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## Ba and Pb–Zn occurrences in the Chañarcillo Group, Northern Chile: Sr and S isotope constraints

by François Lieben<sup>1</sup>, Robert Moritz<sup>1</sup>, Lluís Fontboté<sup>1</sup>, Denis Fontignie<sup>1</sup> and Antony Fallick<sup>2</sup>

### Abstract

Various Ba and Pb–Zn stratiform and vein-type occurrences are hosted by the Lower Cretaceous carbonate rocks of the Chañarcillo Group, Northern Chile, deposited in a back-arc basin setting. The occurrences are at different stratigraphic positions between the underlying volcanic rocks of the Bandurrias Formation and an evaporite-bearing carbonate unit that is also mineralized.

The strontium isotopic compositions of the barites are comprised between the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of Lower Cretaceous seawater and the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the volcanic rocks of the Bandurrias Formation. Their sulfur isotope values are mainly grouped around the Lower Cretaceous seawater value.

The covariation in strontium and sulfur isotopic composition, and strontium content of the barites indicates various degrees of mixing between a hydrothermal fluid that has leached volcanic rocks of the Bandurrias Formation and a locally derived sulfate-bearing fluid, probably with some interaction of the hydrothermal fluid with the carbonate and evaporite host rocks of the Chañarcillo Group.

*Keywords:* barite, Pb–Zn deposit, Sr isotopes, S isotopes, carbonate rock, fluid mixing, Northern Chile.

### Introduction

In the Copiapó-Vallenar area of Northern Chile, Ba and Pb–Zn occurrences are hosted by Lower Cretaceous carbonate rocks of the Chañarcillo Group (DÍAZ, 1986, 1990 a and b). The Chañarcillo Group was deposited in a back-arc basin to the east of the magmatic arc sequence of the Lower Cretaceous Bandurrias Formation (Fig. 1; COIRA et al., 1982). The occurrences investigated in this study are shown in figure 1 and include various small Ba and Pb–Zn past-producing mines and prospects hosted by the Nantoco Formation, the lowermost unit of the Chañarcillo Group in this region.

Barite was produced in the 1980s by small mines in the Quebrada Galena (Mamiña, Triunfo, Gladys) and in the Quebrada Chañarcillo (e.g. Cartija, Tocopilla). The largest Pb–Zn deposit is the Las Cañas mine, exploited in the 1940s. FLORES (1942) reports ore reserves of 30'000 tons and an average grade of 27% Pb. Examination of

old workings suggests that the accumulated production was in the order of a few 100'000 tons of ore with significantly lower Pb grades. Some of the occurrences are rich in Ag, such as the Ag–Zn–Pb–Ba deposit of Jaula with up to 200 g/t of Ag in ore. Barite veins in the Chañarcillo and Las Tunas-Vizcachas districts, major Ag producers of Chile in the 19th century (RUIZ and PEEBLES, 1988), have been also investigated.

Two genetic hypothesis suggested for these ore occurrences are: (1) submarine exhalative processes related to an episode of intermediate to acid volcanic activity (LINO and RIVERA, 1987); and (2) early diagenetic deposition in a sabkha environment (DÍAZ, 1990 a and b). In this contribution we offer an additional hypothesis that involves ore formation by basinal brines in a deep subsurface environment. Indeed, previous lead isotope data of galenas by PUIG (1988) and FONTBOTÉ et al. (1990) support a model whereby the mineralizing fluids circulated through volcanic rocks of the arc before migrating into carbonate

