

## Sulphur isotope geochemistry of the ores and country rocks at the Almadén mercury deposit, Ciudad Real, Spain\*

FRANCIS SAUPÉ and MICHEL ARNOLD

Centre de Recherches Pétrographiques et Géochimiques, BP 20, 54501 Vandoeuvre-lès-Nancy Cedex, France

(Received June 7, 1991; accepted in revised form April 15, 1992)

**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  $\delta^{34}\text{S}$  is narrow within each of the three orebodies, but the  $\delta^{34}\text{S}$  average values differ sufficiently between them (mean  $\delta^{34}\text{S}$ : San Nicolas =  $0.2 \pm 1.1\%$ , San Francisco =  $8.1 \pm 0.7\%$ , San Pedro =  $5.9 \pm 1.0\%$ ) 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 ( $\delta^{34}\text{S} = 5.5\%$ ) or the spilites ( $\delta^{34}\text{S} = 5.1 \pm 1.3\%$ ). For geometric and chronologic reasons, the former seem the best potential source. However, the high  $\delta^{34}\text{S}$  values of the San Francisco cinnabar cannot be explained without addition of heavy S from reduction of seawater sulphate. Orderly distributions of the  $\delta^{34}\text{S}$  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 Nicolas 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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S} = 5.1 \pm 1.3\%$ . The linear relationship between the  $\delta^{34}\text{S}$  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 ( $n = 3$ ;  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  between  $15.0\%$  and  $16.4\%$ , with a mode of about  $8\%$ ; the pyrite rims of the diagenetic dolomite nodules ( $n = 2$ ;  $\delta^{34}\text{S} = -14.7 \pm 0.35\%$ ) 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 GUILLEMANY, 1975; ARNOLD and SAUPÉ, 1985; RYTUBA et al., 1989) and from Hg deposits in general (OZEROVA 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 acceptance 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 SOBRINO, 1985; ORTEGA GIRONES and HERNANDEZ SOBRINO, 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 clastic 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 Llandoveryan (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 anchimeta-morphism (SAUPÉ, 1973; SAN MIGUEL ARRIBAS and PAULITSCH, 1974; SAUPÉ et al., 1977). 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: Llandeillo (Lower

\* Contribution of the CRPG no. 921.

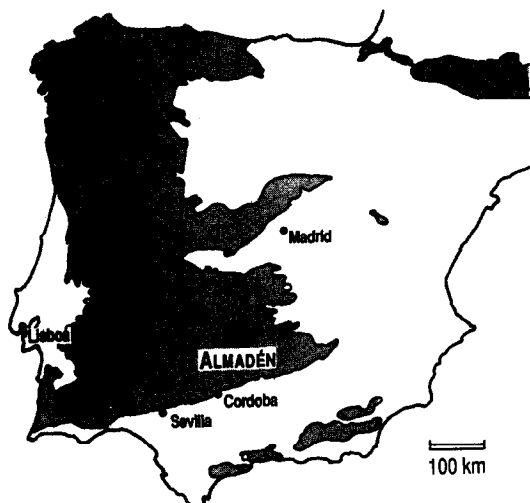


FIG. 1. Geologic sketch map of Spain showing the location of the Almadén district. Stippled pattern: Pre-Mesozoic formations.

Ordovician), Llandovery-Wenlock (Lower to Middle Silurian—beginning immediately after the sedimentation of the Criadero Quartzite), and Middle Devonian. Geological surface and gravity mapping showed that the volume of the erupted basic volcanic rocks is by far larger in the Almadén syncline than elsewhere (SAUPÉ, 1973), but the first episode is missing at the Almadén mine. These rocks belong to an alkali basalt suite that underwent limited magmatic differentiation; they then suffered a general and almost pervasive spilitization, due to reactions with fluids, seawater, or formation waters and  $\text{CO}_2$ . The  $\text{CO}_2$  of the spilitic carbonates was interpreted as mantle derived according to C and O isotope data (weighted means:  $\delta^{13}\text{C} = -6.1 \pm 13\text{‰}/\text{PDB}$ ;  $\delta^{18}\text{O} = 15.3 \pm 1.6\text{‰}/\text{SMOW}$ ) (EICHMANN et al., 1977). Limestones and dolostones are very subordinate in the region. However, derivation of the  $\text{CO}_2$  from the organic matter, abundant in the shales, cannot be ruled out (SAUPÉ, 1990). Indeed, the diagenesis of the organic matter in shales can produce  $\delta^{13}\text{C}$  values formerly considered to be typical for the mantle (IRWIN et al., 1977). The  $\delta^{18}\text{O}$  of the spilitic 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 provisionally 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 explored 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 stratification 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 following 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 Nicolas 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 decentered by approximately 300 m with respect to this reference line. Thus, before folding and erosion the Frailesca lens was surrounded by the sandy 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 interstices between spherules of framboidal pyrite grains. Similarly, they were seen in these pyrite grains between the framboidal 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 mud are evidence for an early arrival of this cinnabar (SAUPÉ, 1973). Similar samples were found, although not *in situ*, in the sixth level

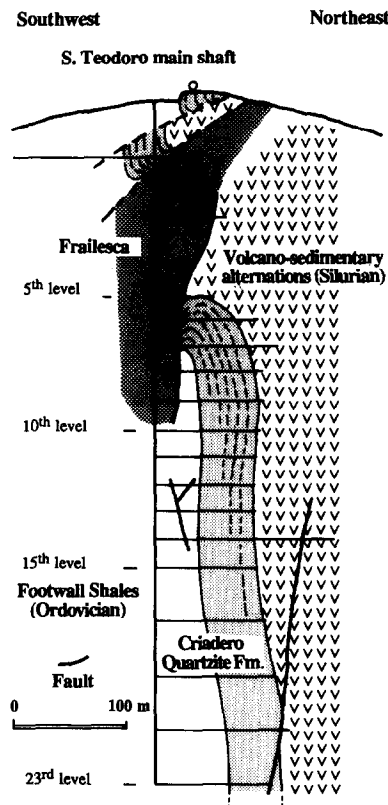


FIG. 2. Vertical geological section through the Almadén mine (Reproduction of Fig. 12 in SAUPÉ, 1990; with kind permission from *Economic Geology*, 1990, Vol. 85, pp. 482–510).

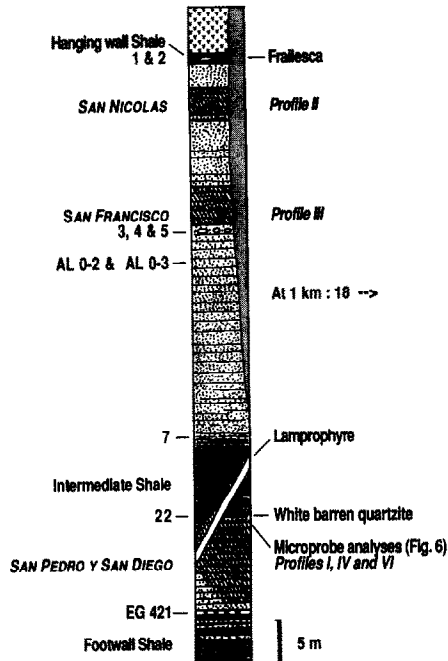


FIG. 3. Stratigraphical profile and position of the samples from the Almadén mine. Cross-hatching and italicized small capitals: orebodies; italics: profiles; plain lettering: sample designation.

of the San Nicolas orebody (oral commun., A. Hernandez and M. Soler, 1975).

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 MACKAY (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.

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 Chillón 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 Concepcion 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  $\mu$ ) at a small scale. After grinding the samples to about 50  $\mu$ ,

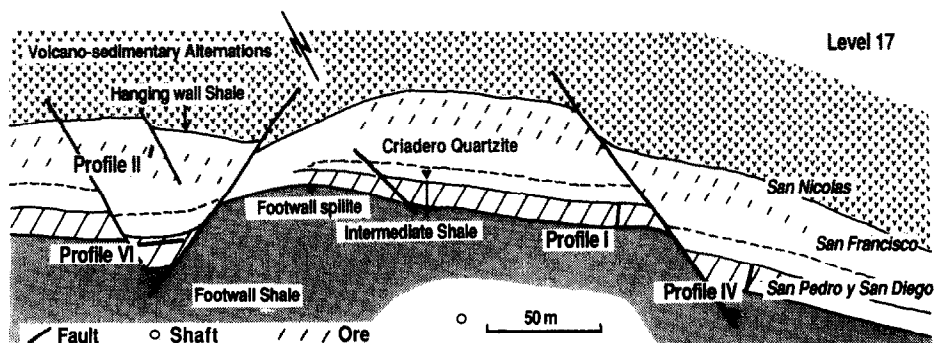


FIG. 4. Sampling profiles in the orebodies reported on the geological map of the seventeenth level of the Almadén mine.

