \( \text{SO}_2 \) concentration of the spilites shows that little seawater anhydrite was preserved in the spilites during cooling of the convectively ascending seawater or that the excess \( \text{SO}_2 \) was completely exported. The low abundance of \( \text{SO}_2 \) (anhydrite), compared to that of S\(^{2-}\), is common to most samples from the oceanic crust. It agrees with the retrograde solubility of anhydrite, but conflicts with the experiments on the seawater basalt interaction (cf. \cite{Mottl1979}) which supposes the formation of anhydrite (\cite{Hubberten1990}). It is best explained by anhydrite dissolution in the late stages of magma cooling.

The reaction temperature of splitzatization was estimated from the O isotope data to be between 130 and 200°C \cite{Saupe1990}. This study also showed that the \( \delta^{16}\text{O} \) of the secondary carbonates was largely controlled by seawater. But only at 255°C would the sulphate/sulphide equilibrium isotopic fractionation give the mean \( \delta^{34}\text{S} \) of 5% determined for the spilite sulphides (read from fig. 10.3 of \cite{Ohmoto1979}). This contradiction is not satisfactorily resolved. The transformations observed in the splitized basalts of Almadén are similar to those described for the Upper Devonian/Lower Carboniferous mafic volcanic rocks of the South-Iberian Pyrite Belt (e.g., \cite{Munna1980}) for which S isotope data on possible source rocks are missing. The spread for the \( \delta^{34}\text{S} \) values of the Almadén spilites (3.1 to 6.8% for 3 samples, \( x = 5.1\%\)) is indicative of variable seawater contamination, whereas the good linear correlation suggests a nearly constant temperature.

The present mine openings in the Frailasca are notably dry and impervious. This suggests that this rock was never percolated by anhydrite transporting solutions. Thus, little \( \text{SO}_2 \) was reduced, and consequently the \( \delta^{34}\text{S} \) of the Frailasca \( \delta^{34}\text{S} = 1.9\% \) is lower than that of the spilites \( \delta^{34}\text{S} = 5.1\% \) and closer to the "mantle" value.

The values found for the three "lamprophyre" veins (Table 5) do not help solve the origin of these highly altered rocks, which are difficult to classify: \cite{Saupe1990} argued that they were probably independent later intrusions. Because, unlike normal lamprophyres, these rocks are enriched in S (0.17 to 1.28% total S, essentially as pyrite), their S content and \( \delta^{34}\text{S} \) variability are related to exchanges with the host rocks and their formation waters.

Black shales

In ancient (e.g., Early Carboniferous of the Yasnopolyan Basin, Russian Platform; \cite{Migdisov1974}, as in present argillaceous sediments (\cite{Azov1974}; \cite{Baltic1969}; \cite{Hartmann1969}; \cite{Lein1983}; \cite{Black1962}) pyrite \( \delta^{34}\text{S} \) is higher in continental and coastal zones than in deep sea sediments. In present sediments, the Eh is one of the factors controlling the pyrite \( \delta^{34}\text{S} \) in anoxic sediments it ranges from −25 to −32%, whereas in the sediments from the oxygenated shallow margins it is in the 0 to 11% range. \cite{Sangster1968} statistically established that the \( \delta^{34}\text{S} \) of pyrite resulting from

---

Footnote:

\(^1\) Average of 20 spilite samples. \( \text{SO}_2 \) is below 100 ppm in 14 samples and has an average of 200 ppm for the remaining six others.
A bacterial reduction of seawater sulphate is shifted by 13.9% towards negative values relative to the contemporary seawater sulphate. The shift is much higher under euxinic conditions and may reach −50%. Schwarcz and Burnie (1973), limiting their investigations to clastic environments, found that a decrease of about 25% (compared to the 13.9% shift of Sangster, 1968) and a large spread of δ34S values are characteristic for shallow sea or brackish water environments (type 1), whereas deep and euxinic basins display a −50% decrease with a narrow spread of δ34S values (type 2). Large fractions can be explained as a combination of the shift due to bacterial reduction of seawater sulphate with shifts induced by intermediate inorganic compounds, such as thiosulphates (Arnold and Saupé, 1988). The abundance of reactive Fe during diagenesis largely controls the formation of pyrite (Canfield, 1989) which in turn controls the isotopic composition of the pyrite S (Gautier, 1987).