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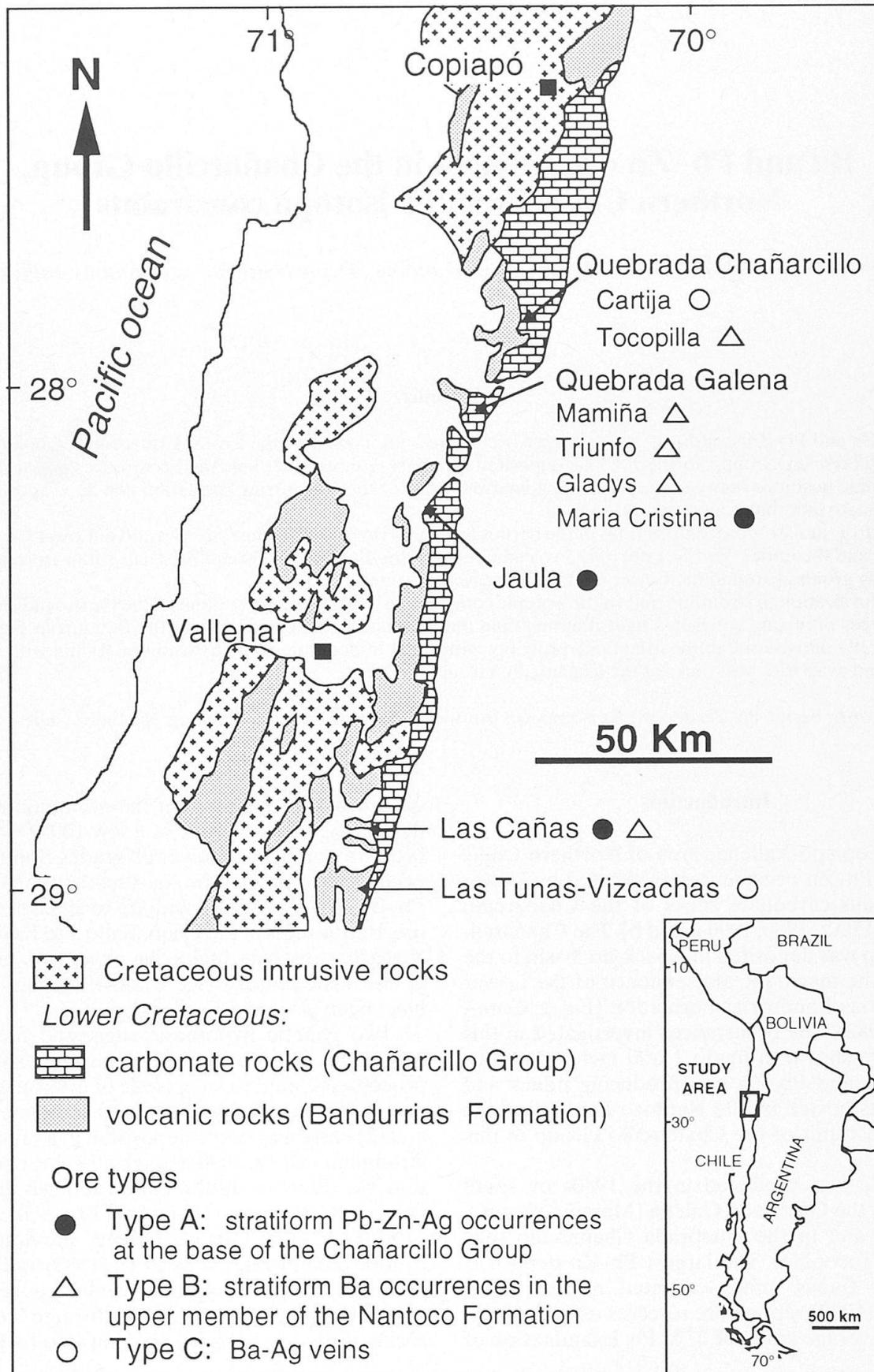


Fig. 1 Simplified geology of the study area (after Mapa Geológico de Chile, Sernageomin, 1982) and location of the Ba and Pb-Zn ore occurrences in the Chañarcillo Group.

Tab. 1 Main characteristics of the Ba and Pb-Zn occurrence types of this study.

