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ARTICLE

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The influence of enclosing rock type on barite deposits, eastern Pyrenees, Spain: fluid inclusion and isotope (Sr, S, O, C) data

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Abstract The Rocabruna and Coll de Pal barite deposits, located in the eastern Pyrenees of Spain, fill karstic cavities within carbonate rocks of Cambrian and Devonian age, respectively. The deposits contain barite, chalcopyrite, tetrahedrite, pyrite and minor sphalerite and galena with saddle dolomite and quartz as gangue. Fluid inclusion data from Coll de Pal quartz and dolomite indicate that the mineralizing fluid was a polysaline $CaCl_2$-rich brine, with temperatures between 125 and 150 °C. C and O isotopic compositions of carbonates in both deposits are consistent with a progressive increase in temperature during deposition. The $\delta^{34}S$ values of barite, which range from 14.2 to 15.9‰ in Coll de Pal, and from 13.9 to 19.3‰ in Rocabruna, together with $^{87}Sr/^{86}Sr$ ratios ranging from 0.7118 to 0.7168 in Rocabruna, and from 0.7115 to 0.7136 in Coll de Pal, indicate two different fluid sources. We propose that these deposits formed as a result of mixing between a Ba-rich, sulfate-poor hot fluid, and sulfate-rich solutions of surficial origin. The different Sr isotope ratios in the deposits indicate that the hot Ba-rich fluids involved in each deposit were equilibrated with different rock types (carbonates and shales), in agreement with the geology of the two areas.

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Introduction

The Rocabruna and Coll de Pal deposits are part of an ore district in the eastern Pyrenees (Fig. 1) characterized by barite and minor tetrahedrite and/or chalcopyrite mineralization. These deposits consist of karst cavity fillings and are associated characteristically with carbonates of Cambro-Ordovician age in Rocabruna and of Devonian age in Coll de Pal. Although the Rocabruna deposit was also mined for Cu, barite has been the main ore of interest in both abandoned deposits. About 20 000 Tm of barite have been mined in each of the two deposits.

The study of radiogenic and stable isotope compositions of ores and their wall rocks coupled with fluid inclusion data in ore and gangue minerals is an essential tool in the understanding of ore-forming processes. Sr isotope studies in barites have proved to be useful in determining the source of Ba. Examples of such studies include those by Kesler et al. (1988), Dill and Carl (1987), Frimmel and Papesch (1990), Boni et al. (1992), Canals and Cardellach (1993) and Galindo et al. (1994) among many others. In carbonate-hosted deposits, detailed studies of C, O and Sr isotopic composition of carbonates may provide valuable information not only about their genesis, but also about the presence of alteration halos around the mineralization that can be used as tracers for locating additional ore bodies.

The purpose of the paper is to understand whether the barite mineralization was formed by fluids buffered by local host-rocks or by fluids whose chemistry retained a signature of a longer distance fluid migration. By integrating fluid inclusion, stable C, O and S isotope and Sr isotope data, we determine the nature and origin of mineralizing fluids and develop a genetic model which explains the processes that gave rise to the karst-filling deposits.

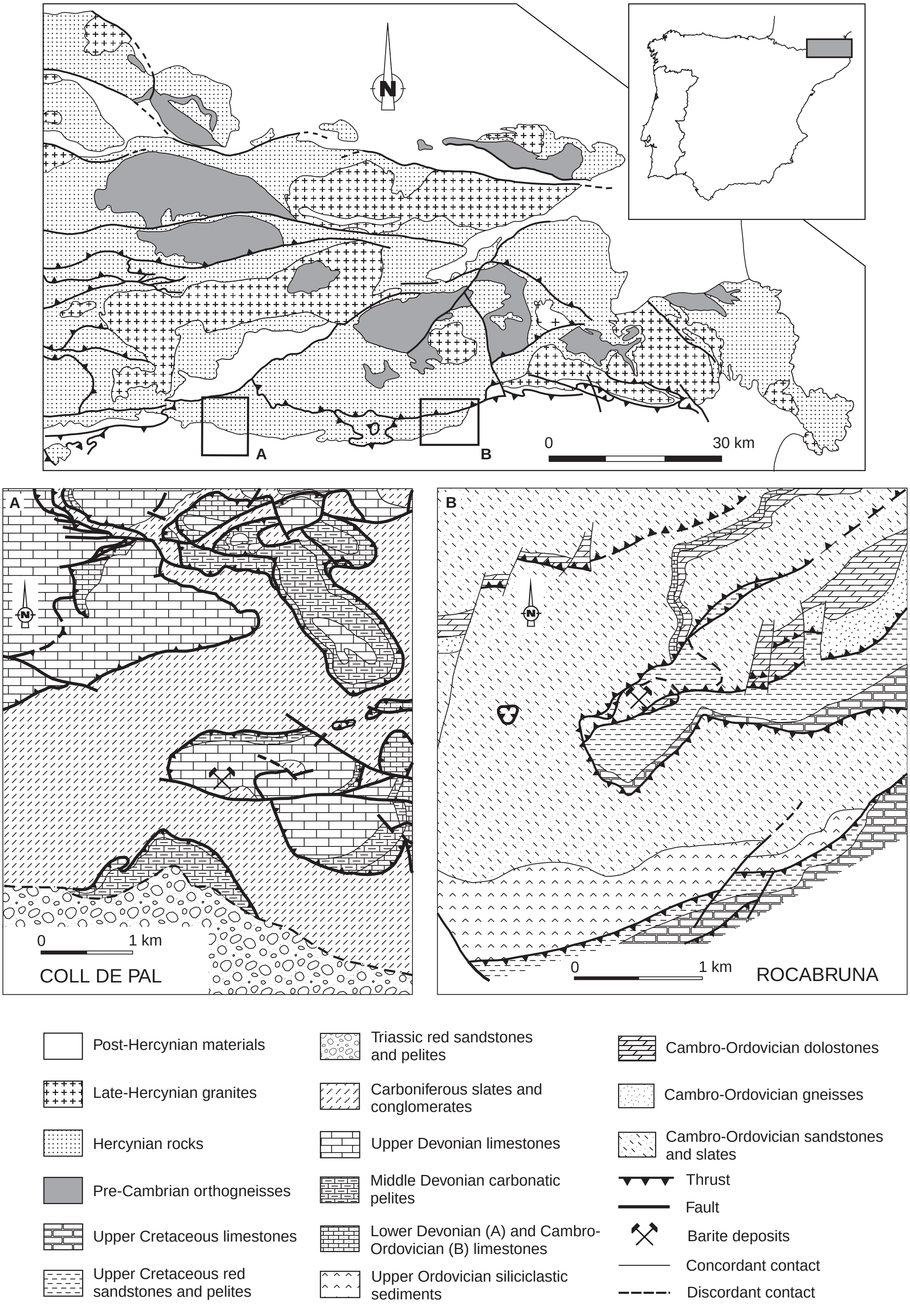

Fig. 1 Simplified geological map of the Eastern Pyrenees. Inset regions: *A* Coll de Pal deposits; *B* Rocabruna deposits