**Application to the black shales of Almadén**

The low δ34S value (−8%) for the Precambrian pyrite found in a greywacke (Table 3) can be compared to the δ34S values of Precambrian seawater sulphate as read from Fig. 9 of Claypool et al. (1980):

- 600 m.y.: δ34S = 30%
- 650 m.y.: δ34S = 21%
- 700 m.y.: δ34S = 15%

The host rock, the predominant rock type in the Precambrian formations, excludes a euxinic environment, and the absence of mineralized fractures does not suggest a later introduction of pyrite. If simple bacterial seawater sulphate reduction in an infinite reservoir is postulated, a δ34S decrease of about 25% (Schwarcz and Burnie, 1973) could be expected. Accordingly, the value at −8% is in better accord with the Riphean age (650–1600 m.y.) proposed for these formations by San José (1983) than with the generally accepted Vendian age (Uppermost Precambrian, 600–650 m.y., by García San Segundo et al., 1986; Molina Camara and Fernandez Carrasco, 1987).

During the Lower Silurian there was an anoxia crisis of wide geographical extension (Sahara, Western and Central Europe) expressed by the Graptolite Shale facies, the equivalent of which in Almadén is the Hanging Wall Shale. This facies is slightly diachronous (Saupé, 1973). Its S isotope geochemistry has been little investigated. The variation range of the pyrite δ34S between the different lithostratigraphic units of a profile through Graptolite Shales (i.s.) in Bavaria, Germany, is broad (−22.1 to 18.8%, with a mean of −4.5% for twenty samples) (Dill and Nielsen, 1986). A broad variability was also found within the different lithostratigraphic units of this profile, e.g., within the stratigraphic equivalent of the Almadén Hanging Wall Shales (−22.1, −16.5, and −1.5%; Dill and Nielsen, 1986). Silurian black shales from the Harz, Germany, have a δ34S below −18%, with a mode between −25 and −30% (Nielsen, 1968).

At the time of deposition of the Criadero quartzite (transition Ordovician/Silurian) and of the Hanging Wall Shale, the δ34S of the seawater sulphate was approximately 28% (Claypool et al., 1980). The large differences in the δ34S of the three black shales (Upper Ordovician/Lower Silurian) cannot be explained by variations of the δ34S of the seawater sulphate because the three samples are almost coeval. The Footwall Shales with a δ34S = 5.5% correspond to seawater sulphate reduced in slightly euxinic conditions (28−5.5 = 22.5%), whereas the δ34S of the Hanging Wall Shales (14.4%) corresponds to normal bacterial reduction (28 14.4 = 13.6%). Only the Intermediate Shales (δ34S = −6.7) denote stronger euxinic conditions or possibly greater kinetic effects. The latter cannot be appreciated because it is not possible to determine the type of organic matter. The observed difference between the pyrite of the Intermediate Shales and the contemporaneous seawater sulphate (Δ = 28% − (−6.7%) = 34.7%) agrees with values for the type 1 distribution of Schwarcz and Burnie (1973) found in shallow marine or brackish-water environments. The respective δ34S figures for the Hanging Wall Shales (14.4%) and for the pyrite (samples 1 and 2) fringing the dolomite nodules hosted by these shales (−14.7%) are odd. They cannot be explained by the dissolution of an early pyrite of the shales and its reorientation around the nodule, which would introduce only a small shift of the δ34S. Nor is it possible to postulate that the pyrite rim crystallized before the disseminated pyrite so that the shift of the δ34S values be positive. Only a two-step process can explain this situation: (1) the disseminated pyrite crystallized first through bacterial sulphate reduction and (2) euxinic conditions developed later by increasing anoxia and the rim pyrite developed by sulphate reduction under euxinic conditions.

A bacterial reduction of Silurian seawater sulphate alone would give pyrite with a δ34S of about 14% following Sangster (1968, 1976) or of about 3%, with a large spread following Schwarcz and Burnie (1973). Thus, the disseminated pyrite in the shales developed under euxinic conditions, with great local variability.