Ore type	Type A Pb-Zn	Type A' Pb-Zn	Type B Ba	Type C Ba
Stratigraphic unit	base of the Chañarcillo Group above the Bandurrias Formation	Nantoco Formation	upper member of the Nantoco Formation	Nantoco Formation, abundant beneath the upper member of the Nantoco Formation
Morphology and textures	stratiform, up to 2 km long and 2 m thick, ore minerals mainly intergranular cements	irregular bodies (Pb-Zn) and slightly discordant layers (Ba)	stratiform, up to 800 m long and 3 m thick zebra textures	NNW to NNE-striking subvertical veins
Host rock	porous bioclastic limestone and tuff, above andesitic and basaltic andesite lavas	recrystallized white limestone and volcaniclastic sandstones, in proximity of small intrusion	intertidal limestones (algal mats)	limestones
Mineralogy	galena, sphalerite, barite, hemimorphite and hydrozincite	sphalerite, galena, pyrite, barite, minor magnetite and marcasite	barite, calcite, iron oxides and minor galena	barite and iron oxides
Hydrothermal alteration	some silicification and chloritization	intense silicification and chloritization of carbonate rocks	not recognized	not recognized
Location	Jaula, Las Cañas	Quebrada Galena (Maria Cristina, Carola)	Quebrada Galena (Mamiña, Triunfo, Gladys), Las Cañas, Quebrada Chañarcillo	Quebrada Chañarcillo, Quebrada Galena

rocks of the back-arc basin. The aim of the present study is to use the strontium and sulfur isotopic composition of barite to further constrain the sources and the pathways of the mineralizing fluids.

### Geological setting

In the Copiapó-Vallenar area, the oldest rocks are Paleozoic magmatic and metamorphic rocks, consisting mainly of schists, phyllites and quartzites. They are overlain by clastic and subordinate carbonate rocks of the Triassic-Liassic Canto del Agua Formation (MOSCOSO et al., 1982). The Lower Cretaceous rocks of the Bandurrias Formation and the Chañarcillo Group have been deposited unconformably upon these formations. The Chañarcillo Group, in the region under study, lies on and interfingers to the west with the volcanic arc constituted by the andesitic flows and volcaniclastic rocks of the Bandurrias Formation (Fig. 1).

Three formations of the Chañarcillo Group are recognized in this region. They are from bottom to top the Nantoco, the Totoralillo, and the Pabellón formations. The Nantoco Formation is subdivided into a lower and an upper member (SEGERSTROM, 1968; CISTERNAS and DÍAZ, 1990). The lower member consists of up to 800 m of bio-

clastic limestone and cherty limestone. The upper member is composed of about 80 m of algal-laminated limestone, ferruginous cherty limestone, and micritic limestone bearing some evaporite pseudomorphs. It is characterized by a stratiform breccia which is a marker horizon in the carbonate sequence. The Totoralillo Formation comprises about 150 m of micritic and bioclastic limestone with marly intercalations. The Pabellón Formation consists of up to 500 m of chert, cherty limestone, phosphate-bearing limestone, and bioclastic limestone (CISTERNAS and DÍAZ, 1990).

The carbonate rocks of the Chañarcillo Group were deposited under shallow marine water conditions, with a regressive episode in the upper member of the Nantoco Formation (CISTERNAS and DÍAZ, 1990). All the units of the Chañarcillo Group contain volcanic and volcaniclastic material, mainly as centrimetric to metric tuff intercalations, volcaniclastic sandstones and subordinate lava flows.

The Lower Cretaceous rocks are unconformably overlain by the clastic continental sedimentary rocks and andesites of the Upper Cretaceous Cerrillos Formation, and by Tertiary volcanic and continental sedimentary rocks. They have experienced various stages of intrusions and thin-skinned tectonics (ARÉVALO and MPODOZIS, 1991). Dykes and sills of basic to intermediate composition are abundant in the carbonate rocks.