Table 1. Sulphur isotope composition of a synthetic and a natural cinnabar standard

Anal. n°	Weight mg	Yield %	$\delta$ ‰	2 $\sigma$ 10
<i>Synthetic standard</i>				
<i>HgS Prolabo batch 25458</i>				
<i>(1000 °C)</i>				
1516	11.5	107	1.7	0.04
1517	23.3	107	2.4	0.03
1518	10.6	108	2.1	0.04
1522	13.3	106	3.5	0.07
1524	16.8	108	1.5	0.04
1527	15.3	107	2.3	0.03
1535	14.3	100	1.8	0.04
1537	19.1	106	1.5	0.03
1538	17.6	109	1.9	0.03
		$\bar{x}$ =	2.1	
		st. dev.	0.6	
<i>Natural standard : AL17-40/4.III</i>				
<i>(1000 °C)</i>				
1523	15.1	108	6.9	0.05
1525	18.7	98	6.2	0.04
<i>(1100 °C)</i>				
1528	15.9	98	6.8	0.06
1529	17.7	104	6.6	0.04
1530	14.7	100	6.5	0.04
1532	13.8	95	6.2	0.05
1533	19.7	99	6.1	0.07
1534	15.0	105	6.6	0.04
		$\bar{x}$ =	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<sub>2</sub> by reacting the sample (10 mg of pyrite or 30 mg of cinnabar) with excess Cu<sub>2</sub>O at 1050°C following the procedure of ROBINSON and KUSAKABE (1975). After removal of the gaseous impurities, the yield is determined with a Hg manometer of known volume. The extraction procedure for HgS was tested with a natural standard and a synthetic standard (commercial HgS). The natural standard (Table 1) was heated to 1000°C and to 1100°C, and no difference was observed between the two series of runs. The natural standard is isotopically more homogeneous than the synthetic (Table 1) and was used as our control standard. Some SO<sub>2</sub> preparations with low yields were retained because microscopic examination showed that the sulphides were only diluted by quartz.

The total S was extracted as SO<sub>2</sub> from the whole rocks (shales and mafic volcanic rocks) by heating in an induction furnace, oxidized with H<sub>2</sub>O<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> and ultimately precipitated as BaSO<sub>4</sub>. BaSO<sub>4</sub>, natural or resulting from extraction of total S from whole-rock samples, was reacted with SiO<sub>2</sub> at 1500°C to liberate SO<sub>2</sub> according to the procedure of HOLT and ENGELKEMEIR (1970). The laboratory standard (commercial SO<sub>2</sub>) is periodically calibrated against the five international standards of MONSTER and REES (1975). The measured values are standardized relative to CDT. The soluble sulphate concentration in the whole rocks was determined separately by turbidimetry.

#### Secondary Ion Mass Spectrometry (SIMS)

The  $\delta^{34}\text{S}$  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  $\mu$ . The analytical procedure is reported by CHAUSSIDON and DEMANGE (1988).

#### RESULTS

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  $\delta^{34}\text{S}$  values for cinnabar within each orebody (Table 2) and notable qualitative and quantitative differences between the three ore bodies (Table 5). In the San Pedro orebody, the  $\delta^{34}\text{S}$  increases stratigraphically upwards (Fig. 5a). In the topmost and richest ore layer of San Pedro the  $\delta^{34}\text{S}$  decreases laterally from the centre outwards. Profile IV (east of San Pedro—Fig. 5a) (av.  $\delta^{34}\text{S}$  = 6.1‰) and profile VI (west of San Pedro) (av.  $\delta^{34}\text{S}$  = 5.2‰) are situated on both sides of profile I (centre of San Pedro) (av.  $\delta^{34}\text{S}$  = 6.4‰). The distributions of the  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  values are highest toward the centres of the lenses and decrease towards the stratigraphic top and bottom (the lateral variation of the  $\delta^{34}\text{S}$  was not investigated in these two orebodies). Thus, both  $\delta^{34}\text{S}$  distribution patterns reproduce the distribution patterns of the ore grades as they can be observed on stope faces. Unfortunately this  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  of 8.5‰, but the fourth lies significantly apart ( $\delta^{34}\text{S}$  = 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  $\delta^{34}\text{S}$  = -8.0‰ (Table 5). The sulphide  $\delta^{34}\text{S}$  (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  $\delta^{34}\text{S}$  is much larger than for cinnabar. Each sulphide morphology exhibits a distinctive range of  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  values near 0‰. Pyrite from another seam (sample 7) has  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  of 7.8‰.

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)

Anal. n°	Sample n°	Mineral	Yield %	$\delta$ ‰	$2\sigma_{10}$
<i>Profile I - San Pedro (perpendicular to stratification)</i>					
1594	AL17-40/4.I	Cinnabar	83	7.3	0.07
	AL17-40/4.III	Cinnabar		6.5	
1583	AL17-40/6.I	Cinnabar	103	5.2	0.03
1587	AL17-40/7.I	Cinnabar	108	6.4	0.04
			$\bar{x} =$	6.4	
3477	AL17/40 (10)	Pyrite	99	7.7	0.03
3478	AL17/40-3a	Pyrite	88	7.3	0.05
3479	AL17/40-3b	Pyrite	90	6.9	0.06
3480	AL17/40-3c	Pyrite	92	8.3	0.07
			$\bar{x} =$	7.6	
<i>Profile II - San Nicolas (perpendicular to stratification)</i>					
4011	II - 11	Cinnabar	108	0.1	0.08
3898	II - 7	Cinnabar	105	-0.3	0.08
3897	II - 5	Cinnabar	104	1.2	0.06
3896	II - 4	Cinnabar	107	0.8	0.07
3895	II - 3	Cinnabar	106	1.2	0.05
3894	II - 2	Cinnabar	104	-1.6	0.07
			$\bar{x} =$	0.2	
3902	II - 10	Pyrite	95	1.6	
3901	II - 7	Pyrite	100	-2.9	0.07
3899	II - 4	Pyrite	99	-15.8	0.06
3900	II - 1	Pyrite	94	-1.0	0.03
<i>Profile III - San Francisco (perpendicular to stratification)</i>					
1579	III - 1	Cinnabar	90	7.4	0.05
1540	III - 2/1	Cinnabar	98	7.3	0.04
1542	III - 2/3	Cinnabar	102	7.3	0.04
1541	III - 3	Cinnabar	105	8.2	0.04
1544	III - 4	Cinnabar	104	8.1	0.05
1547	III - 5	Cinnabar	109	9.0	0.03
1548	III - 7 top	Cinnabar	95	8.4	0.04
1546	III - 7 bottom	Cinnabar	101	8.9	0.02
1552	III - 8	Cinnabar	108	8.1	0.05
1554	III - 9	Cinnabar	107	8.9	0.03
1571	III - 10	Cinnabar	100	7.0	0.06
			$\bar{x} =$	8.1	
			st. dev.	0.7	
<i>Profile IV - San Pedro (E - perpendicular to stratification)</i>					
3904	IV - 1	Cinnabar	105	7.2	0.05
3903	IV - 2	Cinnabar	103	6.9	0.05
3905	IV - 3	Cinnabar	102	6.8	0.06
3906	IV - 5	Cinnabar	100	5.9	0.05
3907	IV - 6	Cinnabar	105	4.9	0.06
3909	IV - 8	Cinnabar	100	4.5	0.04
			$\bar{x} =$	6.1	
3911	IV - 9	Pyrite	99	5.4	0.04
<i>Profile VI - San Pedro (W - parallel to stratification)</i>					
1582	VI - 1	Cinnabar	100	5.8	0.06
1574	VI - 2	Cinnabar	104	4.5	0.05
1581	VI - 3	Cinnabar	106	5.3	0.05
			$\bar{x} =$	5.2	

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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  is positive, up to 6.8‰, deviating from assumed mantle values around 1 to 2‰. (4) The  $\delta^{34}\text{S}$  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 decrepitated, 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  $\delta^{34}\text{S}$  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 at temperatures below 300°C (THOLE and ROBINSON, 1976), a temperature not attained in Almadén during metamorphism (210–270°C, SAUPÉ, 1990). HOEPPNER et al. (1990) showed that isotopic equilibration with liquid S occurs above 250°C in galena and sphalerite, and possibly in cinnabar. At

Table 3. Sulphur isotope composition of various pyrites and rocks from the Almadén mine and area