**Pyrite in the Criadero Quartzite**

Some of the analyzed pyrites (Fig. 3 and Table 3) are unrelated to the Hg mineralization, although they occur only a small distance from the latter (for a detailed description of these pyrites see Maucher and Saupé, 1967, and Arnold et al., 1971). They were included in this study because they provide information on the geologic setting. Pyrite sample 22 (Fig. 3) from a few-centimetre-thick pyrite bed on top of the white quartzite overlying the San Pedro ore lens has a δ34S of 16.4%, strongly differing from the δ34S = −6.7% in the Intermediate Shales situated a few tens of cm stratigraphically higher and from the average 5.9% found for the pyrite layer in the ore (Fig. 8). Pyrite crystals (sample 7) disseminated in seams parallel to the bedding in the black barren sandstone between the San Pedro and the San Francisco orebodies have an average δ34S of 9.2%. Other bedded disseminations (AL 0-2 and AL 0-3) have near zero δ34S values. Three pyrite nodules (samples 3, 4, and 5) collected in a white quartzite bed in the footwall of San Francisco have similar δ34S with surprisingly high values in the centres of the nodules (17.0 and 26.8%; Fig. 6), not explicable by a Rayleigh process, because in such an event the crystallization...
Several intermediate processes may produce the sulphur
of the sulphides and sulphates of the Almadén ores starting
from the two ultimate sources, seawater and mantle. A list
will guide the discussion:

1) derivation from mantle fluids, by degassing slightly pre-
ceeding the intrusion or eruption of the Silurian basalts,
2) convective leaching of S from basalts, not forgetting that
at Almadén most basalts were emplaced on or near sea
bottom, and after the ore (Saüpe, 1990),
3) reduction of contemporary (=Lower Silurian) seawater
sulphate above 300°C in a convective circuit
\[ \text{(SO}_4^-/\text{H}_2\text{S equilibrium reaction)} \]
4) bacterial reduction of the contemporary seawater sulphate,
5) convective remobilization of sulphides contained in the
pre-Silurian formations (Precambrian or Ordovician),
6) a combination of two or several of these different sources.

The unweighted $\delta^{34}$S average for the thirty-one cinnabars
is 5.6%, compared to 5.1% for the three spilites and 5.5%
for the Footwall Shale sample. The small dispersion of the
$\delta^{34}$S within each of the three orebodies eliminates possibilities
(3) and (4). The large difference between the respective $\delta^{34}$S
eliminates the Precambrian pyrite ($\delta^{34}$S = −8.0%) from
possibility (5) but not the Footwall Shale ($\delta^{34}$S = 5.5%). If
the cinnabar S were mantle S, one could indeed expect a
small dispersion but the $\delta^{34}$S should be closer to 1 or 2%0
and should not differ between the orebodies; thus, possibility
(1) is not plausible, except maybe for the San Nicolas orebody
(\(\delta^{34}\) = 0.2%). From this discussion, the Footwall Shales and/
or the spilites seem the most probable source for the cinnabar
sulphur. Because the Footwall Shales are preceding the min-
eralization, they are thought to be the best potential source.
They were also interpreted as the source of the Hg. Both
likely migrated together in direction of the future eruption
centres, evidenced by the frailesca lenses. Mercury was prob-
ably transported as a bisulfide complex (Barnes, 1979),
though other complexes are not ruled out (Krupp, 1988).

The isotopic differences between the three orebodies and the
average $\delta^{34}$S of 8.1% for the San Francisco orebody, higher
than the $\delta^{34}$S of the postulated source, makes improbable a
single sulphur source. Only the addition of S formed by re-
duction of contemporaneous seawater sulphate can explain
the shift toward heavier values observed for San Francisco.

The small spread of the isotopic compositions of three of
the barites indicates constant conditions during their for-
mation. The $\delta^{34}$S value of 8.5% is some 20% below that of
Silurian seawater (28%, Claypool et al., 1980) and elimi-
nates a straightforward seawater origin for the sulphate. As
this figure is approximately the mode of the syn genetic pyrite,
oxidation of the latter may have produced the sulphate S.