Geological setting

The Coll de Pal deposits are located in the Tossa d'Alp massif, eastern Pyrenees, about 150 km north of Barcelona. This massif is enclosed within the Cadí thrust sheet and is composed of Upper Paleozoic to Cenozoic sedimentary and volcanic rocks. Devonian limestones, and Carboniferous Culm facies schists and conglomerates are overlain unconformably by Stephanian to Permian rhyolites and ignimbrites (Domingo et al. 1988). Lower Triassic and Cretaceous sedimentary rocks unconformably overlie the peneplaned Hercynian basement. The Triassic is represented by red-bed facies conglomerate, sandstone and shale. The Cretaceous, unconformably deposited upon the Triassic, consists of limestones. The Cenozoic sequence contains red sandstone and shale. The area has been affected by the Hercynian and Alpine orogenies, resulting in a complex succession of thrusts and faults. The cavities are within the Devonian carbonates of the Tossa d'Alp unit (Domingo et al. 1988), close to a post-Hercynian fault.

The Rocabruna deposit is located about 40 km east of the Coll de Pal area, also within the eastern section of the Pyrenean belt, along the Ribes-Camprodon thrust. The area is characterized by paleozoic rocks, deformed during the Hercynian orogeny, late-Hercynian granitic intrusions, and Upper Cretaceous to Paleocene sedimentary rocks. The Paleozoic rocks consist of pelites and sandstones with some interbedded volcano-sedimentary rocks, conglomerates and carbonates. The ore deposits are hosted by dolostones that have been attributed to the Cambro-Ordovician by comparison with the lithologic facies of Montagne Noire, France. These rocks have been deformed and affected by very low-grade metamorphism during Hercynian time. Upper Cretaceous to Lower Paleocene sedimentary rocks consist of detrital and carbonate rocks and red-bed congomerates followed by a sandstone-shale alternation.

Mineralogy and ore deposit description

The Coll de Pal deposit consists of several karstic cavities in dolostones, up to decametric size, filled with barite and minor sulfides. Barite is also found within fractures and joints connecting the cavities. The bottoms of some cavities are filled partially with finely bedded dolomite (Fig. 2a) containing disseminated crystals of barite. Dolomite pervasively replaces limestone near the joints and karstic cavities, as well as around fractures affecting the Tossa d'Alp thrust. The mineral paragenesis consists of an early generation of ferroan, saddle dolomite, followed by a millimeter-sized band of chalcopyrite and pyrite. A later generation of calcite and quartz precedes precipitation of white barite, the most abundant mineral, which is present as large radial crystals up to meter size. Spar calcite crystals, up to 20 cm, are also found postdating barite. Finally, small calcite crystals (late calcite) fill geodic cavities. The mineralization sequence is shown in Fig. 2b.

The Rocabruna deposit also consists of irregular cavities of meter to decameter size within dolostone. The orebodies developed along the bedding and jointing of carbonates and are interconnected (Fig. 3a). The mineralized bodies are irregular in shape and show evidences of dissolution of the enclosing dolostone. The mineralogy consists mostly of barite and minor tetrahedrite-tennantite, chalcopyrite, galena, pyrite, sphalerite and locally dolomite. Barite is present as radial agreggates of up to meter size. Tetrahedrite-tennantite is the most important sulfide containing up to 0.8 wt.% of Ag (Soler and Ayora 1985). Quartz is scarce and locally replaces enclosing carbonates. Sulfides and quartz form a millimeter to centimeter thick aureole between the enclosing dolostone and barite. Blocks of host rock with partial sulfide coating are found within lower parts of barite bodies. This indicates dissolution and collapse of portions of the host rocks during barite precipitation. The mineralization sequence is shown in Fig. 3b.

The age of the deposits is not known, but some constraints may be inferred from field relationships. At Coll de Pal, carbonate host rocks have been dolomitized around a post-Hercynian fault; therefore dolomitization must be younger than Carboniferous age. At Rocabruna, the mineralization is affected by Alpine thrust faults (Soler and Ayora 1985).

Both deposits share some similarities. However, in contrast to Coll de Pal, Rocabruna is characterized by dissolution structures, more abundant sulfides, scarce saddle dolomite and quartz, and the absence of speleothems. These morphological and mineralogical features indicate physico-chemical differences of the mineralizing fluids between the two types of deposits.

Sampling and analytical techniques

Samples of Coll de Pal were collected from surface outcrops and from underground workings in Rocabruna. For sulfur isotope analyses, sulfides were converted to SO_2 gas by combustion with cupric oxide, and barite was converted to SO_2 by combustion with crushed silica. The isotopic ratios were measured using a Nuclide 6-60 double collector mass spectrometer. For oxygen isotope analysis of quartz oxygen was extracted using the BrF_5 technique (Clayton

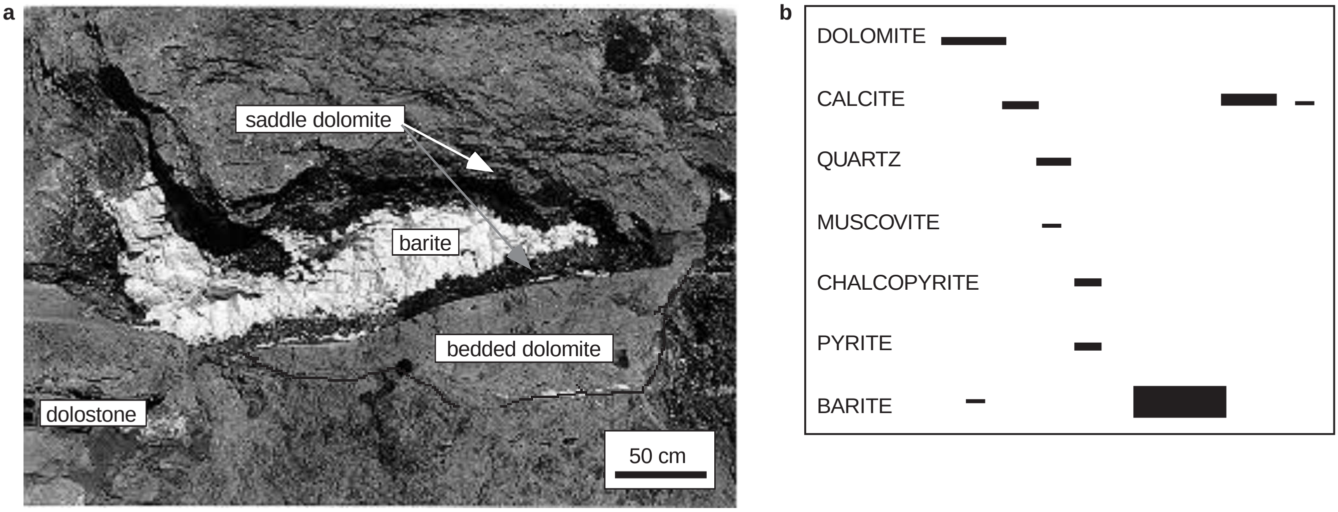

Fig. 2 **a** Finely bedded dolomite filling the bottom of a cavity with a ferroan, saddle dolomite coating and barite at Coll de Pal. **b** Paragenetic sequence of the Coll de Pal mineralization

