

The age and origin of the barite–fluorite (Pb–Zn) veins of the Sierra del Guadarrama (Spanish Central System, Spain): a radiogenic (Nd, Sr) and stable isotope study

C. Galindo^a, F. Tornos^b, D.P.F. Darbyshire^c and C. Casquet^a

^a*Departamento de Petrología y Geoquímica, Universidad Complutense de Madrid, 28040 Madrid, Spain*

^b*Instituto Tecnológico Geominero de España, 28003 Madrid, Spain*

^c*NERC Isotope Geosciences Laboratory, Keyworth NG12 5GG, UK*

ABSTRACT

Fluorite and barite-rich veins (+ sulphides) of the Sierra del Guadarrama (Spanish Central System) are usually hosted by Hercynian granitoids. Zoned fluorites from one of these veins have a Sm–Nd age of 145 ± 18 Ma. This age is similar to the K–Ar ages obtained in other hydrothermal rocks of the Spanish Central System (156–152 Ma) and confirms the existence of an important hydrothermal event during the Late Jurassic, probably related to extensional fracturing accompanying the opening of the North Atlantic Ocean.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio found in fluorite and barite (0.7154–0.7207) is in most cases lower than that found in the host granitoids (0.7194 and 0.7209), suggesting more than one source of strontium. This, in turn, supports previous models that involve mixing of two fluids during mineralization, an ascending hot ($> 300^\circ\text{C}$) and low-salinity fluid and a shallow, cooler ($< 100^\circ\text{C}$) and more saline brine. The ascending fluid probably reacted to a variable extent with the host granitoids, and the most likely source for the shallow fluid derived from a marine/evaporitic environment, with a low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (~ 0.7069 in the Late Jurassic).

The calculated ϵ_{Nd} composition of the fluorites (–8.8 to –7.6) as well as the $^{147}\text{Sm}/^{144}\text{Nd}$ variation found in this mineral (0.153–0.405) do not conflict with the mixing model although they can be largely explained by interaction of the ascending fluid with the host granitoids.

Sulphur isotopic compositions of sulphides range between –3.4 and –0.8‰ and those of barites from +15.5 to +15.8‰. The near 0‰ $\delta^{34}\text{S}$ -value of the sulphides suggests that their sulphur was derived from the hydrothermal leaching of the granitoids by the ascending fluid. The $\delta^{34}\text{S}$ -value of barite is consistent with Upper Jurassic marine sulphate as the source of sulphate in the shallow fluid. The absence of equilibrium between reduced and oxidized sulphur species can be easily interpreted as a consequence of the short residence time of the mixed fluid in the open fractures at temperatures between 250° and 100°C .

Although no pre-Cretaceous sediments are found on this part of the Iberian Hercynian basement, the data presented here support the existence of a shallow platform joining central Spain with the Iberian or the Subbetic realm in Late Jurassic times.

1. Introduction

Granite-hosted and to a lesser extent gneiss-hosted barite–fluorite veins with small amounts of base-metal sulphides (galena, sphalerite and chalcopyrite) are common in the southern part of the Sierra del Guadarrama, 30–60 km northwest of Madrid (Fig. 1; IGME, 1987). These veins were exploited in the past

for barite, fluorite and lead and have been the subject of considerable geologic, petrographic and fluid-inclusion research (Vindel, 1980; Locutura and Tornos, 1985, 1987; Ortega et al., 1988; Tornos et al., 1991; Lillo et al., 1992). However, the age of the veins, origin of the fluids and the precise metallogenic and geological setting are still a matter of debate.

Vindel (1980), Ortega et al. (1988) and

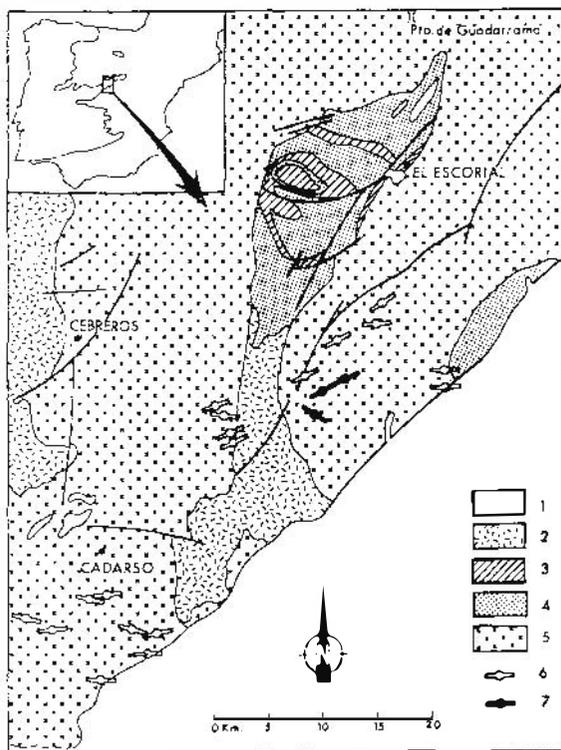


Fig. 1. Geological setting of the mineralizations [1=Cainozoic sediments; 2=schists and gneisses (Precambrian?); 3=ferric paragneisses and augen-gneisses (Precambrian?); 4=orthogneisses (Cambrian-Ordovician); 5=adamellites and granites; 6=barite-rich veins; 7=fluorite-rich veins].

Lillo et al. (1992) consider hydrothermal fluids to be directly related to the Hercynian granitic magmatism. Lillo et al. (1992) argue that the veins were formed under two successive late Variscan tectonic regimes involving extension, concomitant with the emplacement of granites, and later transcurrent faulting. An alternative genetic model, based on geochemical studies, was proposed by Locutura and Tornos (1985, 1987) and Tornos et al. (1991) who favored an unconformity-related origin for the veins that implies mixing of an ascending reduced, hot, low-salinity meteoric fluid and an oxidized, more saline brine of basal origin during late to post-Hercynian times.

The problem of the age of the F-Ba (Pb-Zn) veins has also been addressed elsewhere in the

European and North African Hercynian realm. In some cases, the veins cut across Permo-Triassic or Lower Jurassic rocks, thus excluding any relationship with the Hercynian magmatism (e.g., Thibieroz, 1987; Canals et al., 1992). In the Catalan Coastal Ranges (NW Spain) veins as young as the Miocene can be found (Canals and Cardellach, 1993). Ages of veins, hosted by granitoids or pre-Hercynian rocks, are more difficult to assess on geological grounds only. Available radiometric data indicate a broad span of ages: 266–259 Ma in Cornwall, U.K. (Darbyshire and Shepherd, 1990; Chesley et al., 1991), 206 Ma in the Pennine ore field, U.K. (Halliday et al., 1986), 295–205 Ma in southern Germany (Dill and Nielsen, 1987), 170–140 Ma in the south French Massif Central and Germany (Bonhomme et al., 1987) and 152 Ma in Panasqueira, Portugal (Kelly and Wagner, 1977). This suggests that the barite-fluorite veins present episodic hydrothermal events extended over a long span of time from the Permo-Triassic to Tertiary.

This work provides new isotopic evidence ($^{87}\text{Sr}/^{86}\text{Sr}$, $^{147}\text{Sm}/^{144}\text{Nd}$ and $\delta^{34}\text{S}$) that we believe strengthens the unconformity-related model for the genesis of the veins and confirms the relative youth of them in the Sierra del Guadarrama, leading to new palaeogeographic consequences.