**Sulphur Fractionation Between Cinnabar and Pyrite-
Isotopic Equilibrium**

The S fractionation between cinnabar and pyrite in general
has been considered by a few authors only. Some information
can be obtained using (1) a theoretical approach, (2) data
from experimentation, and (3) consideration of available
analytical data on natural systems.

***Theoretical approach***

No fractionation factor is known so far for the pair pyrite-
cinnabar, but following the indirect data (based on lattice
than for the pyrite-galena (100 In \( Y = 16.5 \) at 0°C) because cinnabar has a lower bond strength than galena. It is safe to take the galena figure as a minimum for cinnabar.

Experimental approach

The S isotopic fractionation factor between cinnabar and other S-containing minerals has not yet been determined experimentally, because of the generally low solubility of Hg and because of low activity product of the sulphides, such as cinnabar \( (K = 10^{-56} \text{ at } 25^\circ C) \).\( \text{HEPLER and OLOFSSON, } 1975.\) HOEPPNER et al. (1990) experimentally investigated the S isotope exchange between synthetic PbS, ZnS, and HgS and natural PbS and ZnS on one hand and liquid S on the other hand. The isotopic exchange rates decrease from PbS to HgS, but the isotopic equilibrium values for natural sulphides differ from those found for synthetic, i.e. pure sulphides. They conclude that "the diffusion coefficients for sulphur isotope exchange in sulphides . . . indicate that sulphur isotope redistribution in sulphide ores is possible within geological time, even at relatively low temperatures" but do not propose a numerical fractionation factor for cinnabar. They noticed a strong isotopic difference in natural cinnabar—metacinnabar pairs which shall be discussed later.

Available analytical data from literature

Table 6 gathers selected data from literature giving paired \( \delta^{34}S \) values for cinnabar and other sulphides, mostly pyrite, from present-day deposition or from various deposits. Papers reporting only data on cinnabar with no associated S containing mineral were omitted, as were papers in which it is apparent that cinnabar is not coeval with other S-bearing species. In most papers the contemporaneity of the mineral pairs is not discussed. The low values of \( \Delta^{34}S_{\text{py-cin}} \) are noticeable at the first glance.

Hot springs provide better information because the \( \Delta^{34}S_{\text{py-cin}} \) can be checked against the temperature of ore deposition, not very different from 100°C. According to Fig. 8, at 100°C the \( \Delta^{34}S_{\text{py-cin}} \) should be of 6.4%, but at this temperature the sulphate/sulphide equilibrium is frozen. Because the measured factors in cinnabar depositing springs are lower, cinnabar must have precipitated under strong isotopic disequilibrium.

Isotopic equilibrium vs. disequilibrium

The observed \( \Delta^{34}S_{\text{py-cin}} \) reported in Table 6 seldom exceed 3.5%. Using this figure for the pair pyrite-galena would give a temperature of 290°C. Assuming that the fractionation factor \( \alpha \) for cinnabar-pyrite exceeds that for galena-pyrite, an unrealistic deposition temperature would be obtained for the cinnabar. Even if deposited at the same temperature, two minerals may not be in isotopic equilibrium if (1) the isotopic composition of the solution varied between the deposition of the two minerals, or (2) if the deposition was excessively rapid (kinetic disequilibrium, ARNOLD, 1984). From the preceding we conclude that cinnabar is frequently deposited in isotopic disequilibrium. The very low solubility of cinnabar rapidly induces oversaturation and must be responsible for this disequilibrium.

Application to the ore minerals of Almadén

The SIMS data (Fig. 9) give a \( \Delta^{34}S_{\text{py-cin}} \) of \(-1.2\%\) or \(-3.7\%\), depending if it is calculated from the disseminated pyrite \( (\delta^{34}S = 3.4\%) \) or the layered pyrite \( (\delta^{34}S = 5.9\%) \), while the cinnabar sulphur has an average of 7.1%. The MS data are in the same range. Thus, either both sulphides were deposited in isotopic disequilibrium or they are not coeval. The second possibility is not supported by microscopic evidence and the Almadén deposit must have been formed under isotopic disequilibrium in short time intervals.