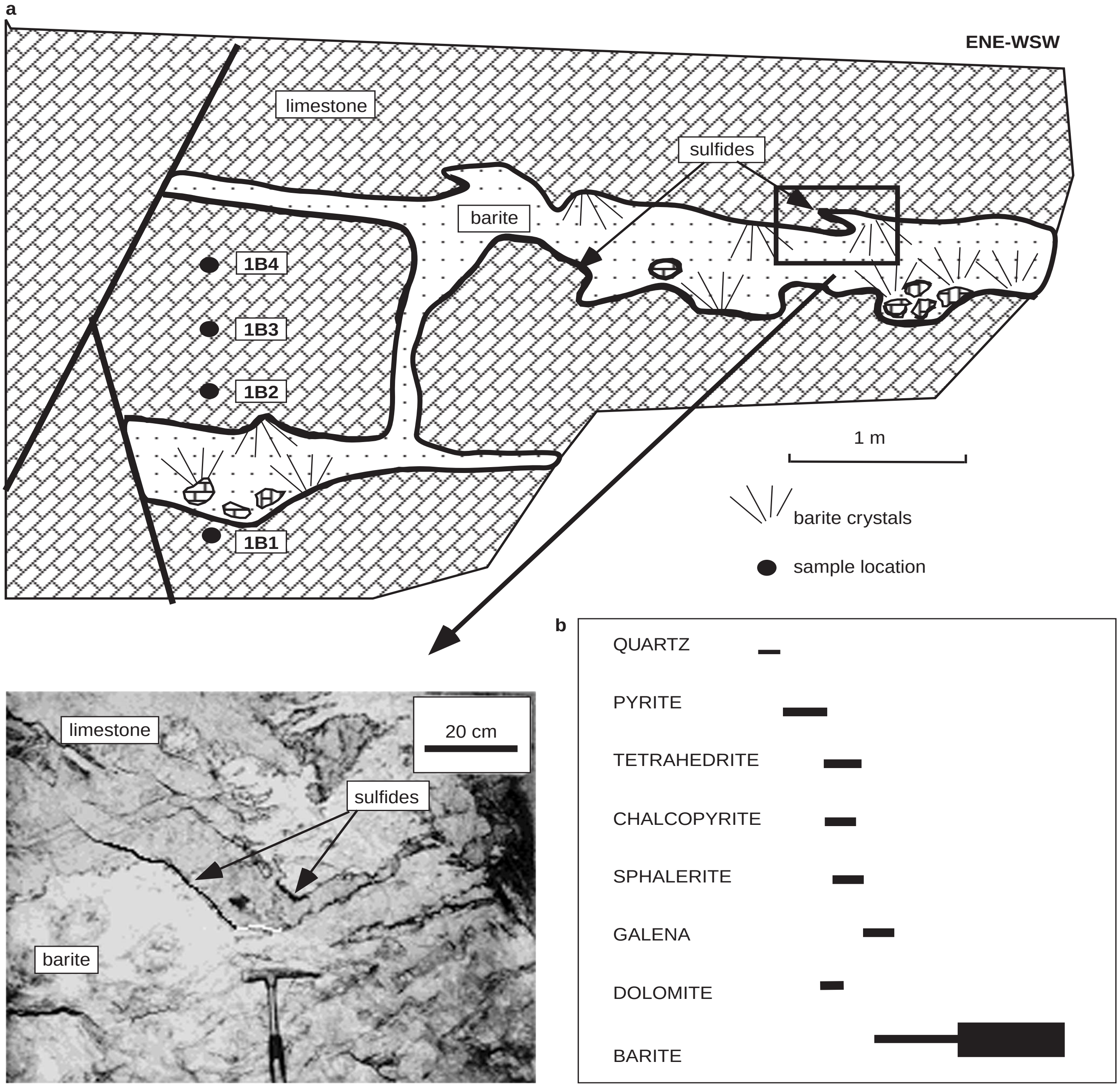

Fig. 3 **a** Replacement of carbonates along bedding and jointing in Rocabruna. Note the sulfide rim along the carbonate-barite contact. **b** Paragenetic sequence in Rocabruna

and Mayeda 1963). Carbon dioxide was extracted from carbonates using phosphoric acid (McCrea 1950). The isotopic ratios of the CO_2 and O_2 gases were measured using a Finnigan Mat 251 mass spectrometer. Isotopic compositions are reported in delta notation relative to CDT for sulfur, VSMOW for oxygen and VPDB for carbon.

For strontium isotope analyses, carbonate and barite chips were first dried for four hours. Barite was leached in 6N HCl at 100 °C overnight, and carbonates were dissolved in 1N HCl at 100 °C. The dry residues of both carbonates and barite were dissolved in 2.5N HCl, and after centrifugation, strontium was separated using standard cation exchange procedures. Sr isotope ratios were measured on a 7 collector Finnigan MAT 262 thermal ionization mass spectrometer. Standard deviation of the analyses was usually ±0.00004. Stable and radiogenic isotope results are presented in Table 1.

Fluid inclusion microthermometric measurements were made on doubly polished sections using a Chaixmeca freezing-heating stage. Some quartz-hosted fluid inclusions were also analyzed using the CRYO-SEM-EDS technique (Ayora and Fontarnau 1991). Sodium, calcium, potassium, magnesium and chlorine were measured with a reproducibility of ±10% or better.

Fluid inclusion results

A microthermometric fluid inclusion study was performed on quartz and dolomite from the Coll de Pal deposit. The small size (< 3 μm) and the scarcity of primary fluid inclusions in Rocabruna minerals precluded their study. Microthermometric data reported below pertain to primary and pseudosecondary inclusions.

Primary fluid inclusions in quartz crystals predating barite in the Coll de Pall deposit range between 5 and 60 μm and are distributed along growth bands. The size of the fluid inclusions in saddle dolomite is less than 5 μm and has only allowed us to obtain homogenization temperatures (*Th*). At room temperature, fluid inclusions in both minerals consist of a vapor and a liquid phase. *Th* values are grouped around 125 °C in saddle dolomite and around 150 °C in quartz (Fig. 4a). Ice melting temperatures in quartz-hosted fluid inclusions are around −16 °C, corresponding to a salinity of 20 wt.% NaCl equivalent. Eutectic temperatures are as low as −57 °C, indicating the existence of a polysaline brine. SEM-EDS analyses of frozen fluid inclusions show that the fluid is composed mainly of $CaCl_2$ and NaCl, with minor amounts of KCl (Fig. 4b). SO_4, Fe or Mg were also analyzed but not detected, therefore their concentrations are below the detection limit of 0.5 wt.%. Many inclusions show trapped crystals of platy morphology composed of Si, Al and K based on SEM-EDS analyses and have been interpreted as muscovite.