2. Geological setting

The Sierra del Guadarrama forms part of the Spanish Central System (SCS) which is a block of Hercynian basement bounded to the north and south by Tertiary-Quaternary basins. The uplift took place for the most part along NE-SW-trending high- to low-angle thrusts, during the Alpine tectogenesis (Lower Miocene). These faults divide the Sierra del Guadarrama itself, into several longitudinal blocks with a "pop-up" geometry (e.g., De Vicente et al., 1992). Most of the barite-fluorite veins are found in the southernmost block, which is also

the one that underwent the least uplift and therefore shows only minor erosion. The rocks hosting the barite–fluorite veins are for the most part granitoids and to a lesser extent high-grade metamorphic rocks. These rocks form the largest part of the Sierra del Guadarrama, which has been interpreted as representing the lower plate of an Hercynian “core complex-like structure” bounded on its sides by extensional shear zones (Casquet et al., 1988).

The granitoids are mainly peraluminous, biotite±cordierite porphyritic to medium-grained adamellites and minor, two-mica, fine-grained to pegmatitic leucogranites. They were emplaced following the Hercynian compressive phases in the time span from 345 to 290 Ma (Ibarrola et al., 1987). Older, small bodies of quartz-diorite to tonalites are also found locally, as well as later massifs of amphibole-bearing adamellites and granites with a monzonitic affinity, which may be as young as 275 Ma (Ibarrola et al., 1987). The majority of metamorphic rocks are orthogneisses (augengneisses and leucogneisses) that have yielded Late Cambrian to Early Ordovician Rb–Sr ages (Viallette et al., 1987). Azoic, pre-Ordovician sediments are more scarce. A striking feature of the Sierra del Guadarrama is the presence of dyke swarms of regional extent. They consist for the most part of granitoid porphyries and minor microdiorites (Huertas, 1991) and crosscut all the Hercynian granitic plutons. They must be older than 275 Ma (Caballero et al., 1992 a, b).

3. Mineralization and controls

The barite–fluorite veins have a lens-shaped geometry and follow two systems of fractures, N60–70°E and N110–125°E. The first corresponds to tension joints, often with an “en échelon” arrangement, and the second to open zones along major strike–slip right-lateral

faults. The vertical extension of the veins is short (100–200 m) and the thickness, generally < 3 m. Length of the veins vary from several metres to few kilometres, a “pinch and swell”-like geometry being common. The veins display a wide variety of textures, with banding, massive open space fillings and different generations of breccias, that reflect repeated activity of the fractures. Breccia fragments consist of reworked vein material as well as host rocks. Fragments of episyenites (i.e. hydrothermally dequartzified granitoids along diffuse fracture zones) correspond to an hydrothermal regional episode dated at 274 ± 6 Ma (Caballero et al., 1992b; Casquet et al., 1992). Mylonites with a strong phyllic alteration are also found, and probably represent the alteration along the shear zones bounding the veins. K–Ar ages of 152 ± 4 and 156 ± 6 Ma have been obtained for a similar alteration consisting of chlorite + sericite + quartz + sulphides in the Sierra del Guadarrama. (Casquet et al., 1991; Caballero et al., 1992a)

In spite of local complexities, the veins display a gross vertical and lateral zoning. They show a deeper and outer quartz zone, an intermediate fluorite zone and a shallower and inner barite zone. Minor amounts of carbonates, ankerite and calcite, are found as void fillings in the central and upper sections of the veins (Tornos et al., 1991). Sometimes a colour zoning is displayed by fluorite with an outer yellow type, an intermediate purple variety and an inner green zone in contact with the barite. Other gangue minerals found in the veins are chlorite, sericite and clay minerals. The ore minerals are galena, sphalerite and chalcopryrite with minor amounts of pyrite, freibergite, pearcite, bismuthinite, native bismuth and Bi–Ag sulphosalts. Alteration at the selvages includes silicification, sericitization and, to a lesser extent, chloritization, argillitization and adularitization. This host-rock alteration also appears to display a vertical zonation with adularitization being more intense at depth and the argillitization restricted to the shallower

TABLE 1

Bulk analysis of the gas fraction of fluid inclusions in quartz, fluorite and barite (in mole%) by mass spectrometry (British Geological Survey)

	Quartz	Fluorite		Barite			CB-
	CB-B1	SE-2	SE-3 ^a	AS-101	AS-53 ^a	AS-104 ^a	
H ₂ O	94.28	98.53	98.28	99.10	97.55	95.96	96.1
CO ₂	5.22	0.85	0.68	0.55	0.66	3.51	1.3
CH ₄	0.12	0.08	0.05	0.06	0.09	0.06	0.0
CO	0.19	0.35	0.01	0.21	0.00	0.19	0.2
H ₂	0.04	0.10	0.77	0.09	1.41	0.28	1.4
N ₂	0.16	0.00	0.22	0.00	0.29	0.00	0.0

^aMean of two analyses.

sections of the vein system (Locutura and Tornos, 1987; Mayor et al., 1989).

Fluid-inclusion data reflect the internal zoning of the veins. Homogenization temperatures in primary inclusions in quartz, fluorite and barite decrease regularly from 300° to 250°C, 270° to 150°C and 200° to 125°C, probably reflecting progressively lower precipitation temperatures (Locutura and Tornos, 1987). Fluid-inclusion studies, chemical analyses of decrepitates and thermodynamic constraints have led to a model of vein evolution consisting of the mixing of an ascending, reduced CO₂-poor and low-salinity fluid (<0.6 *m*) Na-K fluid, with a shallow, oxidized and more saline (>2.8 *m*) Na-K-Ca-Mg brine (Tornos et al., 1991). Fluid pressure was probably <100 bar. Analyses of volatiles contained in fluid inclusions in fluorites and barites by decrepitation under vacuum and mass spectrometry (Shepherd et al., 1991) show that fluids were almost pure water ($X_{H_2O} > 0.95$) with small amounts of CO₂ ($X_{CO_2} < 0.05$) and traces of H₂, CH₄ and CO (Table 1). Precipitation of the ore took place in a near-neutral pH environment and close to the pyrite-haematite-magnetite buffer. Geochemical calculations show that mixing of two such fluids accounts well for the observed zonal arrangement (Tornos et al., 1991).

4. Isotope work

4.1. Sampling and analytical procedure

Sampling was restricted to two of the most important barite-fluorite veins in the area. These veins comprise the Asturiana and Eusebio Mines (AS Mine and SE Mine, respectively; Fig. 1) both of which are hosted by porphyritic biotite adamellites belonging to the same intrusive unit. Samples of barite, fluorite, carbonates and sulphides were separated by hand-picking. Twelve samples of fluorite from the SE Mine, where the colour zoning is best displayed, were analyzed for Nd and ⁸⁷Sr/⁸⁶Sr. Four barites, three of them from the AS Mine, were analyzed for ⁸⁷Sr/⁸⁶Sr. Barites from the AS Mine were also analyzed for $\delta^{34}S$, along with two sphalerites and galena from the same mine. $\delta^{18}O$ and $\delta^{13}C$ were also measured on two calcites from the SE Mine. Stable isotope measurements were carried out at the Scottish Universities Research and Reactor Centre and the Salamanca University Isotope Laboratory. Results are displayed in Tables 2 and 3.