Isotopic Variations of the Cinnabar Sulphur

The variations of the \( \delta^{34}S \) (Fig. 5) determined for the cinnabar of Almadén will be discussed from three aspects: (1) their small spread within each orebody, (2) the variations between the orebodies, and (3) the orderly variations within the orebodies. The discussion is limited because of (1) the isotopic disequilibrium previously shown and of (2) the lack of information on the composition of the cinnabar depositing hydrothermal fluids at Almadén, particularly on their \( \delta^{34}S \) and the speciation of S \( (\text{HS}^- \text{or } S^2^-) \). The S concentration in the hydrothermal solutions can roughly be estimated to be \( 10^{-2} \) or \( 10^{-3} \text{ molal} \) by analogy with known convective circuits of seawater in volcanic rocks (STYRT et al., 1981).

(1) A large spread of \( \delta^{34}S \) values is the rule in most non-orthomagmatic ore deposits, although some exceptions can be quoted. GREGORY and ROBINSON (1984) indicate ranges of similar magnitude for the stratiform massive sulphide deposits of N. Queensland: from 2.5 to 3.6% for pyrite from massive sulphides and from 2.5 to 4.4% for pyrite from stockwork ores at the O.K. mines and ranges of 1.9% for sphalerite and 2.6% for pyrite from the Dianne mine. The \( \delta^{34}S \) varies from \(-1.0 \) to \( 1.1\% \) for forty-four pyrites taken over a 65 m profile in the uniferrous sandstone of the Quirke II deposit (Blind River district, Ontario; HATTORI et al., 1983). Still smaller spreads were found by ARNOLD and SHEPPARD (1981) for hydrothermal S of the black smokers at the East Pacific Rise 21°N: 1.4 to 3.0% for sixteen pyrite and chalcopyrite samples. A small \( \delta^{34}S \) spread is also reported for cinnabar \( (1.3-4.4\%) \) and metacinnabar \( (0.0-3.2\%) \) at New Idria (BOCTOR et al., 1987). Therefore, the small spread observed at Almadén within the three orebodies is as significant as the absolute values.

The small spread of the \( \delta^{34}S \) values observed at Almadén requires that at least two conditions be simultaneously fulfilled: (a) relative uniformity of the S source or a constant mixing ratio if several (uniform) sources are involved, (b) relative constancy of the physicochemical parameters during the formation of a single ore lens, particularly as to \( pO_2, pS_2S, pH, T, \) and \( \delta^{34}S_{SSS} \) (not quantifiable with the presently available data) which are the major factors controlling the sulphide \( \delta^{34}S \) through the \( SO_2^-/H_2S \) equilibrium (OHMOTO, 1972; OHMOTO and RYE, 1979). The fractionation is small or nil if the S results from dissolution of reduced S which remains in reduced state, whereas it is important if the S
Table 6. Selected sulphur isotope data from literature on mineral associations including HgS and FeS\textsubscript{2}

<table>
<thead>
<tr>
<th>LOCALITY</th>
<th>References</th>
<th>Cinnabar</th>
<th>Paired minerals</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample n°</td>
<td>d (^{34})S</td>
<td>Sample n°</td>
<td>d (^{34})S</td>
</tr>
<tr>
<td></td>
<td>Hot springs</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>USSR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>APAPELS'K SPRINGS</td>
<td>Ozernova et al., 1973 a</td>
<td>-9.6</td>
<td>11.7</td>
<td>SO\textsubscript{4} 2-</td>
</tr>
<tr>
<td>GORYAČHI PLYAZ</td>
<td>Ozernova et al., 1971</td>
<td>-2.4</td>
<td>n = 3</td>
<td>-1.5/1.2</td>
</tr>
<tr>
<td>MENDELEEV VOLCANO</td>
<td>Ozernova</td>
<td>-2.4</td>
<td>n = 2</td>
<td>-2.4/1.2</td>
</tr>
<tr>
<td>USA</td>
<td>THE GEYSERS</td>
<td>Brookins, 1970</td>
<td>2.3</td>
<td>-2.9</td>
</tr>
</tbody>
</table>