From these data, we conclude that temperature in the Coll de Pal deposits increased about 20 to 30 °C from dolomite to quartz deposition. The fluids were $CaCl_2$-NaCl-bearing brines with salinities up to 20 wt.% equivalent NaCl and were in equilibrium with muscovite at this temperature. The partial coexistence of quartz with calcite and the presence of muscovite in quartz fluid inclusions constrain the pH between 4 and 5 at about 150 °C, with potassium and calcium concentrations of 0.2 m and 2.8 m, respectively, based on SEM-EDS analyses and the total salinity of the fluid inclusions.

Fluids with similar temperature and salinity are present in many F-Ba-base metals vein systems within the Variscan domain of the Iberian Peninsula (Cardellach et al. 1990; Johnson et al. 1996; Subias and Fernandez-Nieto 1995; Tornos et al. 1991 among others).

Isotopic results and discussion

O and C isotopes

Coll de Pal

The Devonian limestone has a mean $\delta^{13}C$ value of 1.3‰ and a mean $\delta^{18}O$ value of 22‰. Both are within the values for marine carbonates of this age reported by Veizer and Hoefs (1976). Dolostones around the karstic cavities and along the E-W fracture postdating the Tossa d'Alp thrust have $\delta^{13}C$ and $\delta^{18}O$ isotopic values of 1.1 to 1.51‰ and 23.1 to 23.3‰, respectively (Fig. 5 and Table 1), indicating that the dolomitizing fluids were equilibrated isotopically with limestones. This composition is nearly identical to that shown by the bedded dolomite from the bottom of the cavities (1.4‰ and 23.4‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively). However, the large spar calcite crystals have lower values: $\delta^{13}C$ = −2.1‰ and

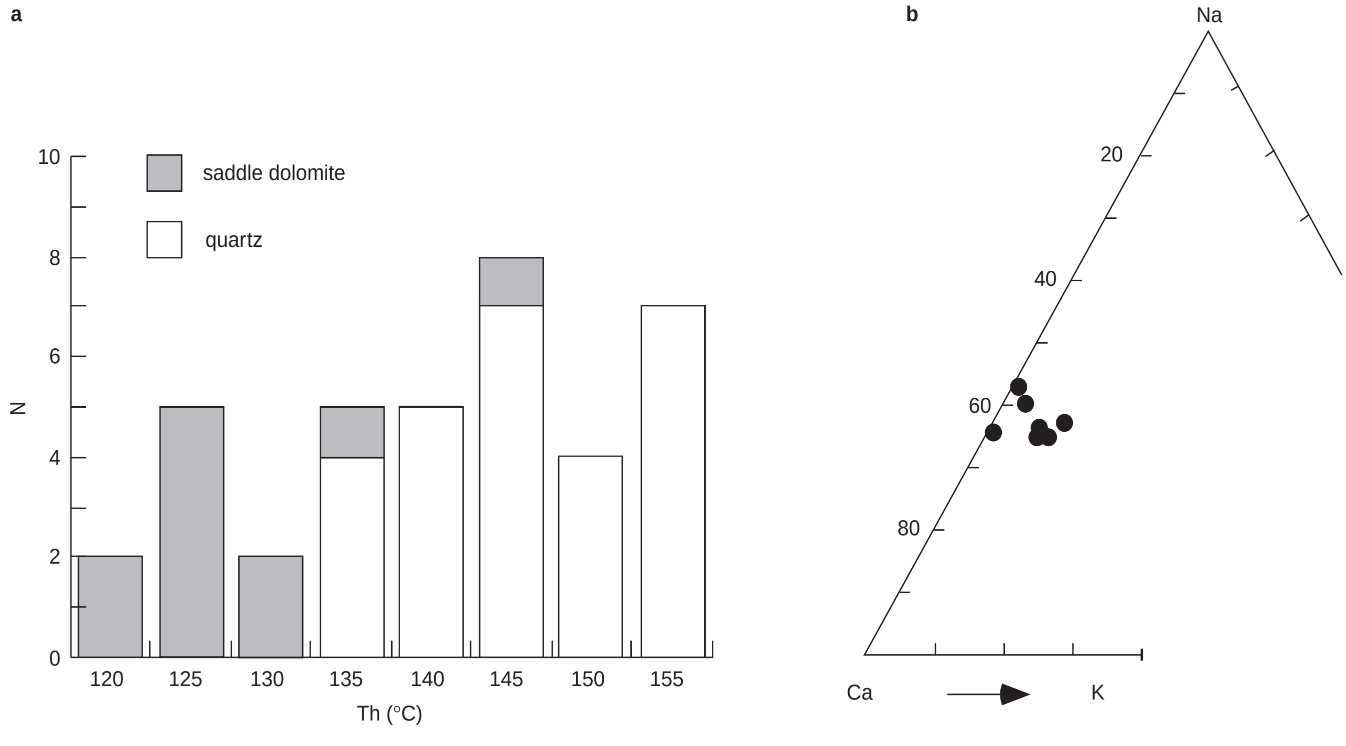

Fig. 4 a Homogenization temperatures (*Th* °C) of primary fluid inclusions in quartz and saddle dolomite from Coll de Pal. *N* = 38. **b** Na:K:Ca wt.% relations of frozen fluid inclusions in quartz from Coll de Pal analyzed by SEM-EDS