Concentrations of Rb and Sr as well as Rb/Sr atomic ratios for the whole-rock samples were determined by X-ray fluorescence spectrometry (Analytical Geochemistry G

TABLE 2

Sm-Nd and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic analyses of Sierra de Guadarrama fluorites, barites and whole-rock samples

Sample	Mineral	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\epsilon\text{Nd}_{145\text{Ma}}$	$(^{87}\text{Sr}/^{86}\text{Sr})_i$
SE	B	—	—	—	—	0.717164	—	—
SEp	F	4.93	15.55	0.1915	0.512219	0.717795	-8.1	—
SE-1p	F	6.33	22.55	0.1697	0.512214	0.717374	-7.8	—
SE-2p	F	6.26	18.40	0.2057	0.512236	0.717170	-8.1	—
SE-g	F	9.79	30.00	0.1970	0.512217	0.720679	-8.3	—
SE-2g	F	13.4	46.50	0.1534	—	0.716279	—	—
SE-5g	F	9.24	29.00	0.1926	0.512224	0.720265	-8.0	—
SEy	F	2.45	3.84	0.3850	0.512413	0.715438	-7.9	—
SE-3y	F	2.15	3.20	0.4055	0.512430	0.717168	-8.0	—
SE-4y	F	0.07	0.30	0.1561	0.512210	0.717274	-7.6	—
SE-8	A	7.96	38.50	0.1250	0.512217	0.726406	-6.9	0.7194
AS-3	B	—	—	—	—	0.716989	—	—
AS-4	B	—	—	—	—	0.715567	—	—
AS-101	B	—	—	—	—	0.716151	—	—
AS-1y	F	3.70	6.75	0.3309	0.512320	0.716934	-8.7	—
AS-y	F	4.25	7.41	0.3466	0.512333	0.716872	-8.8	—
AS-gp	F	3.70	7.24	0.3087	0.512319	0.716893	-8.3	—
AS-12	A	6.90	33.17	0.1258	0.512167	0.729441	-7.9	0.7209

Symbols: A = adamellites; F = fluorites; B = barites; p = purple; y = yellow; g = green; vp = green-purple. — = no data.

British Geological Survey) following the methods of Pankhurst and O'Nions (1973). Sr isotope ratio measurements were made on an automated multicollector Finnigan-MAT[®] 262 mass spectrometer at the NERC Isotope Geosciences Laboratory.

Sm and Nd concentrations were obtained by isotope dilution using a mixed ^{149}Sm - ^{150}Nd spike solution. Sm and Nd were separated using cation-exchange columns filled with Bio-beads[®] coated with bis-di-ethylhexyl hydrogen phosphate (HDEHP). Isotopic analyses were made on an automated multicollector VG[®] 354 mass spectrometer.

Fluorites and barites were decomposed using hydrochloric acid and separation of the required elements for isotopic analysis was by cation exchange and reverse-phase chromatography as described above for the whole-rock samples. Analytical data are presented in Table 2.

Errors are quoted throughout as two standard deviations from measured or calculated

values. The decay constants used are $\lambda^{87}\text{Rb} = 1.42 \cdot 10^{-11} \text{ a}^{-1}$ and $\lambda^{147}\text{Sm} = 6.54 \cdot 10^{-12} \text{ a}^{-1}$ (Steiger and Jäger, 1977). Analytical uncertainties are estimated to be $\pm 0.01\%$ for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, and $\pm 1.0\%$ for both the $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios. ϵ -Values were calculated relative to a chondrite present-day $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.51262 and $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.1967. Replicate analyses of the NBS 987 Sr isotope standard yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710247 ± 0.000024 ($n = 215$). 56 analyses of the Johnson & Matthey[®] Nd standard during 1992 gave a mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.511114 ± 0.000026 .

4.2. Sm-Nd systematics

It is well known that fluorites can be considerably enriched in rare-earth elements (REE), and that total REE content as well as the degree of inter-elemental fractionation can vary significantly within short distances in the min-

eral (e.g., Möller and Morteani, 1983). Application of the Sm–Nd isotope data has recently proved to be a very useful technique to constrain the source of the hydrothermal fluids and to date fluorite deposits (Halliday et al., 1986, 1990; Darbyshire and Shepherd, 1990; Chesley et al., 1991).

Total REE content and chondrite-normalized profiles of the fluorites (SE Mine) show a clear relationship with colour. Total contents vary from 12–39 ppm in the yellow type to 182–192 ppm in the green type, with intermediate values in the purple varieties (89–105 ppm). Thus, the REE content increases inward from the vein wall. The yellow and purple fluorites show a slight relative enrichment in the intermediate and heavy REE + Y relative to the light ones (negative fractionation) and neither have a Eu anomaly (or at the most a very small one). Instead, the green fluorites exhibit relatively flat patterns with a large positive Eu anomaly (Fig. 2). All the fluorite REE profiles are very different to that shown by the host adamellite.

Sm–Nd data of the yellow, green and purple varieties of fluorite from the SE mine and yellow and green-purple fluorite from the AS Mine fluorite are presented in Table 2. The host adamellite from both mines was also analyzed for comparison. The $^{147}\text{Sm}/^{144}\text{Nd}$ ratio varies from 0.153 to single vein (SE Mine), the $^{147}\text{Sm}/^{144}\text{Nd}$ range can be as large as 0.252. Within any colour type (e.g., the SE Mine purple fluorite), the $^{147}\text{Sm}/^{144}\text{Nd}$ range is smaller.

The SE Mine fluorites define an isochron (MSWD=0.5, Fig. 3) yielding an age of 145 ± 18 Ma, with an initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.51205 ± 0.00003 . The mean age value corresponds to the Late Jurassic (Harland et al., 1982). If the error bar is considered, the age can range from the boundary of the Middle–Late Jurassic to the Early Cretaceous (Neocomian). The number of samples and the limited range of $^{147}\text{Sm}/^{144}\text{Nd}$ ratios preclude the determination of a Sm–Nd isochron age for the

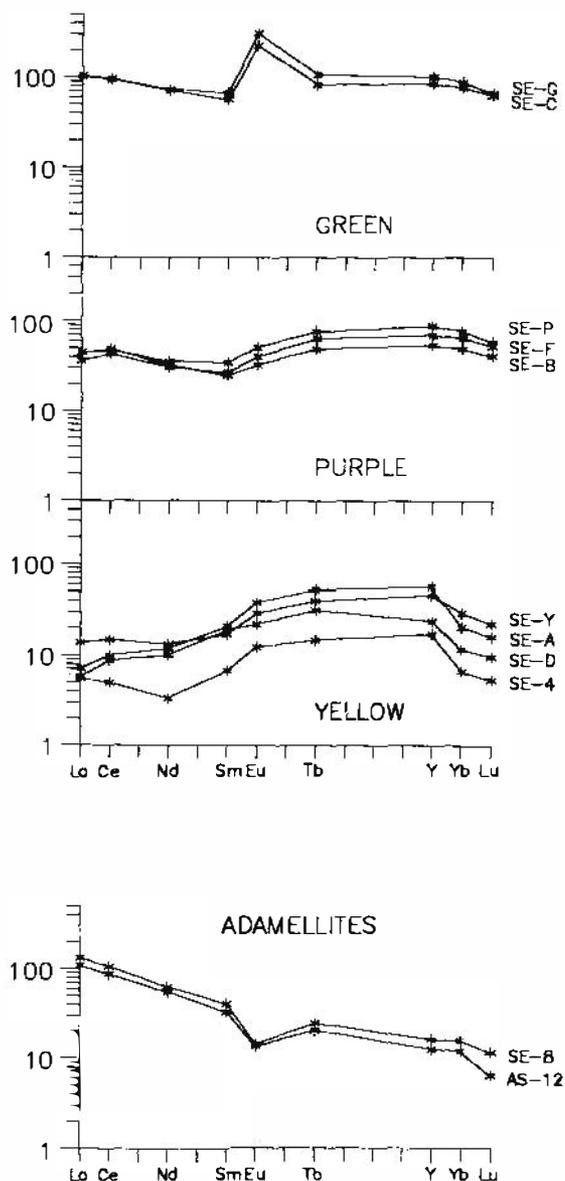


Fig. 2. REE patterns in fluorites from the SE Mine, and in host rocks (adamellites) from the SE and AS Mines.