| Ore deposits and occurrences | |
|----------|----------|----------|----------|----------|
| ITALY    | LA TOLFA | Field and Lombardi, 1972 | 7.4 | n = 7 | \(\delta^{34} \)S = 8.3 | pyrite | 0.9 | Pyrite and cinnabar not in the same deposit; pyrite from a nearby, similar deposit |
| TULMINI | Robinson, 1974 | n = 2 | 1.2/1.3 | n = 2 | 1.1 | chalcopyrite | -0.2 | Champion lode, cinnabar younger than chalcopyrite |
| USSS     | AKTASH | Ozernova et al., 1977 | -14.1 | 13.0 | pyrite | 27.1 | |
| BELOKAMEENOE | Chepynyn et al., 1974 | 5v-b | -3.0 | Ks/73 | 1.7 | pyrite | 4.7 | Disseminations in sandstones |
| NIKITOVKA | Vinogradov, 1963 | 9 | 0.1 | 9 | 0.1 | pyrite | 0.0 | Great pyrite crystals in fissure filled with organic matter, cinnabar in adjacent, smaller fissure |
| NIKITOVKA | Saukov et al., 1972 | n = 6 | -1.7/2.5 | n = 5 | \(\delta^{34} \)S = 2.1 | pyrite | 1.8 | Pyrite impregnating sandstone and associated cinnabar |
| NIKITOVKA | Ozernova et al., 1973 b | n = 2 | -1.2/2.5 | n = 2 | \(\delta^{34} \)S = 13.2 | marcasite | 12.9 | |
| SARAYNSK | Ozernova et al., 1977 | n = 2 | -3.4/3.4 | n = 2 | -0.5 | pyrite | -8.9/2.6 | |
| USSS     | SLAVYANSK | Ozernova et al., 1973 b | 13.6 | n = 3 | 8.0/21.8 | pyrite | -5.6/2.2 | Pyrite of a different generation than cinnabar |
| TAMVATNEI | Ozerova et al., 1977 | n = 2 | \(\delta^{34} \)S = 0.3 | n = 2 | \(\delta^{34} \)S = 3.3 | marcasite | 12.9 | |
| TAMVATNEI/TROGOVOY | Ozernova et al., 1977 | n = 2 | \(\delta^{34} \)S = 7.3 | n = 2 | \(\delta^{34} \)S = 8.2 | pyrite | 1.5 | |
| TCHEMPORIN | Ozernova et al., 1973 a | 2.9 | 3.2 | 0.3 | pyrite | 0.3 | |
| VYSCHIKOV | Ozernova et al., 1973 b | n = 2 | -2.2 | 0.0 | pyrite | 2.2 | |
| USA      | NEW IDRIA | Ozerova et al., 1977 | n = 8 | 1.3/4.4 | n = 3 | 3.1/13.0 | pyrite | -1.3/8.6 | Pyrite and cinnabar are not coeval, precipitation under isotopic disequilibrium |
|          | Boctor et al., 1987 | n = 4 | 0.0/3.2 | metacinnabar | -4.4/1.9 | Interpreted as precipitation under isotopic disequilibrium |
|          | Ozernova et al., 1973 a | n = 2 | -2.1 | metacinnabar | -0.1 | |
| YUGOSLAVIA | IDRIA (= IDRIA) | Ozerova et al., 1973 a | n = 12 | -5.5/8.6 | n = 12 | -0.8 | pyrite | -2.4 | Cinnabar from different ore types |
|          | Ozerova et al., 1973 a | 6.0 | 7.3 | pyrite I | 1.3 | Associated pyrite and cinnabar |
|          | Ozerova et al., 1973 a | 6.0 | 8.4 | pyrite II | 0.3 | |
| MOUNT AVALA | Ozernova et al., 1973 a | n = 2 | 1.1 | 12.5 | pyrite | 8.6 | |
|          | Ozerova et al., 1977 | n = 2 | 10.9/14.0 | pyrite | 2.9/15.1 | |