Anal. n°	Sample n°	Sample description	Mineral	Yield %	$\delta$ ‰	2 $\sigma$ 10
<i>Pyrites from sedimentary rocks</i>						
1598	1	Crust surrounding a dolomite nodule of hanging wall shale	Pyrite	100	-14.3	0.07
1609	2		Pyrite	96	-15.0	0.04
				$\bar{x} =$	$\overline{-14.7}$	
3462	3-x	Pyrite nodule 1 (id. 2)	Pyrite	91	26.8	0.05
3471	4-c	Pyrite nodule 2 in the	Pyrite	95	17.0	0.06
3463	4-a	footwall quartzite of the	Pyrite	96	9.9	0.05
3609	4-c'	San Francisco	Pyrite	80	8.9	0.06
3610	4-i	orebody	Pyrite	84	8.6	
3470	5.1	Pyrite nodule (id. 2)	Pyrite	79	8.9	0.07
3474	5.2	id.	Pyrite	83	8.7	0.07
				$\bar{x} =$	$\overline{7.1}$	
1631	AL0-2	Bedded dissemination	Pyrite	103	0.8	0.05
1633	AL0-3	Bedded dissemination	Pyrite	109	-0.1	0.06
1638	7	Isolated pyrite crystals in	Pyrite	90	9.6	0.04
3468	7	seams	Pyrite	95	8.8	0.06
3475	22	Layer on top barren quartzite	Pyrite	71	16.4	0.06
				$\bar{x} =$	$\overline{7.1}$	
3473	18	Barren Criadero quartzite	Pyrite	39	7.8	0.05
1593	19	Precambrian	Pyrite	103	-8.0	0.05
4104	Footwall	Black shale	Total S	101	5.5	0.07
4105	Intermed.	Black shale	Total S	99	-6.7	0.06
4106	Hang. wall	Black shale	Total S	95	14.4	0.07
<i>Pyrites from hydrothermal veins and igneous rocks</i>						
<i>Massive</i>						
1599	"La Pava"	Galena-pyrite quartz vein	Pyrite	101	4.4	0.06
<i>Disseminated</i>						
3464	EG 423	"Lamprophyre" (Alm. mine)	Pyrite	52	5.8	0.06
3465	EG 424	"Lamprophyre" (Alm. mine)	Pyrite	82	0.9	0.05
3466	EG 425	"Lamprophyre" (Alm. mine)	Pyrite	60	3.4	0.04
				$\bar{x} =$	$\overline{3.4}$	
3625	EG 389	Spilite (N. Concepcion)	Total S	101	6.8	0.07
3626	EG 254	Spilite (Ordovician)	Total S	98	5.3	0.07
3629	EG 421	Spilite (Footwall Alm. mine)	Total S	98	3.1	0.07
				$\bar{x} =$	$\overline{5.1}$	
3628	EG 67	Frailesca (Almadén mine)	Total S	100	1.9	0.08
3467	EG 9	Dolerite (Silurian)	Pyrite	81	1.0	0.07

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 cin-

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

Anal. n°	Sample n°	Mineral	Yield %	$\delta$ ‰	2 $\sigma$ 10
4014	TV 1 (mine run)	Barite	102	8.3	0.06
4015	TV 2 (mine run)	Barite	104	8.5	0.02
4017	AL17-5	Barite	102	8.8	0.07
4393	AL17-54	Barite	98	14.9	0.05
4012		Late cinnabar	102	5.0	0.04
4013		Metacinnabar	103	-14.1	0.06

nabar 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  $\delta^{34}\text{S}$  distributions in the ore lenses were not obliterated, it is possible to conclude that cinnabar did not isotopically reequilibrate during metamorphism.

Late cinnabar ( $\delta^{34}\text{S} = 5.0\text{‰}$ , Table 4) maintains the S isotope composition of the first cinnabar generation (mean  $\delta^{34}\text{S} = 5.6\text{‰}$ ). To the contrary, at Almadén metacinnabar ( $\delta^{34}\text{S} = -14.1\text{‰}$ , Table 4) strongly differs from that of cinnabar (mean  $\delta^{34}\text{S} = 5.6\text{‰}$ ). 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  $345^\circ\text{C}$ ,

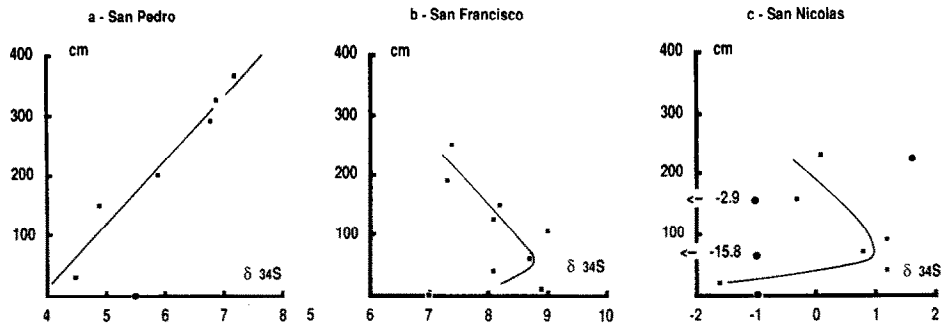


FIG. 5. Isotopic analyses along sampling profiles: a—profile IV (San Pedro—perpendicular to stratification); b—profile III (San Francisco—perpendicular to stratification); c—profile II (San Nicolas—perpendicular to stratification). Squares: cinnabar; dots: pyrite.

POTTER and BARNES, 1978). At New Idria, California, the  $\delta^{34}\text{S}$  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 $\delta^{34}\text{S}$ of the upper mantle

An evaluation of the S geochemistry in the spilites can be attained reviewing the total S concentration and  $\delta^{34}\text{S}$  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  $850 \pm 150$  ppm given by NIELSEN (1978), and a  $\delta^{34}\text{S}$  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.

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

Orebody	Average $\delta^{34}\text{S}$	Sample number	$\sigma_{n-1}$
San Nicolas	0.2	6	1.1
San Francisco	8.1	11	0.71
San Pedro	5.9	13	0.99

The DSDP hole 504 B was drilled at approximately  $1^\circ\text{N}$ , 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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  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

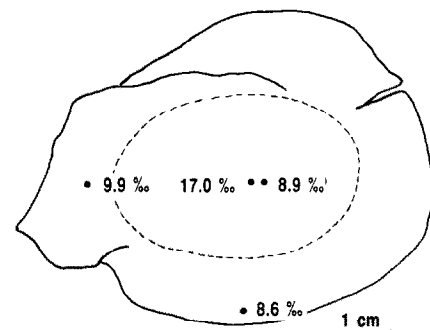


FIG. 6. Isotopic analyses of pyrite from a diagenetic pyrite nodule (the dotted line is a visible discontinuity within the nodule).

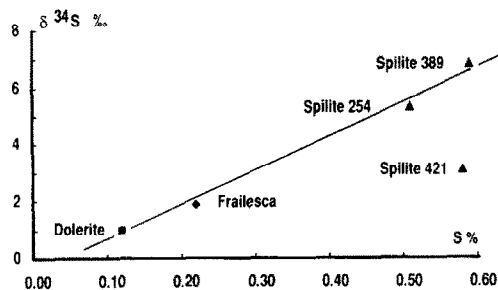


FIG. 7.  $\delta^{34}\text{S}$  vs. wt% S correlation in basic volcanic rocks from Almadén.

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 CRPG by the same procedures [(a) the shales of this study ( $n = 3$ ) and (b) a set of BIF samples ( $n = 16$ ); ARNOLD et al., 1990].

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<sup>†</sup> 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.

UEDA and SAKAI (1984) 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.<sup>†</sup> A S enrichment can be the result of a reduction of seawater sulphate circulating within basalts by oxidation of the  $\text{Fe}^{2+}$  of olivine and pyroxene as proposed by OHMOTO and RYE (1979) and by MOTTLE et al. (1979). The corresponding transformation of  $\text{S}^{6+}$  to  $\text{S}^{2-}$  requires the oxidation of 8  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , i.e., 14 g Fe for 1 g of S. As an average alkali basalt contains 6.2%  $\text{Fe}^{2+}$  (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 sat-

isfied 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  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  was completely exported. The low abundance of  $\text{SO}_4^{2-}$  (anhydrite), compared to that of  $\text{S}^{2-}$ , 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. MOTTLE et al., 1979) which supposes the formation of anhydrite (HUBBERTEN, 1990). It is best explained by anhydrite dissolution in the late stages of magma cooling.

The reaction temperature of spilitization was estimated from the O isotope data to be between 130 and 200°C (SAUPÉ, 1990). This study also showed that the  $\delta^{18}\text{O}$  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 OHMOTO and RYE, 1979). This contradiction is not satisfactorily resolved. The transformations observed in the spilitized 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., MUNHA and KERRICH, 1980) 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,  $\bar{x} = 5.1$ ‰) is indicative of variable seawater contamination, whereas the good linear correlation suggests a nearly constant temperature.