AS Mine fluorites. The data plot slightly below the SE Mine isochron but the significance of this deviation is not yet certain.

The good fit of the isochron to the data points (MSWD=0.5), and the coincidence of the age with the K/Ar ages of the associated phyllic alteration (see below), are here taken as evidence of a fairly uniform $^{143}\text{Nd}/^{144}\text{Nd}$

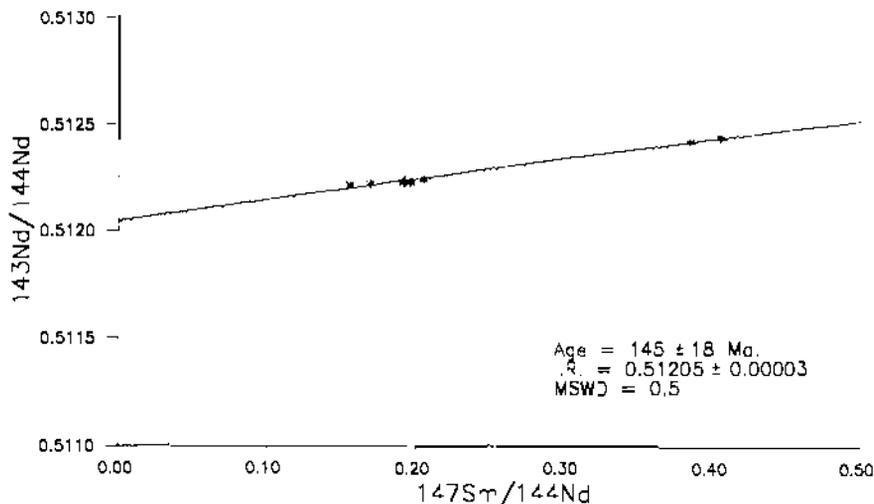


Fig. 3. Sm-Nd isochron from fluorites of the San Eusebio Mine.

composition of the parental hydrothermal fluid. Table 2 shows the ϵ_{Nd} -values calculated at 145 Ma for the SE Mine fluorites and the host adamellites from both mines. Adamellites are by far the most common granitoids exposed in the Sierra del Guadarrama and they can be taken as good representatives of the basement. The ϵ_{Nd} -values found from fluorites (-8.3 to -7.6) rule out any deep mantle-derived contribution in the fluids. Also, the value is lower than that of the host adamellites (-6.9). Disequilibrium of the fluid with the host whole-rock and/or a contribution from a less radiogenic shallow source must be considered.

4.3. Sr isotope composition

The low concentrations of Rb in barite and fluorite favour the use of these minerals for the determination of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the fluid (e.g., Reesman, 1968). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is a powerful tool to constrain the source of the hydrothermal fluid (e.g., Kesler et al., 1983; Lange et al., 1983; Barbieri et al., 1984, 1987; Strong et al., 1984; Ruiz et al., 1985; Dill and Nielsen, 1987; Baumann and Hofmann, 1988; Canals and Cardellach, 1993).

The $^{87}\text{Sr}/^{86}\text{Sr}$ -values in barites and fluorites

from the SE and AS Mines range from 0.7154 to 0.7207 as shown in Table 2. Fluorites from the SE Mine display a clear colour-related composition with highest Sr isotope ratios occurring in the internal green type. The variations found in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are larger than the analytical error (± 0.00002) and indicate differences in the isotopic composition of the hydrothermal fluids with time, and probably from one place to the other. In other words, the fluids were isotopically heterogeneous precluding a derivation of Sr from a single homogeneous source.

4.4. Stable isotopes

The C and O isotope compositions of two samples of carbonate (ankerite) filling late cavities in the AS Mine yielded $\delta^{18}\text{O}_{\text{SMOW}}$ -values of $+21.1$ to $+23.5\text{‰}$ and $\delta^{13}\text{C}_{\text{PDB}}$ of -8.6 to -7.8‰ (Table 3). Oxygen isotopic composition of the fluid calculated at $T=100^\circ\text{C}$, i.e. the estimated temperature of formation of the carbonates, would be $+1.0$ to $+3.5\text{‰}$ [using fractionation factors for ankerite-fluid from Morad et al. (1992)].

Sulphur isotope compositions were determined for barites and sulphides from the AS Mine (Table 3). $\delta^{34}\text{S}_{\text{CDT}}$ -values of two sphalerites are -1.0 and -0.8‰ and one galena is

TABLE 3

Sulphur isotopic composition ($\delta^{34}\text{S}_{\text{CDT}}$) of sulphides and sulphates from San Eusebio (SE) and Asturiana (AS) Mines, and $\delta^{18}\text{O}_{\text{SMOW}}$ and $\delta^{13}\text{C}_{\text{PDB}}$ of carbonates from SE Mine

Sample	$\delta^{34}\text{S}$ (‰ vs. CDT)			
	barite	galena	sphalerite	chalcopyrite
<i>Asturiana Mine (Fresnedillas):</i>				
AS-102			-1.0	
AS-106			-0.8	
AS-100		-3.4		
AS-105	+15.8			
AS-B	+15.8			
AS-101	+15.5			
SCS-36	+14.9			
<i>San Eusebio Mine (Colmenar de Arroyo):</i>				
SCS-12	+15.6	-3.6	-1.6	-1.1
SCS-18	+15.1	-1.8	-1.9	
SCS-28	+15.5	-4.4		
SCS-29	+16.5	-3.4		
Sample	$\delta^{18}\text{O}$ (‰ vs. SMOW)	$\delta^{13}\text{C}$ (‰ vs. PDB)		
AS-CC	+23.5	-7.8		
AS-108a	+21.1	-7.8		
AS-108b	+22.8	-8.6		

SCS samples and the name of locations in brackets are from Lillo et al. (1992).

-3.4‰. $\delta^{34}\text{S}$ -values of barites range from +15.5 to +15.8‰. These values are in agreement with the ranges of $\delta^{34}\text{S}$ found by Lillo et al. (1992) for a larger set of Ba-rich veins (included those studied here), of the SCS (galenas -4.4 to -1.8‰; sphalerites -1.9 to -1.6‰; barites +14.9 to +16.5‰; see Table 3). Similar values in sulphides and sulphates are found all over the world for the so-called zoned polymetallic hydrothermal veins (Field and Fifarek, 1985).