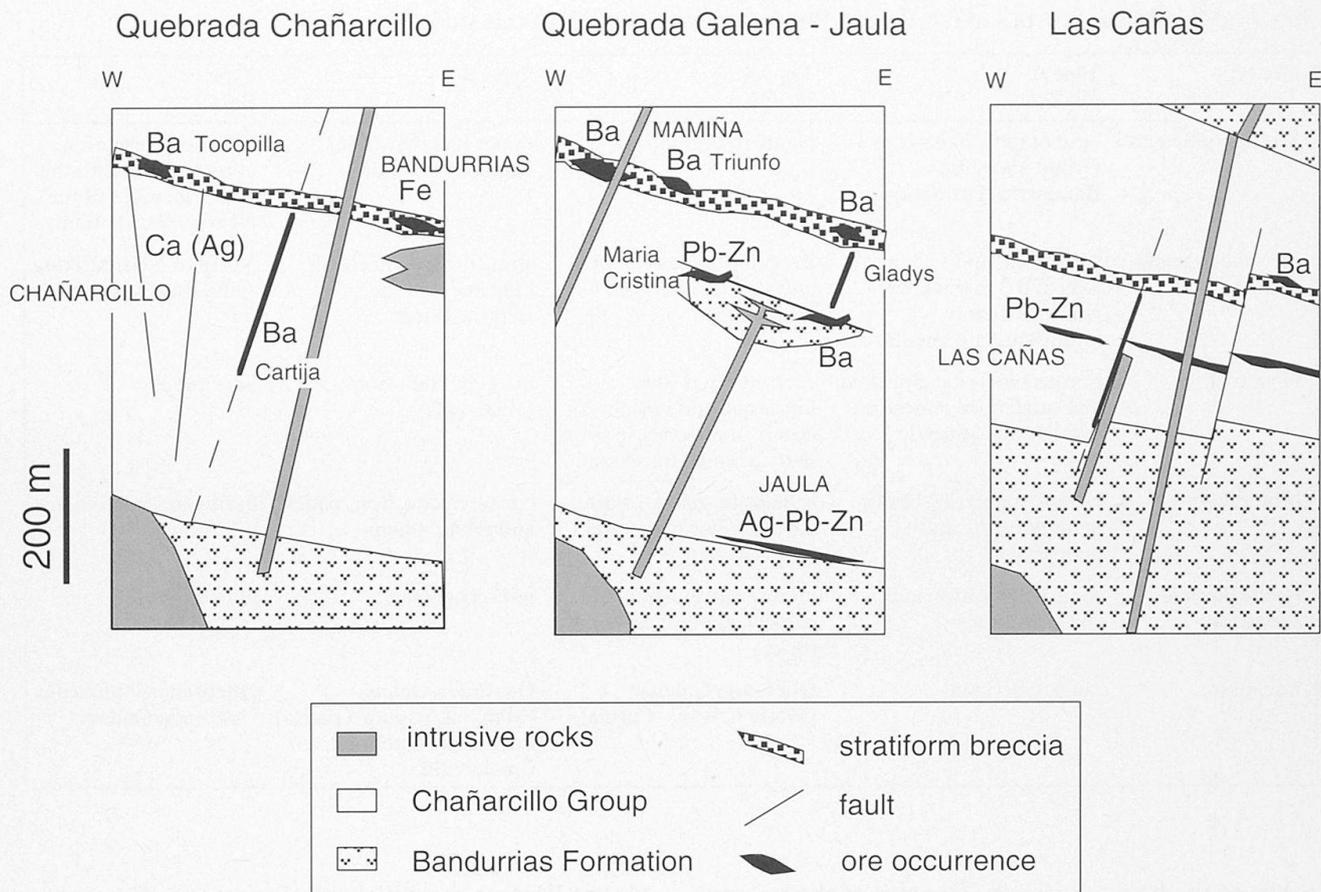


Fig. 2 Synthetic cross sections in the Quebrada Chañarcillo, Quebrada Galena and Las Cañas, showing the ore occurrences under study.

The intrusive rocks of Jurassic to Tertiary age belong to N-S trending belts with ages becoming younger from the Pacific coast toward the east (Moscoso et al., 1982). Large Cretaceous granodioritic, quartz-dioritic and dioritic plutons form a central magmatic belt and intrude the Bandurrias Formation and the Chañarcillo Group. There is no spatial association of the ore occurrences with these batholiths.

### Ore types

Three ore types have been distinguished on the basis of their morphology, paragenesis and stratigraphic position (Tab. 1 and Fig. 2):

Type A are stratiform Pb-Zn ± Ag ore occurrences at the base of the Chañarcillo Group above the Bandurrias Formation. This ore type is found at Jaula and Las Cañas (Figs 1 and 2). The mineralized horizon at Jaula occurs a few meters above volcanic rocks of the Bandurrias Formation. The ore minerals, including hemimorphite, hydrozincite, barite and some galena and sphalerite, ce-

ment a bioclastic limestone (DÍAZ, 1990a). At Las Cañas, a mineralized tuff horizon occurs 100 m above the contact with basaltic andesite lavas of the Bandurrias Formation. The ore consists of galena, with minor sphalerite. High angle normal faults cutting the volcanic rocks are also mineralized. In these type A ore occurrences, the mineralizing fluids appear to have been channeled by the high porosity of the immediate host rock.