The present mine openings in the Frailesca are notably dry and impervious. This suggests that this rock was never percolated by anhydrite transporting solutions. Thus, little  $\text{SO}_4^{2-}$  was reduced, and consequently the  $\delta^{34}\text{S}$  of the Frailesca ( $\delta^{34}\text{S} = 1.9$ ‰) 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: SAUPÉ (1990) 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; MIGDISOV et al., 1974) as in present argillaceous sediments (Azov Sea, MIGDISOV et al., 1974; Baltic Sea, HARTMANN and NIELSEN, 1969; LEIN, 1983; Black Sea, VINOGRADOV et al., 1962), 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. SANGSTER (1968, 1976) statistically established that the  $\delta^{34}\text{S}$  of pyrite resulting from

<sup>†</sup> Average of 20 spilite samples.  $\text{SO}_4^{2-}$  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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  values (type 2). Large fractionations 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 turns controls the isotopic composition of the pyrite S (GAUTIER, 1987).

#### *Application to the black shales of Almadén*

The low  $\delta^{34}\text{S}$  value (-8‰) for the Precambrian pyrite found in a greywacke (Table 3) can be compared to the  $\delta^{34}\text{S}$  values of Precambrian seawater sulphate as read from Fig. 9 of CLAYPOOL et al. (1980):

$$600 \text{ m.y.: } \delta^{34}\text{S} = 30\text{‰}$$

$$650 \text{ m.y.: } \delta^{34}\text{S} = 21\text{‰}$$

$$700 \text{ m.y.: } \delta^{34}\text{S} = 15\text{‰}$$

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  $\delta^{34}\text{S}$  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 GARCIA 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  $\delta^{34}\text{S}$  between the different lithological units of a profile through Graptolite Shales (l.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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  of the seawater sulphate was approximately 28‰

(CLAYPOOL et al., 1980). The large differences in the  $\delta^{34}\text{S}$  of the three black shales (Upper Ordovician/Lower Silurian) cannot be explained by variations of the  $\delta^{34}\text{S}$  of the seawater sulphate because the three samples are almost coeval. The Footwall Shales with a  $\delta^{34}\text{S} = 5.5\text{‰}$  correspond to seawater sulphate reduced in slightly euxinic conditions (28-5.5 = 22.5‰), whereas the  $\delta^{34}\text{S}$  of the Hanging Wall Shales (14.4‰) corresponds to normal bacterial reduction (28-14.4 = 13.6‰). Only the Intermediate Shales ( $\delta^{34}\text{S} = -6.7\text{‰}$ ) 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 ( $\Delta = 28\text{‰} - (-6.7\text{‰}) = 34.7\text{‰}$ ) agrees with values for the type 1 distribution of SCHWARCZ and BURNIE (1973) found in shallow marine or brackish-water environments.

The respective  $\delta^{34}\text{S}$  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 reconcentration around the nodule, which would introduce only a small shift of the  $\delta^{34}\text{S}$ . Nor is it possible to postulate that the pyrite rim crystallized before the disseminated pyrite so that the shift of the  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  of 16.4‰, strongly differing from the  $\delta^{34}\text{S} = -6.7\text{‰}$  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 et the San Francisco orebodies have an average  $\delta^{34}\text{S}$  of 9.2‰. Other bedded disseminations (AL 0-2 and AL 0-3) have near zero  $\delta^{34}\text{S}$  values. Three pyrite nodules (samples 3, 4, and 5) collected in a white quartzite bed in the footwall of San Francisco have similar  $\delta^{34}\text{S}$  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

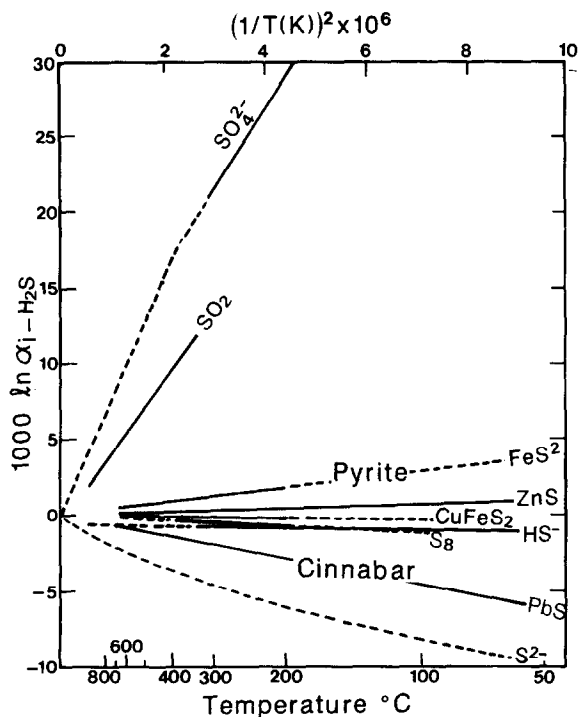


FIG. 8. Equilibrium isotopic fractionation factors among S compounds relative to  $\text{H}_2\text{S}$ . Solid lines—experimentally determined. Dashed lines—extrapolated or theoretically calculated. Caption and figure from fig. 10.3 in OHMOTO and RYE (1979). Cinnabar fractionation factor taken equal to that of galena.

of the nodule should have been centripetal. Quartz associated with one of these nodules has a fibrous habit. This habit is known to develop when  $\text{CaSO}_4$ -bearing brines mix with brackish waters having high  $\text{SiO}_2$  concentrations. Monomeric silica then “salts out” and recrystallizes during aging (ARNOLD and GUILLOU, 1981). These two water types are likely to be found in a delta intersecting a shelf, the palaeogeographic interpretation proposed for the site of the ore deposition at Almadén (SAUPÉ, 1990).

The variations of the  $\delta^{34}\text{S}$  of the quartzite pyrite unrelated to the ore are large, as was noted for the pyrite of the black shales. This variability, normal in clastic environments (see, i.e., HARTMANN and NIELSEN, 1969), is caused by the combination of rapid vertical changes of the Eh in the first centimetres of the sedimentary column, by the variable input of reactive iron, and by the shift of the isotopic composition of the sulphides deposited in a progressively closing system (Rayleigh process). The scatter of the isotopic compositions of the pyrites and the  $\delta^{34}\text{S}$  mode, of 8‰ again, is in accordance with bacterial seawater sulphate reduction in a near-shore environment (SCHWARCZ and BURNIE, 1973). Pyrite collected in the Criadero Quartzite, one km to the east of the mine below the town of Almadén (sample 18), also has a  $\delta^{34}\text{S}$  near 8‰.

#### Sources of the Sulphide and Sulphate Sulphur of the Ore Deposit

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 preceding 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 (SAUPÉ, 1990),
- 3) reduction of contemporary (=Lower Silurian) seawater sulphate above 300°C in a convective circuit ( $\text{SO}_4^{2-}/\text{H}_2\text{S}$  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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  within each of the three orebodies eliminates possibilities (3) and (4). The large difference between the respective  $\delta^{34}\text{S}$  eliminates the Precambrian pyrite ( $\delta^{34}\text{S} = -8.0\text{‰}$ ) from possibility (5) but not the Footwall Shale ( $\delta^{34}\text{S} = 5.5\text{‰}$ ). If the cinnabar S were mantle S, one could indeed expect a small dispersion but the  $\delta^{34}\text{S}$  should be closer to 1 or 2‰ and should not differ between the orebodies; thus, possibility (1) is not plausible, except maybe for the San Nicolas orebody ( $\bar{x} = 0.2\text{‰}$ ). 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 mineralization, 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 probably 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  $\delta^{34}\text{S}$  of 8.1‰ for the San Francisco orebody, higher than the  $\delta^{34}\text{S}$  of the postulated source, makes improbable a single sulphur source. Only the addition of S formed by reduction 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 formation. The  $\delta^{34}\text{S}$  value of 8.5‰ is some 20‰ below that of Silurian seawater (28‰, CLAYPOOL et al., 1980) and eliminates a straightforward seawater origin for the sulphate. As this figure is approximately the mode of the syngenetic 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

vibrations) gathered by BACHINSKI (1969) it should be higher than for the pyrite-galena ( $1000 \ln \alpha = 16.5$  at  $0^\circ\text{C}$ ) 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 ( $K = 10^{-36}$  at  $25^\circ\text{C}$ , HEPLER and OLOFSSON, 1975). HOEPPENER 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  $\delta^{34}\text{S}$  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  $\Delta^{34}\text{S}_{\text{py-cin}}$  are noticeable at the first glance.