Sulphide-sulphate isotope thermometry, based on data from Lillo et al. (1992) for the SE Mine and equations of Field and Fifarek (1985, table 6.5), gives unreasonably high values (324-381°C) that are above the upper thermal limits found for the precipitation of fluorite on the basis of fluid-inclusion studies (270-300°C). It suggests that these minerals

did not form in isotopic equilibrium. This disequilibrium is to be expected in these low-temperature veins due to the lack of exchange between aqueous sulphide and sulphate after mixing (Ohmoto and Rye, 1979; Ohmoto and Lasaga, 1982; Field and Fifarek, 1985; Ohmoto, 1986).

5. Chronological considerations

The age of the fluorite-barite veins coincides within the limits of error, with the K-Ar ages of 152 ± 4 and 156 ± 6 Ma found for the spatially associated phyllic alteration (Casquet et al., 1991). Both types of hydrothermal rocks are probably the consequence of a common tectonic event. These results are clearly at odds with the Hercynian magmatic-related hypotheses proposed for these veins by Vindel

(1980), Ortega et al. (1988), and Lillo et al. (1992).

Late Jurassic ages have also been found for other barite veins in other parts of the European Hercynian realm. Kelly and Wagner (1977; see also Thadeu, 1982) obtained a fission-track age of 152 Ma for the Pb-Zn-Ba veins at Panasqueira. Bonhomme et al. (1987) have found K-Ar ages of 170–150 Ma for clay minerals associated with barite occurrences in the south French Central Massif and Germany. This supports the hypothesis of Ziegler (1988) that the European Hercynian basement underwent widespread fracturing during the Late Mesozoic, probably related to the opening of the North Atlantic.

6. Constraints on the provenance of the fluids

The data presented here strongly support the conclusions of Tornos et al. (1991) that two contrasting fluids were probably involved in the genesis of the barite-fluorite veins. The possible provenance of these fluids are now considered.

The occurrence of a pervasive hydrothermal alteration at the selvages of the veins, suggests that the hydrothermal fluids interacted with the host rocks. The Sr isotope composition of the adamellites calculated at $t = 145$ Ma is 0.7194 and 0.7209 at the ES and AS Mines, respectively. These values are higher than those of the fluorite with the exception of two samples of the green variety from the SE Mine that are slightly higher, but still within the limits of error. On the basis of this limited sampling an exclusive contribution to the fluid components by the crystalline basement is unlikely and another less radiogenic source is required. In the absence of other suitable lithologies in the area [orthogneisses are more evolved radiogenically than the same granitoids; ($^{87}\text{Sr}/^{86}\text{Sr}$)_{145\text{Ma}}} for the Abantos Gneiss range from 0.7383 to 1.0064; Vialette et al., 1987], Sr must have been derived from external fluids.

Sr isotope ratios of seawater (and meteoric

water) are low (present-day value is 0.70907). However, this ratio has varied during geological time as a consequence of plate interactions and sea-floor spreading (Burke et al., 1982). These authors provide a $^{87}\text{Sr}/^{86}\text{Sr}$ vs. time curve for the Phanerozoic, fitting values obtained from marine sediments collected from all over the world. A value of ~ 0.7068 , which is also the lowest Phanerozoic ratio, is found for the Late Jurassic seawater. Koepnick et al. (1990), in a thorough review of the Triassic–Jurassic portion of the curve, show that this should be considered more properly a band with values of the Sr isotope ratio varying between 0.70608 and 0.70702 at 145 Ma, with a mean value of ~ 0.70691 . Mixing of different proportions of seawater (or meteoric water) and an ascending hot fluid having interacted with the host adamellites would explain the Sr isotope compositions found in barites and fluorites as well as their variations in time and space. Because of the probable presence of highly radiogenic metamorphic pre-Hercynian rocks in the emerged areas, the Sr isotope ratio of the shallow water was probably higher thus reducing the importance of the shallow contribution. This shallow contribution was probably very small for the case of the two green fluorites of the SE Mine that show ($^{87}\text{Sr}/^{86}\text{Sr}$)_{145\text{Ma}}} values close to 0.720.

Baumann and Hofmann (1988) have reviewed in detail the problem of the fluid source for barite-fluorite veins in different geological settings of the Hercynian basement in Germany. High Sr isotope compositions that overlap our data, i.e. 0.715–0.720, are found in fluorites and barites from the Central and Southern Black Forest, southwest Germany, where most of the veins are also hosted by granitoids and orthogneisses. Baumann and Hoffman conclude that no direct relationship exists between the Sr isotope compositions in the vein minerals and the host rocks. In their opinion, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios represent the averaged time-integrated compositions of the underlying rocks. Taking into account that

barite-fluorite veins are almost everywhere related to unconformities (e.g., Dill and Nielsen, 1987), the influence of shallow marine or meteoric waters should not be disregarded in this case.

Mixing of relatively high- and low- ϵ_{Nd} components, from the host adamellites and from a hypothetical seawater or meteoric water, respectively, could explain the calculated composition of the fluid as well as the observed $^{147}Sm/^{144}Nd$ variations.

Stille et al. (1989) have defined the Nd isotope composition of Jurassic seawater on the basis of data from metasediments and Mn ores collected at the Pennine realm in the Alps, Central Europe. They obtained an average $^{143}Nd/^{144}Nd$ initial value of 0.512105 ± 0.000018 ($\epsilon_{Nd} = -6.7 \pm 0.6$) calculated at 150 Ma. This value is high relative to the SE Mine fluid, in spite of the fact that extreme figures of $\epsilon_{Nd(150Ma)}$ as low as -7.7 are found in the Mn ores. However, these values correspond to deep seawater with no detrital influence. In our case if seawater existed in Jurassic times above the Sierra del Guadarrama realm, the depth of the water had to be very shallow. Large amounts of metamorphic rocks were probably exposed at these times in the source areas, on account of the erosion level, and could lead to decreased ϵ_{Nd} -values compared with deep seawater (Piepgras and Wasserburg, 1980). In fact, Michard et al. (1985) have found values of ϵ_{Nd} as low as -11.2 to -8.8 for Jurassic sediments in Lorraine, France, a paleogeographic environment similar to the Sierra del Guadarrama. These values attest to an important metamorphic component in the sediments and therefore to correspondingly low ϵ_{Nd} -values in the waters. Meteoric waters of the same age within the Tethys realm could also show the same isotopic signature as deduced for seawater.

However, a more realistic explanation of the low ϵ_{Nd} -values shown by the fluorites involves the dissolution behaviour of the host-rock minerals during the hydrothermal alteration.

This seems particularly true for the two green fluorite samples discussed above, which on the basis of Sr isotopes suggest a minimum shallow fluid contribution. In spite of this, these fluorites show very low ϵ_{Nd} -values (-6.9 for the adamellite vs. -8.3 and -8.0 in the fluorites).