Table 1 Isotopic results of the analyzed samples

Sample	Mineral	$\delta^{13}C$	$\delta^{18}O$	$\delta^{34}S$	$^{87}Sr/^{86}Sr$
Coll de Pal					
CP-1	Limestone	0.5	21.4		
CP-2	Limestone				0.7097
CP-3	Limestone	1.5	22.3		0.7090
CP-4	Limestone	1.8	22.2		
CP-5	Dolostone	1.5	23.1		0.7107
CP-6	Dolostone				0.7106
CP-7	Dolostone	1.1	23.3		
CP-8	Bedded dolomite	1.5	23.2		
CP-9	Bedded dolomite	1.3	23.4		
CP-10	Bedded dolomite	1.4	23.7		0.7109
CP-11	Saddle dolomite	−1.6	22.7		
CP-12	Saddle dolomite	−0.1	22.1		
CP-13	Saddle dolomite	1.2	22.7		
CP-14	Saddle dolomite	1.2	22.9		0.7115
CP-15	Saddle dolomite	−0.8	22.9		
CP-16	Saddle dolomite	−0.2	23.1		
CP-17	Saddle dolomite	0.1	22.6		
CP-18	Saddle dolomite	0.5	22.5		
CP-19	Saddle dolomite				0.7139
CP-20	Saddle dolomite				0.7126
CP-21	Calcite	−0.3	19.4		
CP-22	Calcite	0.2	20.3		
CP-23	Calcite	0.0	20.3		
CP-24	Calcite	−0.1	19.3		
CP-25	Calcite	0.6	18.3		
CP-26	Calcite	0.1	19.1		0.7134
CP-27	Spar calcite	−2.4	21.1		
CP-28	Spar calcite	−4.1	21.5		0.7126
CP-29	Spar calcite	0.0	20.9		0.7128
CP-30	Late calcite	−6.2	24.8		
CP-31	Late calcite	−6.1	24.4		
CPB-1	Barite			15.9	
CPB-2	Barite			15.8	
CPB-3	Barite			15.1	
CPB-4	Barite			15.4	
CPB-5	Barite			15.7	
CPB-6	Barite			15.6	0.7123
CPB-7	Barite			15.7	0.7136
CPB-8	Barite			14.8	0.7115
CPB-9	Barite			15.1	0.7128
CPB-10	Barite				0.7126
CPB-11	Barite			14.2	
CPS-1	Chalcoprite			11.1	
CPS-2	Chalcoprite			10.8	
CPS-3	Chalcoprite			−0.9	
CPS-4	Chalcoprite			−1.2	
CPQ-1	Quartz		21.0		
CPQ-2	Quartz		21.3		
Rocabruna					
ARES-1	Regional dolostone	0.0	23.3		
ARES-2	Regional dolostone	−0.6	22.7		
1B1	Dolostone	−2.4	20.4		0.7160
1B2	Dolostone	−2.7	19.3		
1B4	Dolostone	−3.1	20.4		0.7155
1B7	Dolostone	−2.7	21.0		
1B8	Dolostone	−2.4	20.5		0.7182
1B9	Dolostone	−1.4	21.7		
1B10	Dolostone	−3.0	20.7		
1B13	Dolostone	−2.8	20.3		
1A3	Dolostone	−3.0	20.5		
2X2	Dolostone	−7.3	15.5		
3A2	Dolostone	−2.4	21.6		0.7162
1A1	Barite			19.0	0.7131
1B1W	Barite			18.7	0.7129
1B2W	Barite			15.7	0.7151
1B3W	Barite			16.6	0.7139

Table 1 Continued

Sample	Mineral	$\delta^{13}C$	$\delta^{18}O$	$\delta^{34}S$	$^{87}Sr/^{86}Sr$
1B4W	Barite			16.2	0.7144
1B5W	Barite			13.9	0.7124
1X54	Barite			19.3	0.7134
2A2	Barite			17.2	0.7122
2A3	Barite			17.6	0.7118
2A4	Barite			17.6	0.7132
2A5	Barite			18.4	0.7118
2D1	Barite				0.7168
2X6	Barite			17.9	0.7123
3A2	Barite			18.3	0.7126
3B2	Barite			18.6	0.7142
ZA-11	Tetrahedrite			1.1	
RB-Tr	Tetrahedrite			1.4	
RB-cpy	Chalcopyrite			8.0	
1B2	Chalcopyrite			8.1	

$\delta^{18}O = 21.1‰$. Late calcite has lower $\delta^{13}C$ values (−6.1‰), but higher $\delta^{18}O$ values (24.6‰).

The ferroan saddle dolomites have $\delta^{13}C = 0‰$ and $\delta^{18}O = 22.6‰$ (Fig. 5 and Table 1). As fluid inclusion data indicate that precipitation took place around 125 °C, the $\delta^{18}O$ value of water in equilibrium with the dolomites was about 5‰ based on the dolomite-water fractionation equation of Land (1983). Hydrothermal calcite coexisting with quartz shows almost constant $\delta^{13}C$ values of about 0‰, but variable $\delta^{18}O$ values between 18.3 and 20.3‰. This is compatible with precipitation from a fluid of constant composition, with a temperature increase from 125 to 150 °C according to the fluid inclusion data.

Taking a temperature of 150 °C and a mean $\delta^{18}O$ value for quartz of 21.1‰, the calculated $\delta^{18}O$ of water in equilibrium with quartz is 4.9‰, based on the quartz-water fractionation equation of Clayton et al. (1972). This value is similar to that reported for the saddle dolomite deposition. This figure corresponds to the lowest values assumed for magmatic waters but is also compatible with meteoric or marine waters that have elevated $\delta^{18}O$ values due to different processes, including evaporation from a restricted basin or exchange with subsurface rocks, a possibility supported by the $CaCl_2$-rich nature of the brines. Late calcite has $\delta^{13}C = -6.1‰$ and $\delta^{18}O = 24.6‰$, probably reflecting late meteoric waters invading the system.

Rocabruna

Compared to the mean value for Cambrian dolostone of the area ($\delta^{13}C = -0.3‰$ and $\delta^{18}O = 23‰$), host dolostones have lower mean isotopic values ($\delta^{13}C = -3‰$ and $\delta^{18}O = 20.2‰$) as a result of an interaction with isotopically light fluid. Consequently, the use of carbonate isotopic composition could be a prospective tool in this area. Dolomite host rock samples collected across one of the karstic cavities (samples S1B1 to S1B10; Table 1 and Fig. 3a) do not show significant C and O isotopic variations, and do not delineate any special alteration pattern at the scale of the cavity. Only one value (sample 2X2) (Table 1) is clearly different from the others and could be the result of a precipitation of dolomite at higher temperature or at higher fluid/rock ratios.

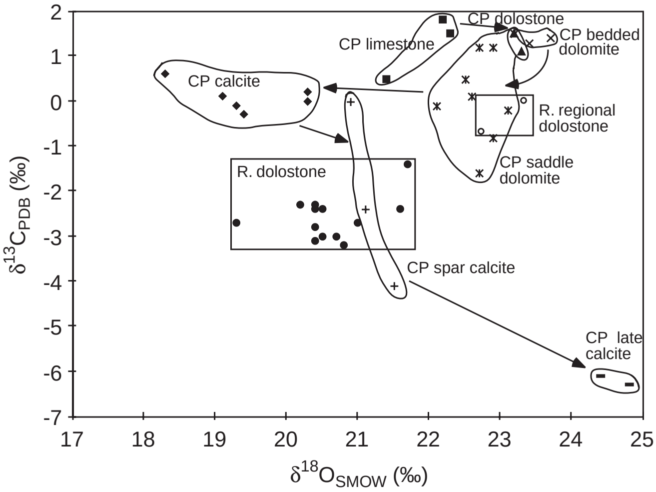

Fig. 5 $\delta^{13}C$ versus $\delta^{18}O$ diagram of the analyzed carbonates. Rocabruna (*R*). The *arrows* show the paragenetic sequence of the different generations of carbonates in Coll de Pal (*CP*)

As the temperature of dolomite formation is unknown, the isotopic composition of the dolomitizing fluids cannot be estimated. However, from the C isotopic composition it is possible to conclude that the lower $\delta^{13}C$ values might be related to an organic carbon source, possibly to the metapelites surrounding the carbonate units of this area. Except for one value, the isotopic results for carbonates from Rocabruna show a narrower range than those from Coll de Pal.