Hot springs provide better information because the  $\Delta^{34}\text{S}_{\text{py-cin}}$  can be checked against the temperature of ore deposition, not very different from  $100^\circ\text{C}$ . According to Fig. 8, at  $100^\circ\text{C}$  the  $\Delta^{34}\text{S}_{\text{py-cin}}$  should be of  $6.4\text{‰}$ , 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  $\Delta^{34}\text{S}_{\text{py-cin}}$  reported in Table 6 seldom exceed  $3.5\text{‰}$ . Using this figure for the pair pyrite-galena would give a temperature of  $290^\circ\text{C}$ . 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  $\Delta^{34}\text{S}_{\text{py-cin}}$  of  $-1.2\text{‰}$  or  $-3.7\text{‰}$ , depending if it is calculated from the disseminated pyrite ( $\delta^{34}\text{S} = 3.4\text{‰}$ ) or the layered pyrite ( $\delta^{34}\text{S} = 5.9\text{‰}$ ), while the cinnabar sulphur has an average of  $7.1\text{‰}$ . 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  $\delta^{34}\text{S}$  (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  $\delta^{34}\text{S}$  and the speciation of S ( $\text{HS}^-$  or  $\text{S}^{2-}$ ). The S concentration in the hydrothermal solutions can roughly be estimated to be  $10^{-2}$  or  $10^{-3}$  molal by analogy with known convective circuits of seawater in volcanic rocks (STYRT et al., 1981).

(1) A large spread of  $^{34}\text{S}$  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  $3.6\text{‰}$  for pyrite from massive sulphides and from 2.5 to  $4.4\text{‰}$  for pyrite from stockwork ores at the O.K. mines and ranges of  $1.9\text{‰}$  for sphalerite and  $2.6\text{‰}$  for pyrite from the Dianne mine. The  $\delta^{34}\text{S}$  varies from  $-1.0$  to  $1.1\text{‰}$  for forty-four pyrites taken over a 65 m profile in the uraniferous 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  $21^\circ\text{N}$ :  $1.4$  to  $3.0\text{‰}$  for sixteen pyrite and chalcopyrite samples. A small  $\delta^{34}\text{S}$  spread is also reported for cinnabar ( $1.3$ – $4.4\text{‰}$ ) and metacinnabar ( $0.0$ – $3.2\text{‰}$ ) 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  $\delta^{34}\text{S}$  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  $p\text{O}_2$ ,  $p\text{S}_{2\text{S}}$ ,  $p\text{H}$ ,  $T$ , and  $\delta^{34}\text{S}_{2\text{S}}$  (not quantifiable with the presently available data) which are the major factors controlling the sulphide  $\delta^{34}\text{S}$  through the  $\text{SO}_4^{2-}/\text{H}_2\text{S}$  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<sub>2</sub>

LOCALITY References	Cinnabar		Paired minerals			Comments
	Sample n°	d 34S	Sample n°	d 34S	Mineral	
<b>Hot springs</b>						
<b>URSS</b>						
APAPEL'SK SPRINGS Ozerova et al., 1973 a		-9.6		11.7	SO <sub>4</sub> 2-	21.3 Kamchatka
GORYACHI PLYAZ Ozerova et al., 1971		-2.4	n = 3	-1.5/1.2 $\bar{x} = -0.6$	pyrite and marcasite	0.9/3.6 1.8 Mendeleev volcano
MENDELEEV VOLCANO Ozerova		-2.4		-2.4/1.2	pyrite	0.0/3.6 Solfataric zone
<b>USA</b>						
THE GEYSERS Brookins, 1970		2.3		-2.9 -6.7	sulphur metastibnite	-5.2 -9.0 Hot spring deposit Metastibnite thought to have formed from gas phase
<b>Ore deposits and occurrences</b>						
<b>ITALY</b>						
LA TOLFA Field and Lombardi, 1972		7.4	n = 7	$\bar{x} = 8.3$	pyrite	0.9 Pyrite and cinnabar not in the same deposit; pyrite from a nearby, similar deposit
<b>NEW ZEALAND</b>						
TUI MINE Robinson, 1974	n = 2	1.2/1.3 $\bar{x} = 1.3$	n = 2 n = 2	1.1 2.7	chalcopyrite pyrite II	-0.2 1.5 Champion lode, cinnabar younger than chalcopyrite Ruakake lode
<b>USSR</b>						
AKTASH Ozerova et al., 1977		-14.1		13.0	pyrite	27.1 -
BELOKAMENNOE Chernytsin et al., 1974	5v-b	-3.0	Kh/73	1.7	pyrite	4.7 Disseminations in sandstones
NIKITOVKA Vinogradov, 1963	9	0.1	9 g	0.1	pyrite	0.0 Great pyrite crystals in fissure filled with organic matter, cinnabar in adjacent, smaller fissure
NIKITOVKA Saukov et al., 1972	56 g n = 6	0.2 -1.7/2.5 $\bar{x} = 0.3$	56 a n = 5 n = 2	0.3 $\bar{x} = 2.1$ $\bar{x} = 13.2$	pyrite pyrite marcasite	0.0 1.8 12.9 Pyrite impregnating sandstone and associated cinnabar
NIKITOVKA Ozerova et al., 1973 b	n = 6	-1.7/2.5 $\bar{x} = 0.3$		1.2	pyrite	-1.3/2.7 Pyrite and associated cinnabar from a vein, no direct association of cinnabar and pyrite.
SARASYSK Ozerova et al., 1977	n = 2	-3.4/3.4 0.0		-5.5	pyrite	-8.9/-2.6 -
SLAVYANSK Ozerova et al., 1973 b		13.6	n = 3	8.0/21.8 13.4	pyrite	-5.6/8.2 Pyrite of a different generation than cinnabar $\bar{x} = -0.2$
TAMVATNEI / PIERVENETS Ozerova et al., 1977			n = 2	$\bar{x} = 7.3$	metacinnabar sulphur	- Hypogene sulphur
TAMVATNEI / TROGOVOY Ozerova et al., 1977		7.1	n = 3	7.7/8.6 $\bar{x} = 8.2$	pyrite	0.6/1.5 $\bar{x} = 1.1$ -
TCHEMPOURINE Ozerova et al., 1973 a		2.9		3.2	pyrite	0.3 -
VYSCHKOV Ozerova et al., 1973 b		-2.2		0.0 -2.1	pyrite metacinnabar	2.2 -0.1 -
<b>USA</b>						
NEW IDRIA Boctor et al., 1987	n = 8	1.3/4.4 $\bar{x} = 2.6$	n = 3 n = 4	3.1/13.0 $\bar{x} = 7.3$ 0.0/3.2 $\bar{x} = 2.1$	pyrite metacinnabar	-1.3/8.6 $\bar{x} = 4.7$ -4.4/1.9 $\bar{x} = -0.5$ Pyrite and cinnabar are not coeval, precipitation under isotopic disequilibrium Interpreted as precipitation under isotopic disequilibrium
<b>YUGOSLAVIA</b>						
IDRIJA (= IDRJA) Ozerova et al., 1973 a	n = 12	-5.5/8.6 $\bar{x} = -0.8$		-1.6	pyrite	-2.4 Cinnabar from different ore types
MARIA RIJEKA Ozerova et al., 1973 a		6.0		7.3	pyrite I	1.3 Associated pyrite and cinnabar
MOUNT AVALA Ozerova et al., 1973 a	n = 2	3.9	n = 2 n = 2	6.2 12.5 22.2	pyrite II pyrite barite	0.2 8.6 18.3 -
MOUNT AVALA Ozerova et al., 1977	n = 6	-1.1/8 $\bar{x} = 4.0$	n = 2	10.9/14.0 $\bar{x} = 12.5$	pyrite	2.9/15.1 $\bar{x} = 8.5$ -

results from sulphate reduction. The small "within"  $\delta^{34}\text{S}$  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).

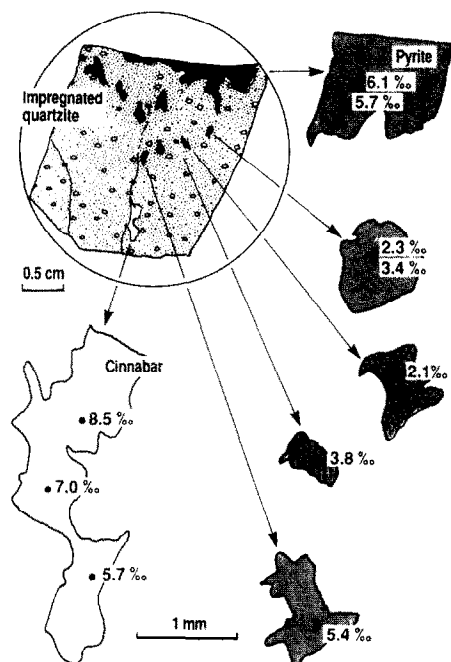


FIG. 9.  $\delta^{34}\text{S}$  determinations by SIMS on sample AL 17-40/3 (rich ore from the uppermost San Pedro ore lens): cinnabar remobilized into a fracture (white), bedded and disseminated pyrite (stippled).