Low Sm/Nd ratios of feldspars relative to the accessory minerals such as apatite, zircon and sphene (Hanson, 1980), along with mass-balance considerations, could explain the isotopic composition of fluorites. The incongruent dissolution of feldspars during phyllic alteration (quartz + sericite + chlorite) is probably the main process controlling the isotopic composition of the ascending fluid. Most of the REE contained in accessory minerals and biotite are probably retained in spite of chloritization (Alderton et al., 1980) and therefore do not contribute to a large extent to the fluid composition. This can explain the fairly uniformity of the initial $^{143}Nd/^{144}Nd$ argued above, as well as the low ϵ_{Nd} -values, on account of the lower Sm/Nd ratios of feldspars relative to the whole rock, largely controlled by the accessory minerals and biotite (Alderton et al., 1980). Variations in the Sm/Nd ratio in the fluorite can be the consequence of a combination of factors like Sm/Nd fractionation among fluid and feldspars as a function of variations in the fluid/rock ratio (Rosing, 1990), or among feldspars and sericite, as well as of kinetic constraints. Very low total REE contents expected in the shallow fluid will not modify to a significant extent the above considerations. Therefore the Sm/Nd data do not conflict with the mixing model, although taken alone cannot be considered conclusive.

The fluid sulphur isotope signatures calculated from the sulphides fractionation curves at temperature between 300° and $150^\circ C$ vary in the range -1.5 to $+0.1\%$, which is within the range of igneous derived sulphur in reduced magmas ($\delta^{34} = -3$ to $+3\%$; Ohmoto, 1986). Since there is no evidence of magmatic fluids involved in the system, sulphur was most

likely derived from leaching of pyrrhotite in the host granitoids (Ohmoto and Rye, 1979).

The interpretation of the sulphur isotope data of the barites is less straightforward. In this type of a system some oxidation of the aqueous sulphide to sulphate might be expected, leading to a variable range of $\delta^{34}\text{S}$ -values in barites and more negative $\delta^{34}\text{S}$ -values in sulphides (Ohmoto and Rye, 1979). However, the restricted range of $\delta^{34}\text{S}$ in barites, found in the SE and AS Mines as well as in other similar veins in the Sierra de Guadarrama, argue for a very limited oxidation and supports derivation of sulphate strictly from marine sources.

The isotopic compositions of barites from the SE and AS Mines closely match the $\delta^{34}\text{S}$ signature of Middle Triassic to Late Jurassic seawater ($+16 \pm 1.5\%$; Claypool et al., 1982). These $\delta^{34}\text{S}$ signatures are distinctly different from Permian sulphates ($\delta^{34}\text{S} = +10.5 \pm 1.0\%$) and younger sulphates (Cretaceous seawater is heavier except for a minimum of $\sim +14\%$ at the Aptian-Albian; Claypool et al., 1982). However, Utrilla (1989) has recently found that the range of $\delta^{34}\text{S}$ -values of Triassic-Liassic sulphates in northeastern Spain is very broad (from $+10.2$ to $+19.2\%$) and very variable even at the local scale. This opens the possibility of the sulphate in barites being derived from dissolution of pre-Late Jurassic evaporites. In fact, Upper Triassic (Keuper) and Liassic evaporites are common in the Iberian realm, to the east of the studied area. However, $\delta^{34}\text{S}$ composition of sulphate in fluids

evaporites should probably display a variability at the regional scale that is not observed in the barites of the SCS. Also, out of 23 determinations of Keuper evaporites by Utrilla (1989), 20 are lower than $+15\%$, i.e. below the values found in the barite veins. Therefore, a provenance of the sulphur by dissolution of older evaporites seems unlikely.

Mixing of two solutions without subsequent S isotope exchange between aqueous S species

could well lead to the observed sulphur isotopic compositions. Short residence time of fluids,

controlled hydrothermal systems, would inhibit a significant oxidation of the aqueous H_2S in the ascending fluid (Ohmoto and Rye, 1979; Ohmoto and Lasaga, 1982), thus preserving the original "igneous" signature in the sulphides. On the other hand, "per descensum" sulphates would retain the original marine/evaporitic isotopic signatures

The oxygen isotope values of carbonates found in the uppermost zones of the veins are consistent with an evolved marine or evaporitic origin. The $\delta^{13}\text{C}$ -values are relatively low and suggest a derivation of the carbon from marine water. Similar values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ have also been found by Morad et al. (1992) in diagenetic carbonate cements in Permian to Triassic sandstones east of the SCS. However, these authors argue for a meteoric origin for the fluid,

resulting from complex changes during diagenesis and controlled by climatic conditions.

7. Palaeogeographic implications

The data presented in this work demonstrate that at least some of the barite-fluorite veins of the Sierra del Guadarrama are probably Late Jurassic in age. The $^{87}\text{Sr}/^{86}\text{Sr}$ and sulphur isotopic composition argue for mixing of an ascending hot meteoric fluid, modified by reaction with the host rocks, with a shallow brine probably of marine/evaporitic provenance.

The sediments resting unconformably on the Hercynian basement in the Sierra del Guadarrama are Upper Cretaceous continental to marine materials. To the east and northeast of the Sierra del Guadarrama, mostly continental Triassic sediments, including important thicknesses of Keuper evaporites, and Lower Jurassic marine carbonates are found unconformably overlain by the Cretaceous. An Upper Jurassic coastline has been well defined far to

the northeast, in the Iberian Ranges by Alonso and Mas (1990), but evidence for Middle to Upper Jurassic sediments in central Spain is still lacking.

It is clear that the sedimentation of the Cretaceous was preceded by an important period of uplift and erosion corresponding to the Neokimmerian tectonic phase. The importance of the erosion is still unknown in the Sierra del Guadarrama realm, and the possibility that Triassic and probably Lower Jurassic sediments once existed here cannot be ruled out. With regard to the Middle to Upper Jurassic, a sea entrance from the south remains a possibility. The existence of a shallow platform joining central Spain with the Iberian or the Subbetic realm in the south is not in conflict with our data.

8. Conclusions

Barite-fluorite veins in the southern Sierra del Guadarrama are of Late Jurassic age. Isotopic data support previous conclusions by Tornos et al. (1991) that show that fluid mixing is an important mechanism in the genesis of the "unconformity-related" F-Ba veins. The isotopic composition of the first fluid resulted from fluid-host rock interaction at depth; no evidence for magmatic or deeper mantle derivation has been found. This fluid ascended along the opened fractures. The second fluid was shallow and contained seawater sulphate. This water probably derived from a shallow platform realm or a close-to-the-shore evaporitic environment. A re-entrant of the Upper Jurassic coastline from the south, stretching at least to the Sierra del Guadarrama, constitutes a feasible palaeogeographic explanation.

Mixing of the two fluids was a nonequilibrium process for the sulphur isotopes, probably because of short residence times in the open fractures. The isotope signatures of the ascending and the shallow fluids have been preserved in the sulphides and sulphates, respectively.

Acknowledgements

This work has in part been financed by the DGICYT Spanish Project No. PB88-124 "Posthercynian Hydrothermal Activity in the Spanish Central System". Funds for the stay of two of the authors at the NERC at Nottingham for some of the isotopic and fluid-inclusion work were provided by the DGICYT project and a British Council Grant (C.G.), and the Spanish-British Joint Action Programme No. PB-88 (F.T.). To all these Institutions we are grateful. Our thanks go also to J.M. Caballero, Dr. J.M. Gonzalez Casado and J. Locutura for their help and critical comments with regard to the hydrothermal evolution of the Spanish Central System. Special thanks are extended to Drs. N.J. Snelling, T.H.E. Heaton and T.J. Shepherd for providing valuable comments to this paper and substantial help in the fluid-inclusion analysis (T.J.S.). The paper has benefited by suggestions by Dr. R.O. Rye and another anonymous reviewer.