S isotopes

Coll de Pal

Sulfur isotopic compositions of barite of the Coll de Pal deposit are homogeneous with a mean value of δ^{34}S = 15.3‰ and without systematic variations with the position of the samples within the cavities. This value is in good accordance with Triassic sea water or with a solution leaching Triassic evaporites. The δ^{34}S values of chalcopyrite predating barite ranges from −1.2 to 11.1‰. These data suggest the existence of two groups of sulfides with contrasting isotopic compositions. Two possible mechanisms can explain this wide variation: (1) a reduction of sulfate to H_2S in a closed or partially closed system and (2) changes in fO_2 during sulfide deposition.

Rocabruna

Sulfur isotopic compositions of barite are higher (mean δ^{34}S = 17.5‰) and less homogeneous than in Coll de Pal with an overall variation of 5‰. Barite δ^{34}S values increase as one goes from the bottom to the center of mineralized cavities (Fig. 7: samples 2A2 to 2A5 and 1B1W to 1B5W). Therefore, since barite precipitation started at the bottom, the mineralizing fluids became ^{34}S-enriched with time. The δ^{34}S values of chalcopyrite and tetrahedrite range from 1.1 to 8.1‰, forming two groups, similar to the Coll de Pal sulfides. The location of sulfides as thin rims around the cavities (see Fig. 3a) in both deposits suggests a similar mechanism of formation. Finally, the difference in barite δ^{34}S values between the two deposits indicates different sulfate sources or different physico-chemical conditions during precipitation.

Strontium isotopes

Coll de Pal

In order to monitor possible changes in the fluid compositions during the mineralizing event ^{87}Sr/^{86}Sr ratios of carbonates and barite have been measured. The lowest value corresponds to the limestone host rock (0.7090) in good accordance with values reported by Burke et al. (1982) for marine carbonates of Devonian age. Dolostones have ^{87}Sr/^{86}Sr ratios slightly higher than the regional limestones but lower than other carbonates related to mineralization. In carbonates filling cavities there was an increase of the ^{87}Sr/^{86}Sr ratio with time. Values range from 0.7109 in bedded dolomite to 0.7134 in hydrothermal calcite coexisting with quartz. Saddle and ferroan dolomite are also more radiogenic than the regional limestone: 0.7115 to 0.7139 (samples CP14 and CP19, respectively) and the spar calcite has a ratio of 0.7126. Barite yields ^{87}Sr/^{86}Sr ratios between 0.7115 and 0.7136 (Table 1).

The higher ^{87}Sr/^{86}Sr ratios of the carbonates and barite compared to the host-rock values cannot be explained by in situ growth of ^{87}Sr as these minerals have a Rb/Sr ratio too low to significantly alter the initial isotopic ratio at the time of crystallization. This means that ferroan and saddle dolomite, calcite, barite and spar calcite crystallized from a fluid enriched in radiogenic Sr with respect to sea water and local rocks.

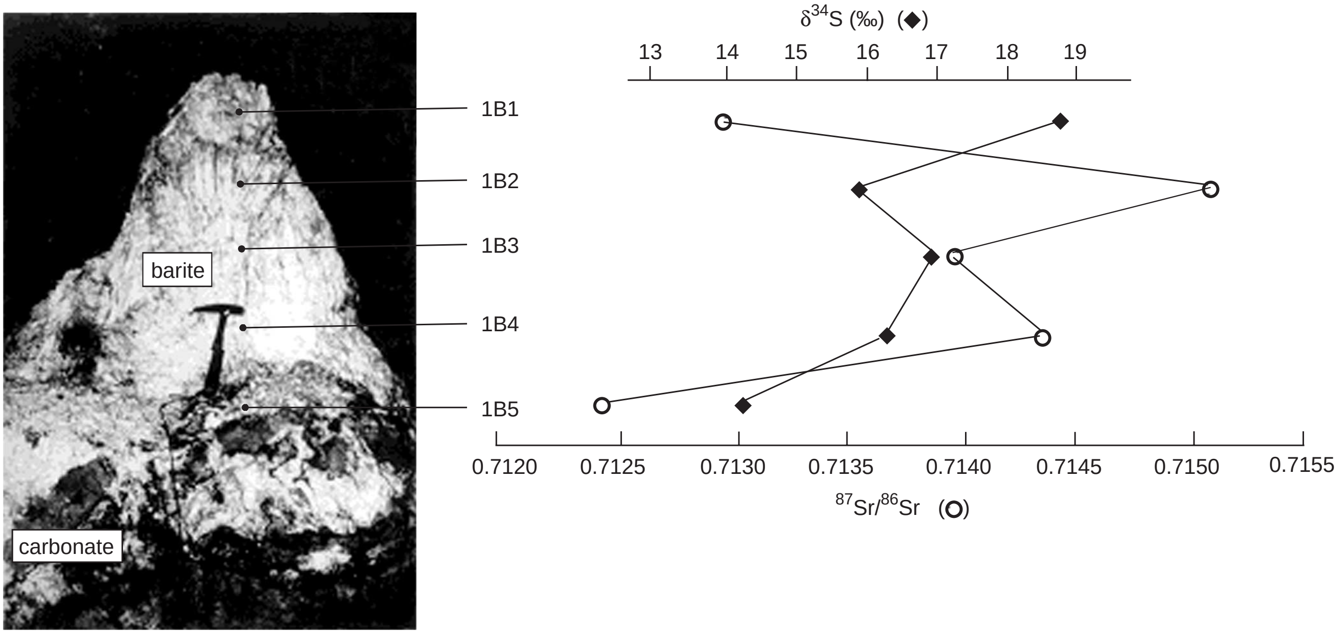

Fig. 6 δ^{34}S and ^{87}Sr/^{86}Sr pattern in one of the systematically sampled cavity at Rocabruna