(2) The mean  $\delta^{34}\text{S}$  values of the three Almadén orebodies are significantly different. Therefore, it is possible to conclude that the formation conditions were not uniform and that the three orebodies were formed during three different episodes, under different physicochemical conditions. The geological observation showed the individuality of San Pedro with respect to San Francisco and San Nicolas. The two latter now appear to be different one from the other. These differences have a bearing on the genetic hypotheses: if the S were purely mantle derived, such large differences would not be observed.

(3) Systematic variations of  $\delta^{34}\text{S}$  within orebodies (and between), as those first mentioned for Almadén by ARNOLD and SAUPÉ (1985), are not frequently recorded in the literature. In the Rammelsberg orebodies (Germany) the  $\delta^{34}\text{S}$  increases from 7 to 20‰ from bottom to top (ANGER et al., 1966; p. 521). The reverse tendency, a decrease toward the top, is mentioned in the South Iberian massive sulphide deposits (MUNHA and KERRICH, 1980, p. 198) where the pyrite of the lower central zone of the bodies is isotopically heavier (average  $\delta^{34}\text{S} = 3\text{‰}$ ) than the pyrite of the border zone (average  $\delta^{34}\text{S} = 2\text{‰}$ ). "Although there are variations among different deposits, at a single mine the sulphur isotopic compositions of pyrites from each of the different paragenetic types tend to be similar." (MUNHA and KERRICH, 1980, p. 197; The "different" paragenetic types include stockwork, disseminations, veins, and massive ore). Two variation trends are reported for the sulphide  $\delta^{34}\text{S}$  (OHMOTO and RYE, 1979): (1)  $\delta^{34}\text{S}$  values decreasing upward in the stratigraphic section are observed in stratabound volcanogenic deposits (as reported for the Shakanai, Japan, kuroko-type deposit by RYE and OHMOTO, 1974) and (2) the  $\delta^{34}\text{S}$  increase upwards in "biogenic" deposits (see also Table 10 of LARGE, 1980).

Three processes may lead to the orderly distributions found in the orebodies of Almadén: (i) a Rayleigh process, (ii) a progressive change of  $p\text{O}_2$  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 $\text{SO}_4^{2-}/\text{H}_2\text{S}$ equilibrium reaction

Given a S source of constant isotopic composition, the sulphate ion is the predominant species at higher  $p\text{O}_2$  values and its  $\delta^{34}\text{S}$  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  $p\text{O}_2$  and its  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  (closer to the source value) indicates (OHMOTO and RYE, 1979) a lower  $\text{SO}_4^{2-}/\text{H}_2\text{S}$  ratio in the ore-forming fluid, that is a lower  $p\text{O}_2$  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  $p\text{O}_2$ -pH domain, an increase in  $p\text{O}_2$  of one log unit or in pH of one unit can cause a decrease in  $\delta^{34}\text{S}$  of as much as 20‰ (OHMOTO, 1972).

A shift in a  $\text{SO}_4^{2-}/\text{H}_2\text{S}$  equilibrium reaction cannot explain the  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  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  $\delta^{34}\text{S}$  of the pyrite unrelated to cinnabar and hosted by the Criadero Quartzite is an estimate of the environmental  $\delta^{34}\text{S}$  (8 to 9‰). It is not very different from the average cinnabar  $\delta^{34}\text{S}$ ; therefore, mixing will not change

substantially the isotopic composition of cinnabar. Also, in 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 OHMOTO, 1974). It is explained by a small-scale metamorphic S remobilization within the orebodies.

### CONCLUSIONS

The disseminated pyrite of the black shales ( $\delta^{34}\text{S}$  between  $-6.7\text{‰}$  and  $14.4\text{‰}$ ) 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  $-15.0\text{‰}$  and  $26.8\text{‰}$ ). 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 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 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 centers 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 ( $\delta^{34}\text{S} = 5.6\text{‰}$ ) is close to the composition of the Footwall Shales ( $\delta^{34}\text{S} = 5.5\text{‰}$ ) and to the mean for the volcanic rocks ( $\delta^{34}\text{S} = 5.1\text{‰}$ ). Either one is therefore a possible 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 S, for which the only source is seawater sulphate, partially reduced in a

convective circuit. Further, it is unlikely that the cinnabar 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 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 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  $\Delta^{34}\text{S}_{\text{py-cin}}$  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 S isotope. Thus, the latter must result from dissolution of cinnabar followed by reprecipitation. Barite was formed during a later, independent episode. Its S is not directly derived from seawater.

*Acknowledgments*—FS is indebted to the successive Presidents of the Board and Central Technical Directors of Minas de Almadén y Arrayanes S. A. for permission to undertake this study, to the local mine managers, and to the geological staff for technical support during mine work and sampling and to all for their continuous interest. He acknowledges critical reading of the manuscript and thoughtful comments by M. Chaussidon, who also contributed the isotopic determinations by SIMS, and by L. A. Derry, F. L. Mauder, and E. M. Ripley. Permission by B. Skinner to reproduce Fig. 2 from an article in *Economic Geology* is gratefully acknowledged. B. Jacquier is thanked for his careful sample preparation and analytical work.

*Editorial handling*: G. Faure

### REFERENCES

- ALMELA SAMPER A. and FEBREL MOLINERO T. (1960) La roca frialesca de Almadén: Un episodio tobaceo en una formacion basaltica del Siluriano superior. *Notas y Comunicaciones Inst. geol. min. Espana* **59**, 41–72.
- ALT J. C., ANDERSON T. F., and BONELL L. (1989) The geochemistry of sulfur in a 1.3 km section of hydrothermally altered oceanic crust, DSDP hole 504 B. *Geochim. Cosmochim. Acta* **53**, 1011–1023.
- ANGER G., NIELSEN H., PUCHELT H., and RICKE W. (1966) Sulfur isotopes in the Rammelsberg ore deposit (Germany). *Econ. Geol.* **61**, 511–536.
- ARNOLD M. (1984) Applications géothermométriques des isotopes du soufre. In *Thermométrie et barométrie géologiques* (ed. M. LAGACHE), Vol. 2, pp. 629–660. Société française de Minéralogie et Cristallographie.
- ARNOLD M. and GUILLOU J. J. (1981) Croissance naturelle de paracristaux de quartz dans une saumure sulfatée calcique à basse température. *Bull. Minéral.* **106**, 417–442.
- ARNOLD M. and SAUPÉ F. (1985) Sulfur isotope data for the Almadén mercury deposit (Ciudad Real, Spain) (abstr.). *Fortschr. Mineral.* **63** (Beiheft 1), 11.
- ARNOLD M. and SAUPÉ F. (1988) A propos de la réduction bactérienne. 12<sup>ème</sup>, *Réun. Sci. Terre*, p. 6. Soc. géol. France.
- ARNOLD M. and SHEPPARD S. M. F. (1981) East Pacific Rise at latitude 21°N: Isotopic composition and origin of the hydrothermal sulfur. *Earth Planet. Sci. Lett.* **56**, 148–156.
- ARNOLD M., MAUCHER A., and SAUPÉ F. (1971) Syngenetic pyrite and associated sulphides at the Almadén mercury mine (Ciudad Real, Spain). In *Ores in Sediments (Proceed. 9th Int. Congr. Sed-*