References

- Alderton, D.H.M., Pearce, J.A. and Potts, P.J., 1980. Rare earth element mobility during granite alteration: Evidence from southwest England. *Earth Planet. Sci. Lett.*, 49: 149-165.
- Alonso, A. and Mas, R., 1990. El Jurásico superior marino en el Sector Demanda-Cameros (La Rioja-Soria). *Cuad. Geol. Iberica*, 14: 173-198.
- Barbieri, M., Masi, U. and Tolomeo, L., 1984. Strontium geochemical evidence for the origin of the barite deposits from Sardinia, Italy. *Econ. Geol.*, 79: 1360-1365.
- Barbieri, M., Bellanca, A., Neri, R. and Tolomeo, L., 1987. Use of strontium isotopes to determine the sources of hydrothermal fluorite and barite from northwestern Sicily (Italy). *Chem. Geol. (Isot. Geosci. Sect.)*, 66: 273-278.
- Baumann, A. and Hofmann, R., 1988. Strontium isotope systematics of hydrothermal vein minerals in deposits of West Germany. *Geol. Rundsch.*, 77(3): 747-762.
- Bonhomme, M.G., Baudron, J.C. and Jebrak, M., 1987. Minéralogie, géochimie, terres rares et âge K-Ar des argiles associées aux minéralisations filoniennes. In: N. Clauer and S. Chaudhuri (Editors), *Isotopes in the Sedimentary Cycle. Chem. Geol. (Isot. Geosci. Sect.)*, 65: 321-339 (special issue).

- Burke, W.H., Denison, R.E., Hetherington, E.A., Koepnick, R.B., Nelson, H.F. and Otto, J.B., 1982. Variation of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ throughout Phanerozoic time. *Geology*, 10: 516-519.
- Caballero, J.M., Casquet, C., Galindo, C., Gonzalez-Casado, J.M., Snelling, N. and Tornos, F., 1992a. Dating of hydrothermal events in the Sierra del Guadarrama, Iberian Hercynian Belt (Spain). *Geogaceta*, 11: 18-22.
- Caballero, J.M., Casquet, C., Galindo, C., Gonzalez-Casado, J.M., Pankhurst, R. and Tornos, F., 1992b. Geocronología por el método Rb-Sr de las episienitas de la Sierra del Guadarrama, Sistema Central Español. *Geogaceta*, 13: 16-18.
- Canals, A. and Cardellach, E., 1993. Strontium and sulphur isotope geochemistry of low-temperature barite-fluorite veins of the Catalonian Coastal Ranges (NE Spain): a fluid mixing model and age constraints. *Chem. Geol. (Isot. Geosci. Sect.)*, 104: 269-280.
- Canals, A., Cardellach, E., Rye, D.M. and Ayora, C., 1992. Origin of the Atrevida Vein (Catalonian Coastal Ranges, Spain): mineralogic, fluid inclusion, and stable isotope study. *Econ. Geol.*, 87: 142-154.
- Casquet, C., Fuster, J.M., Gonzalez-Casado, J.M., Peinado, M. and Villaseca, C., 1988. Extensional tectonics and granite emplacement in the Spanish Central System — A discussion. In: E. Banda and L.A. Mendes-Victor (Editors), Fifth EGT Workshop: The Iberian Peninsula. European Science Foundation, Estoril, pp. 65-75.
- Casquet, C., Caballero, J.M., Galindo, C., Gonzalez-Casado, J.M., Pellicer, M.J. and Tornos, F., 1991. Dating of hydrothermal events in the Sierra del Guadarrama, Iberian Hercynian Belt, Spain. *Terra Abstr.*, 3: 2.
- Casquet, C., Tornos, F., Caballero, J.M. and Galindo, C., 1992. A revised model for the formation of dequartzified and alkalinized granites (episyenites). *Water-Rock Interaction*, Vol. 2. A.A. Balkema, Rotterdam, pp. 1481-1484.
- Chesley, J.T., Halliday, A.N. and Scrivener, R.C., 1991. Samarium-neodymium direct dating of fluorite mineralization. *Science*, 252: 949-951.
- Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H. and Zak, I., 1982. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chem. Geol.*, 28: 199-260.
- Darbyshire, D.P.F. and Shepherd, T.J., 1990. Rb-Sr and Sm-Nd constraints on the age of mineralization and the origin of hydrothermal fluids in SW England. 7th Int. Conf. Geochronol. Cosmochronol. *Isot. Geol.*, Canberra, A.C.T., Sept. 24-29 1990 (unpublished data).
- De Vicente, G., Gonzalez-Casado, J.M., Bergamin, J.F., Tejero, R., Babin, R., Rivas, A., H. Enrile, J.L., Giner, J., Sanchez Serrano, F., Muñoz, A. and Villamor, P., 1992. Alpine structure of the Spanish Central System. III Congr. Geol. España, 1: 284-288.
- Dill, H. and Nielsen, H., 1987. Geochemical and geological constraints on the formation of unconformity-related vein baryte deposits of Central Europe. *J. Geol. Soc. London*, 144: 97-105.
- Field, C.W. and Fifarek, R.H., 1985. Light stable-isotope systematics in the epithermal environment. *Rev. Econ. Geol.*, 2: 99-128.
- Halliday, A.N., Shepherd, T.J., Dickin, A.P., MacLaren, F. and Darbyshire, F., 1986. Sm-Nd dating and fingerprinting of the north Pennine fluorite deposits. *Terra Cognita*, 6: 2 (abstract).
- Halliday, A.N., Shepherd, T.J., Dickin, A.P. and Chesley, J.T., 1990. Sm-Nd evidence for the age and origin of a Mississippi Valley type ore deposit. *Nature (London)*, 344: 54-56.
- Hanson, G.N., 1980. Rare earth elements in petrogenetic studies of igneous systems. *Annu. Rev. Earth Planet. Sci.*, 8: 371-406.
- Harland, W.B., Cox, A.V., Llewellyn, P.G., Piekton, C.A.G., Smith, A.G. and Walters, R., 1982. *A Geologic Time Scale*. Cambridge University Press, London, 128 pp.
- Huertas, M.J., 1991. Las asociaciones filonianas tardihercénicas en la Sierra del Guadarrama (Sistema Central Español). Universidad Complutense de Madrid, Madrid, 336 pp.
- Ibarrola, E., Villaseca, C., Vialette, Y., Fuster, J.M., Navidad, M., Peinado, M. and Casquet, C., 1987. Dating of Hercynian granites in the Sierra de Guadarrama (Spanish Central System). In: F. Bea, A. Carnicero, J.C. Gonzalo, M. Lopez-Plaza and M.D. Rodriguez Alonso (Editors), *Geología de los Granitoides y Rocas Asociadas del Macizo Hespérico*. Rueda, Madrid, pp. 377-383.
- IGME (Instituto Geológico y Minero España), 1987. Mapa Metalogenético de España, No. 45. *Inst. Geol. Miner. España*, Madrid (scale 1:200,000).
- Kelly, W.C. and Wagner, G.A., 1977. Paleothermometry by combined application of fluid inclusion and fission track methods. *Neues Jahrb. Mineral., Monatsh.*, 1: 1-15.
- Kesler, S.E., Ruiz, J. and Jones, L.M., 1983. Strontium-isotopic geochemistry of fluorite mineralization (Coahuila, Mexico). *Isot. Geosci.*, 1: 65-75.
- Koepnick, R.B., Denison, R.E., Burke, W.H., Hetherington, E.A. and Dahl, D.A., 1990. Construction of the Triassic and Jurassic portion of the Phanerozoic curve of seawater $^{87}\text{Sr}/^{86}\text{Sr}$. *Chem. Geol. (Isot. Geosci. Sect.)*, 80: 327-349.
- Lange, S., Chaudhuri, S. and Clauer, N., 1983. Strontium isotopic evidence for the origin of barites and sulfides from the Mississippi Valley-type ore deposits in southeast Missouri. *Econ. Geol.*, 78: 1255-1261.
- Lillo, J., Oyarzun, R., Lunar, R., Doblas, M., Gonzalez, A. and Mayor, N., 1992. Geological and metallogenic aspects of late Variscan Ba-(F)-(base metal) vein de-