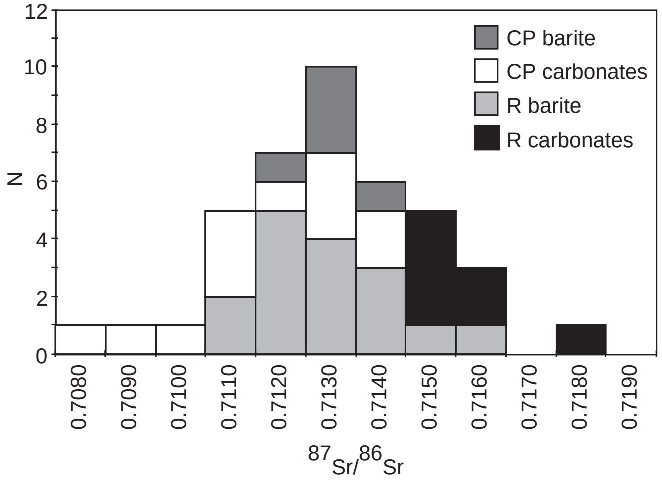

Fig. 7 $^{87}Sr/^{86}Sr$ ratios of carbonates and barites. $N = 40$

Rocabruna

The $^{87}Sr/^{86}Sr$ ratios in carbonates range from 0.7155 to 0.7182 and no correlation exists between their values and the location of the samples within the mineralized cavities. All of these ratios are higher than Cambro-Ordovician marine carbonates (Burke et al. 1982) and higher than $^{87}Sr/^{86}Sr$ ratios in paragenetically later barites. It is interesting to point out that in Coll de Pal this tendency is the opposite, with early carbonates having lower $^{87}Sr/^{86}Sr$ ratios than late-stage sulfates. Barites in both localities have similar $^{87}Sr/^{86}Sr$ ratios (Fig. 7). In Rocabruna, the two systematically sampled cavities (Fig. 6) display saw tooth strontium isotopic ratio pattern, with maximum differences of 0.0013 and 0.0026 for cavities A and B, respectively, indicating that the infux of the radiogenic fluid into the system was not constant with time.

Covariation between Sr and O in carbonates

In Coll de Pal there is a tendency toward lower $\delta^{18}O$ values with increasing $^{87}Sr/^{86}Sr$ ratios from regional limestone to calcite precipitated before barite. We attribute this $\delta^{18}O$-shift to an increase in temperature rather than a change in composition, since the $\delta^{18}O$ value of the fluid which precipitated the hydothermal carbonates (ferroan dolomite, saddle dolomite and calcite) stayed constant at about 5‰. The relatively higher $\delta^{18}O$ values and lower $^{87}Sr/^{86}Sr$ ratio of spar calcite (Fig. 8) suggest that the system evolved toward lower temperatures and nearly host-rock equilibrated fluid during the late stages. Similarly, the range in $\delta^{18}O$ values of carbonates in Rocabruna is also probably due to a temperature effect rather than to variations in the water/rock ratio or changes in fluid composition at constant temperature during an exchange process. If the latter were true, a correlation between strontium and oxygen isotopes should exist but no correlation is observed.

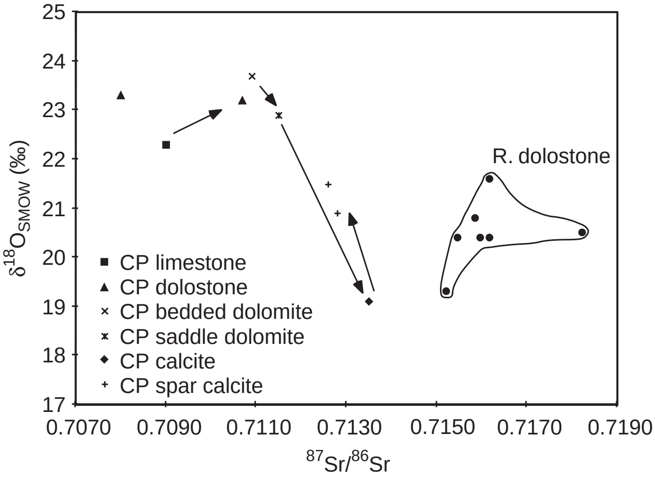

Fig. 8 $\delta^{18}O$ versus $^{87}Sr/^{86}Sr$ diagram of carbonates from the two deposits. The *arrows* show the paragenetic sequence of the carbonates in Coll de Pal

Covariation between Sr and S in barites

In the two systematically sampled cavities of Rocabruna (Fig. 6) the pattern displayed by the strontium isotopic ratios is also shown by the $\delta^{34}S$ values but with an antithetic behavior. The cavity having larger strontium variations has also the larger sulfur isotopic variation, of 1.2‰ in A and 4.8‰ in B, indicating that the fluid carrying the more radiogenic strontium had the lower $\delta^{34}S$ values of oxidized sulfur.

Sulfur isotope compositions of barite span a much larger range in Rocabruna than in Coll de Pal. This variation might be attributed to two different causes: (1) a redox change during barite precipitation or (2) a mixing between two distinct sulfate sources. As the first hypothesis could not explain the relationship of lower $\delta^{34}S$ values to higher $^{87}Sr/^{86}Sr$ ratios, the latter hypothesis seems more plausible. Thus, the lower $\delta^{34}S$ sulfate source would be related to a solution leaching or rubidium-rich rocks such as the pelites enclosing the dolostones. Oxidation of H_2S-bearing fluids would produce lowered $\delta^{34}S$ sulfate molecules which in turn would mix with a higher $\delta^{34}S$ sulfate source of surficial origin.

Genetic model

The fluid inclusion and isotope data allow us to determine the composition of the hydrothermal solution(s) which formed the mineralization at Coll de Pal. Although the formation age of the karst system is not known and bedded dolomite present at the bottom of some cavities have similar C, O and Sr isotope compositions as the dolostone developed around the karstic cavities, joints and fractures, microscopic textures provide evidence that this bedded carbonate formed before dolomitization. This initial dolomitization phase was probably due to the interaction of the host limestone with fluids whose C and O had equilibrated isotopically with the regional carbonate rocks but with a slightly higher $^{87}Sr/^{86}Sr$ ratio. As this dolomitization affects the post-Hercynian fractures, the process has to be Carboniferous age or younger. An increase in temperature, up to 125 °C, due to influx of hot waters into the system, induced recrystallization of the early dolomite and precipitation of a centimeter thick dark brown ferroan saddle dolomite, from fluids having higher $^{87}Sr/^{86}Sr$ ratios.

The co-precipitation of saddle dolomite and sulfide can be linked through a reaction such as:

$$2Ca^{2+} + 2SO_4^{2-} + Mg^{2+} + 2CH_4 \rightleftharpoons CaMg(CO_3)_2 + Ca^{2+} + 2H_2O + 2H_2S$$

which involves the reduction of sulfate by organic matter, represented here by methane (Anderson 1983). This reaction produces H_2S which combines with metals (Fe, Cu…) to deposit sulfides. The small amount of saddle dolomite and sulfides indicates that reduction of sulfate was not a quantitatively important process. This is supported by the lack of carbonate dissolution accompanying sulfide precipitation. The coexisting low and high $\delta^{34}S$ values of chalcopyrite could be indicative of reduction of sulfate in locally closed systems. The reduction of sulfate did not affect the overall $\delta^{34}S$ value of dissolved sulfate as the sulfur isotopic composition of barite is nearly constant in all samples.

Lower O isotope values of carbonates ($\delta^{18}O \approx 19.4‰$) are found in hydrothermal calcite precipitated after saddle dolomite and before quartz. This is in accordance with a general trend of increasing temperature recorded by fluid inclusions in dolomite and quartz. This calcite also shows a more radiogenic $^{87}Sr/^{86}Sr$ values (0.7134) compared to earlier minerals, supporting the idea that external hydrothermal fluids progressively invaded the system. Coexistence of quartz with calcite and the presence of muscovite in quartz-hosted fluid inclusions constrains the pH to values of 4 to 5 at 150 °C, supporting the idea of minor pH changes due to sulfide precipitation.