results from sulphate reduction. The small “within” \(\delta^{34} \)S dispersion can be explained by a rapid precipitation and/or, following OHMOTO (1972), by low S concentrations in the fluids. A short time interval would also favour a small spread by keeping the different parameters nearly constant. In view of the generally low cinnabar solubility, it was postulated that cinnabar depositing geothermal systems must have been active over long time intervals (cf. SAUPÉ, 1976; at least \(10^5 \) years). The Steamboat Springs system, Nevada, has been active for 2 or 3 million years (SILBERMANN et al., 1979). Beyond this gross picture, there is good evidence that the discharge of such a system is pulsatory and not continuous. Ore-forming episodes are short and separated by long time intervals during which no ore deposition occurs. Evidence for such pulsations is found, for example, at Sulphur Banks, California, where during the last 150,000 years, six short cinnabar depositing episodes were recorded in the sediments (SIMS and WHITE, 1981).
Three processes may lead to the orderly distributions found in the orebodies of Almadén: (i) a Rayleigh process, (ii) a progressive change of $pO_2$ and/or $T$, the major physicochemical factors controlling fractionation, or (iii) mixing of two fluids having different $S$ isotope composition.

**Rayleigh process**

This process can explain the distribution in San Pedro (Fig. 5a), but not that in San Francisco and San Nicolas. It would imply that the ore-deposition proceeded upwards in the sediment pile.

**Change of physicochemical parameters in a $SO_2^+/H_2S$ equilibrium reaction**

Given a $S$ source of constant isotopic composition, the sulphate ion is the predominant species at higher $pO_2$ values and its $\delta^{34}S$ will approximately be that of the $S$ source, whereas the sulphide will be much lighter by an amount given by the fractionation factor (e.g., 26% at 300°C). Inversely, the sulphide is dominant at lower $pO_2$ and its $\delta^{34}S$ will be little different from that of the source, but in both cases it will be isotopically lighter than the source (OHMOTO, 1972). It follows that for a source of constant isotopic composition, a higher sulphide $\delta^{34}S$ closer to the source value) indicates a lower $SO_2^-/H_2S$ ratio in the ore-forming fluid, that is a lower $pO_2$ or else higher temperature and thus a smaller fractionation. With the data available for Almadén, it is not possible to estimate the different parameters because in a zone where hydrothermal fluids mix with cold waters, equilibrium may not be attained. In the geologically important $pO_2$-$pH$ domain, an increase in $pO_2$ of one log unit or in $pH$ of one unit can cause a decrease in $\delta^{34}S$ of as much as 20% (OHMOTO, 1972).

A shift in a $SO_2^-/H_2S$ equilibrium reaction cannot explain the $\delta^{34}S$ distribution in the San Pedro orebody: its top was in contact with seawater, where the temperature was lower than at the site of ore deposition, and this situation could not lead to higher $\delta^{34}S$ values on top as observed. It seems possible for San Francisco and San Nicolas, if reduced hydrothermal solutions flow into a permeable horizontal bed soaked with seawater, a higher $\delta^{34}S$ can be expected in the zone of influx because of a progressively outward cooling by mixing with the colder seawater, making plausible the higher values in the centre of the orebodies. However, in view of the isotopic disequilibrium shown before, it is doubtful that changes of the physicochemical parameters play a major role.

**Mixing**

The just described effect on the $\delta^{34}S$ controlling physicochemical parameters of hydrothermal $S$ and $Hg$ carrying solutions flowing into cold, seawater-soaked reducing sediments can be enhanced or substituted by simple mixing of these two waters containing $S$ of different isotopic compositions. The average $\delta^{34}S$ of the pyrite unrelated to cinnabar and hosted by the Criadero Quartzite is an estimate of the environmental $\delta^{34}S$ (8 to 9%). It is not very different from the average cinnabar $\delta^{34}S$, therefore, mixing will not change.
Each of the bodies, the variation range of \( \delta^{34}\text{S} \) is small (2 to 3%).

A negative (not positive like at Almadén) \( \delta^{34}\text{S} \) vs. grade correlation is reported for Homestake, South Dakota (Rye and Ohmuoto, 1974). It is explained by a small-scale metamorphic \( \text{S} \) remobilization within the orebodies.