- posits of Spanish Central System. *Trans. Inst. Min. Metall. (Sect. B: Appl. Earth Sci)*, 101: 24-32.
- Locutura, J. and Tornos, F., 1985. Consideraciones sobre la metalogenia del sector medio del Sistema Central. *Rev. R. Acad. Cienc. Exactas Fis. Nat. Madrid*, 79: 589-615.
- Locutura, J. and Tornos, F., 1987. Aspectos genéticos de las mineralizaciones de F (Ba-Pb) del area de Colmenar de Arroyo (Sistema Central español). *Bol. Geol. Min.*, 98: 680-694.
- Mayor, N., Lunar, R. and Oyarzun, R., 1989. Fenómenos de alteración-mineralización en los yacimientos de Ba-F-(Pb-Zn-Cu-Ag) de la Sierra de Guadarrama. *Bol. Soc. Esp. Min.*, 12: 273-282.
- Michard, A., Gurriet, P., Soudant, M. and Albarède, F., 1985. Nd isotopes in French Phanerozoic shales: External vs. internal aspects of crustal evolution. *Geochim. Cosmochim. Acta*, 49: 601-610.
- Möller, P. and Morteani, G., 1983. On the geochemical fractionation of rare earth elements during the formation of Ca minerals and its application to problems of the genesis of ore deposits. In: *The Significance of Trace Elements in Solving Petrogenetic Problems and Controversies* Theophrastos, Athens, pp. 747-791.
- Morad, S., Al-Aasm, I.S., Ramseyer, K., Marfil, R. and Aldahan, A.A., 1992. Diagenesis of carbonate cements in Permo-Triassic sandstones from the Iberian Range, Spain: evidence from the chemical composition and stable isotopes. *Sediment. Petrol.*, 67: 281-295.
- Ohmoto, H., 1986. Stable isotope geochemistry of ore deposits. In: J.W. Valley, H.P. Taylor, Jr. and J.R. O'Neil (Editors), *Stable Isotopes in High Temperature Geological Processes*. Mineral Soc. Am., *Rev. Mineral.*, 16: 491-556.
- Ohmoto, H. and Lasaga, A.C., 1982. Kinetics of reactions between aqueous sulfates and sulfides in hydrothermal systems. *Geochim. Cosmochim. Acta*, 46: 1727-1745.
- Ohmoto, H. and Rye, R.O., 1979. Isotopes of sulfur and carbon. In: H.L. Barnes (Editor), *Geochemistry of Hydrothermal Ore Deposits*. Wiley, New York, N.Y., 2nd ed., pp. 509-567.
- Ortega, L., Vindel, E. and Lunar, R., 1988. Estudio de los filones de baritina intragraníticos del sector Cenicientos-Cadalso de los Vidrios (Sistema Central). *Bol. Soc. Esp. Min.*, 11: 89-99.
- Pankhurst, R.J. and O'Nions, R.K., 1973. Determination of Rb/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of some standard rocks and evaluation of X-ray spectrometry in Rb-Sr geochemistry. *Chem. Geol.*, 12: 127-136.
- Piepgras, D.J. and Wasserburg, G.J., 1980. Neodymium isotopic variations in seawater. *Earth Planet. Sci. Lett.*, 50: 128-138.
- Reesman, R.H., 1968. Strontium isotope compositions of gangue minerals from hydrothermal vein deposits. *Econ. Geol.*, 63: 731-736.
- Rosing, M.T., 1990. The theoretical effect of metasomatism on Sm-Nd isotopic systems. *Geochim. Cosmochim. Acta*, 54: 1337-1341.
- Ruiz, J., Kesler, S.E. and Jones, L.M., 1985. Strontium isotope geochemistry of fluorite mineralization associated with fluorine-rich igneous rocks from the Sierra Madre Occidental, Mexico: Possible exploration significance. *Econ. Geol.*, 80: 33-42.
- Shepherd, T.J., Bottrell, S.H. and Miller, M.F., 1991. Fluid inclusion volatiles as an exploration guide to black shale hosted deposits, Dolgellau gold belt, North Wales, UK. *J. Geochem. Explor.*, 42: 5-24.
- Steiger, R.H. and Jäger, E., 1977. Subcommission on Geochronology: Convention on the use of decay constants in geo- and cosmochronology. *Earth Planet. Sci. Lett.*, 36: 359-362.
- Stille, P., Clauer, N. and Abrecht, J., 1989. Nd isotopic composition of Jurassic Tethys seawater and the genesis of Alpine Mn-deposits: Evidence from Sr-Nd isotope data. *Geochim. Cosmochim. Acta*, 53: 1095-1099.
- Strong, D.F., Fryer, B.J. and Kerrich, R., 1984. Genesis of the St. Lawrence fluor spar deposits as indicated by fluid inclusion, rare earth element, and isotopic data. *Econ. Geol.*, 79: 1142-1158.
- Thadeu, D., 1982. Gîtes filoniens à Pb, Zn et Ba post-hercyniens au Portugal. *Bull. BRGM (Bur. Rech. Géol. Min.)*, Sect. II, No. 2, pp. 207-209.
- Thibieroz, J., 1987. Metallogenie triasique au nord et au sud des Pyrénées. *Cuad. Geol. Iber.*, 11: 739-758.
- Tornos, F., Casquet, C., Locutura, J. and Collado, R., 1991. Fluid inclusion and geochemical evidence for fluid mixing in the genesis of Ba-F (Pb-Zn) lodes of the Spanish Central System. *Mineral. Mag.*, 55: 225-234.
- Utrilla, R., 1989. Les composicions isotòpiques ($\delta^{18}\text{O}$, $\delta^{34}\text{S}$) del sulfat com indicadors de l'origen de les evaporites del Mesozoic i del Cenozoic de la Península Ibèrica i de les Illes Balears. Ph.D. Thesis, Universidad Central de Barcelona, Barcelona.
- Vialette, Y., Bellido, F., Fuster, J.M. and Ibarrola, E., 1987. Données géochronologiques sur les granites de La Cabrera. *Cuad. Geol. Iberica*, 7: 327-335.
- Vindel, E., 1980. Estudio mineralógico y metalogénico de la Sierra de Guadarrama (Sistema Central Español). Doctoral Thesis, Universidad Complutense de Madrid, Madrid, 249 pp.
- Ziegler, P.A., 1988. Evolution of the Arctic-North Atlantic and the western Tethys. *Mem. Am. Assoc. Pet. Geol.*, 43: 1-198.