The sulfur isotope values of barite around $\delta^{34}S = 15.1‰$, indicate a homogeneous source of sulfur presumably originating by leaching evaporites or directly from seawater sulfate. However, the strontium isotopic ratios of these barites indicate that another fluid besides seawater was involved in the mineralizing event. We envision a scenario where the karst system was saturated with SO_4-rich water and was invaded by Ba and metal-bearing hot fluids. The mixing of these two solutions could have caused barite precipitation. The higher $\delta^{18}O$ values and lower $^{87}Sr/^{86}Sr$ ratios of spar calcite compared to earlier calcite supports the idea that the system evolved toward lower temperatures during late stages, probably due to the waning of the flow of hot waters into the cavities.

The $\delta^{18}O$ value of water in equilibrium with saddle dolomite and quartz is around 5‰. This value together with the chemical composition of the fluids (polysaline $CaCl_2$-rich brines with minor amounts of KCl and saturated with muscovite), point to an evolved meteoric water or connate water that interacted with basement rocks.

The lack of fluid inclusion data in Rocabruna does not allow us to compare the chemistry and temperature of the mineralizing fluids with the Coll de Pal deposit. It is interesting to note that the Rocabruna deposit has not been deformed by the Hercynian orogeny, but has been affected by thrusts of Alpine age, whereas dolomitization related to Coll de Pal deposit affects Hercynian thrusts. Although a similar mixing model can be envisioned, there are some important differences that should be considered. From the morphological point of view, the Rocabruna deposit is characterized by the presence of dissolution structures before and/or contemporaneous to sulfide precipitation. This is represented by the corrosive shape of the rim sulfides around the carbonates and the accumulation of dolomite blocks partially coated by sulfides at the bottom of the barite-filled cavities (Fig. 3a). Thus, compared to Coll de Pal, the mineralizing fluids seem to have been more reactive probably due to interaction with a different type of aquifer, which would not be able to buffer the fluid to a neutral pH as indicated by the absence of karstic sediments in the cavities. The lack of dissolution structures in Coll de Pal could also be related to a higher calcium content of the mineralizing fluids.

The antithetic pattern of sulfur and strontium isotopes of barites in the two systematically sampled cavities points to a precipitation mechanism where a hot, radiogenic fluid carrying small amounts of low $\delta^{34}S$ oxidized sulfur mixed with a less radiogenic, ^{34}S-enriched sulfate-rich fluid. Thus, $\delta^{34}S$ value of the sulfate-rich fluid in Rocabruna was significantly higher than the one present in the Coll de Pal mineralizing system. These Rocabruna barites are less radiogenic than carbonates. Carbonates in Rocabruna are notably more radiogenic than Coll de Pal carbonates or even Coll de Pal barites, indicating that the hot radiogenic fluid involved in the Rocabruna mineralizing system equilibrated with rocks having higher rubidium content than those that equilibrated with Coll de Pal hot fluid. This is consistent with the presence of a thick carbonate sequence in the Coll de Pal area compared to the thin carbonate host rock horizon interbedded within metapelites at Rocabruna. The presence of a calcium-rich brine in Coll de Pal fluid inclusions supports this hypothesis.

Although a similar mixing model involving a Ba-rich, sulfate-poor hot fluid with a sulfate-rich solution of surficial origin can be applied to both deposits, isotopic data show, that the hot Ba-rich fluids involved in each deposit equilibrated with different rock types, in agreement with the geology of the two areas. The sulfate-rich solutions also had different sulfur isotopic values (Coll de Pal: $\delta^{34}S \approx 15‰$ and Rocabruna $\delta^{34}S \geq 19‰$) reflecting different reservoirs. Assuming that the main sulfate source in the surficial solution was from leaching of evaporites, the possible reservoirs are evaporites of Triassic (Coll de Pal) and Tertiary age (Rocabruna). The broad range in the sulfur isotopic composition of barites from Rocabruna and their correlation with the strontium isotopic data compared to the homogeneous values of Coll de Pal indicate that in Rocabruna deposits more than one source of sulfate was involved.

Conclusions

The Coll de Pal and Rocabruna deposits consist of barite and minor Cu-sulfides (chalcopyrite and tetrahedrite) filling karstic cavities within carbonates of Devonian and Cambrian age respectively. The mineralogy is composed of barite, chalcopyrite, tetrahedrite, pyrite and minor sphalerite and galena with saddle dolomite and quartz as gangue. Fluid inclusion data from Coll de Pal quartz and dolomite indicate that deposition took place between 125 and 150 °C from a polysaline $CaCl_2$-rich brine. Temperature and composition of these $CaCl_2$-rich brines are similar to those found in the Ba-F vein type deposits in the Catalonian Coastal Ranges, or in the Variscan domain of Western Europe and Northern Africa (Cardellach et al. 1990; Behr et al. 1987; Jebrak 1984).

In Coll de Pal, saddle dolomite and sulfide precipitation may be linked to sulfate reduction by organic matter. This process produced H_2S which combined with metals to form sulfides. There is also a shift of O isotopes toward $\delta^{18}O$ lower values with increasing $^{87}Sr/^{86}Sr$ ratios from regional limestone to calcite precipitated before barite. This might be attributed to an increase in temperature associated with the presence of a fluid with a high $^{87}Sr/^{86}Sr$ ratio. The relatively higher δ^{18} values and lower $^{87}Sr/^{86}Sr$ ratio of spar calcite suggest that the system evolved toward lower temperatures during the late stages. Sulfur isotope compositions of barite span a much larger range in Rocabruna than in Coll de Pal. The relationship of lower $\delta^{34}S$ values to higher $^{87}Sr/^{86}Sr$ ratios in Rocabruna points to ^{34}S-enriched sulfate source related to the oxidation of H_2S-bearing fluid that leached strontium from rubidium-rich rocks.

We propose that a hot Ba-rich sulfate-poor fluid mixed with sulfate-rich solutions of surficial origin. Isotopic data show that the hot Ba-rich fluid involved in each deposit equilibrated with different rocks in agreement with the geology of the two areas. The sulfate-rich solutions also had different sulfur isotopic compositions (Coll de Pal: $\delta^{34}S \approx 15‰$ and Rocabruna $\delta^{34}S \geq 19‰$) indicating that they were derived from two different reservoirs. Assuming that the main sulfate source in the surficial solution is from leaching of evaporites, the possible reservoirs are evaporites of Triassic (Coll de Pal) and Tertiary age (Rocabruna). The broad range in the sulfur isotopic composition of barites from Rocabruna and their correlation with strontium isotopic data compared to the homogeneous values of Coll de Pal indicate the involvement of more than one sulfate source at Rocabruna.

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