- imentology, Heidelberg) (ed. G. C. AMSTUTZ and A. J. BERNARD), pp. 7–19. Springer.
- ARNOLD M., ALIBERT C., and JACQUIER M. (1990)  $\delta^{34}\text{S}$  in Hamersley BIF, W Australia: The role of bacterial activity and thio-sulfates as an alternative to the hydrothermal model (abstr.). *7th Intl. Conf. Cosmochronol. Isot. Geol., Geol. Soc. Australia, Abstracts* 27, 4.
- BACHINSKI D. J. (1969) Bond strength and sulfur isotopic fractionation in co-existing sulfides. *Econ. Geol.* 64, 56–65.
- BARNES H. L. (1979) Solubilities of ore minerals. In *Geochemistry of Hydrothermal Ore Deposits* (ed. H. L. BARNES), pp. 404–460. Wiley Interscience.
- BOCTOR N. Z., SHIEH Y. N., and KULLERUD G. (1987) Mercury ores from the New Idria mining district, California: Geochemical and stable isotope studies. *Geochim. Cosmochim. Acta* 51, 1705–1715.
- BROOKINS D. G. (1970) Metastibnite from the Geysers, Sonoma County, California. *Amer. Mineral.* 55, 2103–2104.
- CALVO CALVO F. A. and GUILLEMANY J. M. (1975) Structure and origin of the mercury ore from Almadén, Spain. *Trans. Inst. Min. Metall.* (Sect. B: Appl. Earth Sci.) 84, B146–149.
- CANFIELD D. E. (1989) Reactive iron in marine sediments. *Geochim. Cosmochim. Acta* 53, 619–632.
- CHAUSSIDON M. (1988) Géochimie du soufre dans le manteau et la croûte océanique: apport de l'analyse isotopique in situ par sonde ionique. Dr. INPL dissertation, INPL Nancy.
- CHAUSSIDON M. and DEMANGE J. C. (1988) Instrumental mass fractionation in ion microprobe studies of sulfur isotopic ratios. In *Secondary Ion Mass Spectrometry* (ed. A. BENNINGHOVEN et al.), Vol. 6, pp. 937–940. J. Wiley & Sons.
- CHAUSSIDON M., ALBAREDE F., and SHEPPARD S. M. F. (1989) Sulphur isotope variations in the mantle from ion microprobe analyses of micro-sulphide inclusions. *Earth Planet. Sci. Lett.* 92, 144–156.
- CHERNITSYN V. B., NETREBA A. V., BUADZE, V. I., BOBOVNIKA A. N., KAVILADZE M. SH., MESECHKO A. YA., and RAD'KO V. I. (1974) Isotopic composition of sulfur in mercury deposits of the northern Caucasus. *Dokl. Akad. Nauk* 216, 1154–1157.
- CLAYPOOL G. E., HOLSER W. T., KAPLAN I. R., SAKAI H., and ZAK I. (1980) The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chem. Geol.* 28, 199–260.
- DILL H. and NIELSEN H. (1986) Carbon-sulphur-iron variations and sulphur isotope patterns of Silurian Graptolite Shales. *Sedimentology* 33, 745–755.
- EICHMANN R., SAUPÉ F., and SCHIDLOWSKI M. (1977) Carbon and oxygen isotope studies in rocks of the vicinity of the Almadén mercury deposit (Province of Ciudad Real, Spain). In *Time- and Strata-Bound Ore Deposits* (ed. D. D. KLEMM and H. J. SCHNEIDER), pp. 396–405. Springer.
- FAURE G. (1986) *Principles of Isotope Geology*, 2nd ed. J. Wiley & Sons.
- FIELD C. and LOMBARDI G. (1972) Sulfur isotopic evidence for the supergene origin of alunite deposits, Tolfa district, Italy. *Mineral. Deposita* 7, 113–125.
- GARCIA SAN SEGUNDO J., LORENZO ALVAREZ S., and ORTEGA GIRONES E. (1986) Mapa geológico de España 1:50,000, hoja 782, Siruela. Inst. geol. min. España, Madrid.
- GAUTIER D. L. (1987) Isotopic composition of pyrite: Relationship to organic matter type and iron availability in some North American Cretaceous shales. *Chem. Geol.* 65 (Isotope Geosci. 6), 293–303.
- GREGORY P. W. and ROBINSON B. W. (1984) Sulphur-isotope studies of the Mt Molloy, Dianne and O.K. stratiform sulphide deposits, Hodgkinson Province, North Queensland, Australia. *Mineral. Deposita* 19, 36–43.
- GRINENKO L. N., BOSHVAROV V. I., and KOTORGIN N. F. (1987) Sulfur contents and  $\delta^{34}\text{S}$  for komatiite-series rocks. *Geochem. Intl.* 24, (4), 23–30.
- GRINENKO V. A., DMITRIEV L. V., MIGDISOV A. A., and SHARASKIN A. Y. (1975) Sulfur contents and isotope composition for igneous and metamorphic rocks from Mid-Ocean Ridges. *Geochem. Intl.* 12, (1), 132–137.
- HARTMANN M. and NIELSEN H. (1969)  $\delta^{34}\text{S}$ —Werte in rezenten Meeressedimenten und ihre Deutung am Beispiel einiger Sedimentprofile aus der westlichen Ostsee. *Geol. Rundsch.* 59, 621–655.
- HATTORI K., CAMPBELL F. A., and KROUSE H. R. (1983) Sulphur isotope abundances in Aphebian clastic rocks: Implications for the coeval atmosphere. *Nature* 302, 323–326.
- HEPLER L. and OLOFSSON G. (1975) Mercury: Thermodynamic properties, chemical equilibria, and standard potentials. *Chem. Rev.* 75, 585–602.
- HERNANDEZ SOBRINO A. (1985) Estructura y genesis de los yacimientos de mercurio de la zona de Almadén. Ph.D. dissertation abstract, Univ. Salamanca.
- HOLT D. and ENGELKEMEIR A. G. (1970) Thermal decomposition of barium sulfate to sulfur dioxide for mass spectrometric analysis. *Anal. Chem.* 42, 1451–1453.
- HOEPPNER U. D., KRAMAR U. E., and PUCHELT H. (1990) Sulphur isotope exchange between sulphides and fluid sulphur: Consequences for geothermometric application. *European J. Mineral.* 2, 655–665.
- HUBBERTEN H.-W. (1990) Die Fraktionierung der Schwefelisotope bei der Entstehung und Veränderung der ozeanischen Kruste. *Chem. Erde* 50, 39–57.
- IRWIN H., CURTIS C., and COLEMAN M. (1977) Isotopic evidence for source of diagenetic carbonates formed during burial of organic rich sediments. *Nature* 269, 209–213.
- JOHNSON A. E. (1972) Origin of Cyprus pyrite deposits. *Proc. 24th Intl. Geol. Congr.*, Vol. 4 (Mineral Deposits), pp. 291–298.
- KANEHIRA K., YUI S., SAKAI H., and SASAKI A. (1973) Sulfide globules and sulfur isotope ratios in the abyssal tholeiite from the Mid-Atlantic Ridge near 30°N latitude. *Geochem. J.* 7, 89–96.
- KRUPP R. (1988) Physicochemical aspects of mercury metallogenesis. *Chem. Geol.* 69, 345–356.
- LARGE D. (1980) Geological parameters associated with sediment-hosted, submarine exhalative Pb-Zn deposits: An empirical model for mineral exploration. *Geol. Jahrbuch, Reihe D* 40, 59–130.
- LEIN A. YU. (1983) Biogeochemistry of the anaerobic diagenesis of recent Baltic Sea sediments. In *Environmental Biogeochemistry* (ed. R. HALLBERG); *Ecol. Bull.* 35, pp. 441–461.
- MACKAY R. A. (1946) Control of impounding structures. *Econ. Geol.* 41, 13–46.
- MAUCHER A. and SAUPÉ F. (1967) Sedimentärer Pyrit aus der Zinnober-Lagerstätte Almadén (Provinz Ciudad Real, Spanien). *Mineral. Deposita* 2, 312–317.
- MIGDISOV A. A., CHERKOVSKIY S. L., and GRINENKO V. A. (1974) The effect of formation conditions on the sulfur isotopes of aquatic sediments. *Geochem. Intl.* 11, 1028–1047.
- MITCHELL R. H. and KROUSE H. R. (1975) Sulphur isotope geochemistry of carbonatites. *Geochim. Cosmochim. Acta* 39, 1505–1513.
- MOLINA CAMARA J. M. and FERNANDEZ CARRASCO J. (1987) Mapa geológico de España 1: 50,000, hoja 782, Valdemanco de Esteras. Inst. Geol. min. España, Madrid.
- MONSTER J. and REES C. E. (1975) Sulphur isotope secondary standards: Interlaboratory comparisons and discussions, McMaster University Internal Report.
- MOORE J. G. and FABBI B. P. (1971) An estimate of the juvenile sulfur content of basalt. *Contrib. Mineral. Petrol.* 33, 118–127.
- MOORE J. G. and SCHILLING J.-G. (1973) Vesicles, water, and sulfur in Reykjanes Ridge basalts. *Contrib. Mineral. Petrol.* 41, 105–118.
- MOTTL M. J., HOLLAND H. D., and CORR R. F. (1979) Chemical exchange during hydrothermal alteration of basalts by seawater-II. Experimental results for Fe, Mn and sulfur species. *Geochim. Cosmochim. Acta* 43, 869–884.
- MUNHA J. and KERRICH R. (1980) Sea water basalt interaction in spilites from the Iberian pyrite belt. *Contrib. Mineral. Petrol.* 73, 191–200.
- NIELSEN H. (1968) Schwefel-Isotopenverhältnisse aus St. Andreasberg und anderen Erzvorkommen des Harzes. *Neues Jahrb. Mineral. Abh.* 109, 289–321.
- NIELSEN H. (1978) Sulfur isotopes in nature. In *Handbook of Geochemistry* (ed. K. H. WEDEPOHL), Vol. II-2, Chap. 16, pp. B1–B40. Springer.
- NORTHROP D. A. and CLAYTON R. N. (1966) Oxygen-isotope