**CONCLUSIONS**

The disseminated pyrite of the black shales (\( \delta^{34}\text{S} \) between -6.7% and 14.4%) and the different pyrite types known from previous studies to be unrelated to the cinnabar impregnation display a wide range of \( \delta^{34}\text{S} \) values (between -15.0% and 26.8%). At closer observation, half of the pyrite \( \delta^{34}\text{S} \) values concentrate around 9%. They are typical of pyrite in very low-grade metamorphic formations. The variations result from the interaction of various well-known factors: (1) rapid changes of Eh in the upper first centimetres of the sedimentary column (Hartmann and Nielsen, 1969), (2) the availability of reactive iron, and (3) an incipient Rayleigh process due to the progressive closing of the sedimentary system. These are compatible with the sedimentary environment, a combination of a delta and a flat shore, as deduced from earlier sedimentologic studies. The strong linear correlation observed in the volcanic rocks between the \( \delta^{34}\text{S} \) and the \( \text{S} \) concentration indicates contamination of "normal" mantle material (a pristine \( \delta^{34}\text{S} \) of 0.6% can be calculated from the regression line of Fig. 7 for a postulated initial sulphur concentration of 1000 ppm) by \( \text{S} \) from an external source. Because of this strong linear correlation, a source with constant characteristics is more probable. Thus, seawater is a more likely source than the sediments or formation waters and the reaction temperature must have been rather constant.

The cinnabar \( \delta^{34}\text{S} \) values show remarkable features: (1) The distribution of the \( \delta^{34}\text{S} \) within the orebodies follows clear trends, with the highest values in the centres of San Francisco and San Nicolas, or on top in San Pedro. In other words, the \( \delta^{34}\text{S} \) is positively correlated with the ore grade which is also highest on top of San Pedro and in the centres of San Francisco and San Nicolas, but this relation could not be quantified. (2) The difference between the mean values of the three orebodies is larger than the analytical variation and indicate that they were formed during three distinct episodes, under slightly different physicochemical conditions. This is an independent confirmation of the conclusion developed on other bases, of the formation of the ore soon after the deposition of the sediments and at or near a sediment/water interface: if the ore were deposited long after the sediments, there would be no reason for having the three lenses formed under different conditions.

The mean isotopic composition of cinnabar (\( \delta^{34}\text{S} = 5.6\% \)) is close to the composition of the Footwall Shales (\( \delta^{34}\text{S} = 5.5\% \)) and to the mean for the volcanic rocks (\( \delta^{34}\text{S} = 5.1\% \)). Either one is therefore a possible \( \text{S} \) source. Because of their larger volume and because on geological evidence the volcanic rocks erupted slightly after the cinnabar deposition, the Footwall Shales are the preferred source. However, the average \( \delta^{34}\text{S} \) of 8.1% for San Francisco can only be explained by addition of an isotopically heavier \( \text{S} \), for which the only source is seawater sulphate, partially reduced in a convective circuit. Further, it is unlikely that the cinnabar \( \text{S} \) of Almadén resulted from bacterial sulphate reduction in spite of the stratigraphically upward increasing \( \delta^{34}\text{S} \) in the San Pedro orebody. Where pyrite and cinnabar are coeval, they were deposited in isotopic disequilibrium.

Because there is no indication that \( \text{HgS} \) was first deposited as metacinnabar which later transformed into cinnabar, the ore deposition occurred below 345°C, the temperature of the phase transition between these two minerals (Potter and Barnes, 1978). This is also in accordance with the general knowledge on the formation conditions of \( \text{Hg} \) deposits (H. L. Barnes and T. M. Seward, unpubl. data) and the geological history of the Almadén zone. The low and sometimes negative values of the \( \Delta^{34}\text{S}_{\text{in}} \) suggest a rapid precipitation in isotopic disequilibrium as made possible by the low solubility of this sulphide. Subsequent remobilization of the cinnabar I to cinnabar II did not lead to fractionation, whereas metacinnabar strongly fractionates the light \( \text{S} \) isotope. Thus, the latter must result from dissolution of cinnabar followed by reprecipitation. Barite was formed during a later, independent episode. Its \( \text{S} \) is not directly derived from seawater.

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Sulfur isotope geochemistry of the Hg ores of Almadén, Spain


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