- fractionations in systems containing dolomite. *J. Geol.* **74**, 174–196.
- OHMOTO H. (1972) Systematics of sulfur and carbon isotopes in hydrothermal ore deposits. *Econ. Geol.* **67**, 551–578.
- OHMOTO H. and RYE R. O. (1979) Isotopes of sulfur and carbon. In *Geochemistry of Hydrothermal Ore Deposits* (ed. H. L. BARNES), 2d ed., pp. 509–567. J. Wiley.
- ORTEGA GIRONES E. and HERNANDEZ SOBRINO A. (1992) The mercury deposits of the Almadén syncline. *Chron. Recherche Min.* **506**, 3–24.
- OZEROVA N. A., NABOKO S. I., and VINOGRADOV V. I. (1971) Sulphides of mercury, antimony and arsenic forming from the active thermal springs of Kamchatka and Kurile Islands. In *Proc. IMA-IGOD Meetings '70, Joint Symposium Volume, Soc. Mining Geol. Japan, Spec. Issue 2*, 164–170.
- OZEROVA N. A., LEBEDEV L. M., VINOGRADOV V. I., GOROKHOV L. V., and LAPUTIN I. P. (1973a) Some mineralogical-geochemical peculiarities of present formation of mercury ores (exemplified by active hydrotherms of Kamchatka, Kurile Islands, California and other regions) (in Russian). In *Abstract of the Geochemistry of Selected Elements* (ed. F. K. SHIPULIN and K. M. FEODOTIEV), pp. 50–93. Izdat. Nauka.
- OZEROVA N. A., VINOGRADOV V. I., MLAKAR I., FEDORCHUK V. P., and TITOV I. N. (1973b) Isotopic composition of the sulfur of some ores from ore deposits in the western part of the Mediterranean mercury belt (Russian). In *Abstract of the Geochemistry of Selected Elements* (ed. F. K. SHIPULIN and K. M. FEODOTIEV), pp. 275–310. Izdat. Nauka.
- OZEROVA N. A., VINOGRADOV V. I., BABKIN P. V., and ROSENBLUM I. S. (1977) On the source of the sulphur from mercury deposits in belts of ultramafic rocks. In *Geochemistry of the Migration Processes of the Elements of Ore Deposits* (ed. N. I. KHITAROV et al.), pp. 68–86. Izdat. Nauka.
- POTTER R. W. and BARNES H. L. (1978) Phase relations in the binary Hg-S. *Amer. Mineral.* **63**, 1143–1152.
- ROBINSON B. W. (1974) The origin of mineralization at the Tui mine, Te Aroha, New Zealand, in the light of stable isotope studies. *Econ. Geol.* **69**, 910–925.
- ROBINSON B. W. and KUSAKABE M. (1975) Quantitative preparation of sulfur dioxide for  $^{32}\text{S}/^{34}\text{S}$  analyses from sulfides by combustion with cuprous oxide. *Anal. Chem.* **47**, 1179–1181.
- RYE R. O. and OHMOTO H. (1974) Sulfur and carbon isotopes and ore genesis: A review. *Econ. Geol.* **69**, 826–842.
- RYTUBA J. J., RYE R. O., HERNANDEZ A. M., DEAN J. A., and ARRIBAS A., SR. (1989) Genesis of Almadén type mercury deposits, Almadén, Spain. In *28th Intl. Geol. Congress Abstracts*, Vol. 2, p. 2.741.
- SAKAI H., DES MARAIS D. J., UEDA A., and MOORE J. G. (1984) Concentrations and isotope ratios of carbon, nitrogen and sulfur in ocean-floor basalts. *Geochim. Cosmochim. Acta* **48**, 2433–2441.
- SAN JOSÉ M. A. (1983) El complejo sedimentario pelítico-grauvackico. In *Geología de España, libro jubilar de J. M. Rios*, pp. 91–99. Inst. geol. minero España, Madrid.
- SAN MIGUEL ARRIBAS A. and PAULITSCH P. (1974) Petrofabrics of Almadén-Quartzites. In *Proc. 1st Congr. Intl. del Mercurio (Barcelona-España)*, Vol. 1, 201–205.
- SANGSTER D. F. (1968) Relative sulfur isotope abundances of ancient seas and stratabound sulphide deposits. *Geol. Assoc. Canada Proc.* **19**, 79–91.
- SANGSTER D. F. (1976) Sulphur and lead isotopes in strata-bound deposits. In *Handbook of Strata-Bound and Stratiform Ore Deposits* (ed. K. H. WOLF), Vol. 2, pp. 219–266. Elsevier.
- SAUKOV A. A., AYDIN'YAN N. KH., and OZEROVA N. A. (1972) *Summary of the Geochemistry of Mercury*. Izdat. Nauka (in Russian).
- SAUPÉ F. (1967) Note préliminaire concernant la genèse du gisement de mercure d'Almadén (Province de Ciudad Real, Espagne). *Mineral. Deposita* **2**, 26–33.
- SAUPÉ F. (1973) La géologie du gisement de mercure d'Almadén (Province de Ciudad Real, Espagne). *Sci. Terre, Mém.* **29**.
- SAUPÉ F. (1974) Elements for a reappraisal of the geology of the Almadén mercury deposit (Province of Ciudad Real, Spain). In *Proc. 1st Congr. Intl. del Mercurio (Barcelona-España)*, Vol. 2, 483–489.
- SAUPÉ F. (1976) Mercure et volcanisme (Aspects géologiques du problème). *Mém. h. sér. Soc. géol. France* **7**, 143–147.
- SAUPÉ F. (1990) The geology of the Almadén mercury deposit. *Econ. Geol.* **85**, 482–510.
- SAUPÉ F., DUNOYER DE SEGONZAC G., and TEICHMÜLLER M. (1977) Etude du métamorphisme régional par la cristallinité de l'illite et la réflectance de la matière organique dans la zone du gisement de mercure d'Almadén (Province de Ciudad Real, Espagne). *Sci. Terre* **21**, 251–269.
- SCHNEIDER A. (1970) The sulfur isotope composition of basaltic rocks. *Contrib. Mineral. Petrol.* **25**, 95–124.
- SCHWARCZ H. P. and BURNIE S. W. (1973) Influence of sedimentary environments on sulfur isotope ratios in clastic rocks: A review. *Mineral. Deposita* **8**, 264–277.
- SILBERMANN M. L., WHITE D. E., KEITH T. E. C., and DOCKTER R. D. (1979) Duration of hydrothermal activity at Steamboat Springs, Nevada from ages of spatially associated volcanic rocks. *USGS Prof. Paper* 458-D.
- SIMS J. D. and WHITE D. E. (1981) Mercury in the sediments of Clear Lake, California. *USGS Prof. Paper* 1141, 237–241.
- STYRT M. M., BRACKMANN A. J., HOLLAND H. D., CLARK B. C., PISUTHA-ARNOLD V., ELDRIDGE C. S., and OHMOTO H. (1981) The mineralogy and the isotopic composition of sulfur in hydrothermal sulfide/sulfate deposits of the East Pacific Rise, 21°N latitude. *Earth Planet. Sci. Lett.* **53**, 382–390.
- THOLE R. H. and ROBINSON B. W. (1976) Isotopic evidence on the origin of the Shamrock copper mine, Rhodesia. *Mineral. Deposita* **11**, 298–310.
- UEDA A. and SAKAI H. (1984) Sulfur isotope study of quaternary volcanic rocks from the Japanese Islands Arc. *Geochim. Cosmochim. Acta* **48**, 1837–1848.
- VINOGRADOV V. I. (1963) Isotopic composition of sulfur in rocks and minerals of the Nikitovka mercury deposits in the Donbass (Russian). *Trudy Inst. Geol. ore depos., Petrogr. Mineral. Geochem.* **99**, 154–164.
- VINOGRADOV A. P., GRINENKO V. A., and USTINOV V. I. (1962) Isotopic composition of sulfur compounds in the Black Sea. *Geokhymia*, 973–997 (in Russian).
- VON GEHLEN K. (1988) Sulfur in the Earth's mantle—A review. *Terra Cognita* **8**, 222.