A subtype A' represents the Maria Cristina and Carola Pb-Zn occurrences in the Quebrada Galena that are spatially associated with a volcanic intercalation and with small intrusions in the carbonate rocks. The ore occurrences are characterized by irregular morphologies and in part intense hydrothermal alteration (Tab. 1).

Type B are stratiform Ba occurrences in the upper member of the Nantoco Formation. Various lenses of this ore type occur in the Quebrada Galena (Mamiña belt). Other examples are found in the Quebrada Chañarcillo and at Las Cañas (Figs 1 and 2). The barite lens at Mamiña is conformable with the bedding of the host algal-laminated limestone and presents a zebra texture of

Tab. 2 Comparison of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios for barites partially dissolved in HCl 6N and for barites completely dissolved by fusion with  $\text{Na}_2\text{CO}_3$ .

Sample	HCl 6N leaching	Fusion $\text{Na}_2\text{CO}_3$
FX-303	0.70485	0.70495
FX-317-3	0.70511	0.70512
FX-326-5	0.70499	0.70502
FX-346	0.70594	0.70596

alternating barite and barite-carbonate bands (DÍAZ, 1990b). Dolomite occurs as an early cement in some parts of the mine, and as large euhedral crystals on the border of the barite bands, while barite is a late cement. The regionally extending stratiform breccia contains clasts of the banded barite, and therefore postdates the barite mineralization stage. At Las Cañas, a lens consisting predominantly of barite and quartz with subsidiary galena occurs about 30 m above the main ore-bearing Pb-Zn horizon and immediately above the regional stratiform breccia. Primary fluid inclusions in quartz in this barite lens yield homogenization temperatures of 80–140 °C and salinities of 10–30 wt% NaCl equivalent.

Type C are subvertical Ba ± Ag veins with no apparent wallrock alteration that crosscut the Nantoco Formation. They occur notably in the Quebrada Chañarillo, in the Las Tunas-Vizcachas Ag district, and in the Quebrada Galena (Figs 1 and 2). The main mineral is barite accompanied by iron oxides. The veins are particularly abundant beneath the upper member of the Nantoco Formation which is the upper limit to this type of mineralization (MAYER, 1988).

### Analytical methods

For the strontium isotope determinations, approximately 100 mg of finely ground barite was partly dissolved overnight in HCl 6N at 100 °C. The solution was evaporated and the residue dissolved in HCl 2.5N. Strontium was separated in cation exchange columns and analyzed on a Finnigan MAT 262 thermal ionization mass spectrometer at the University of Geneva. Replicate strontium isotope analyses with complete dissolution of the barites by fusion with  $\text{Na}_2\text{CO}_3$  yielded identical results within the error limits ( $\pm 0.00005$ ,  $2\sigma$ ; Tab. 2). For the strontium concentration, the fused barite samples were dissolved in  $\text{H}_2\text{O}$ , filtrated and redissolved in HCl 1N for the analysis by atomic absorption. A reproductibility of  $\pm 5\%$  has been monitored by repeated analyses of laboratory reference samples. The rubidium content has

also been measured by atomic absorption at the University of Geneva.

The sulfur isotope analyses were performed by the Ottawa Carleton Geoscience Centre, Canada, and at the Scottish Universities Reactor and Research Centre, Glasgow. The SURRC technique for barite  $\delta^{34}\text{S}$  has been described in detail in HALL et al. (1991). The analyses in Canada were made on a triple collector VG SIRA 12 mass spectrometer on  $\text{SO}_2$  produced by the combustion with copper oxide. The routine precision ( $2\sigma$ ) of the analyses was  $\pm 0.2\%$ . The data are reported as per mil (‰) deviations relative to the Canyon Diablo Troilite (CDT) standard.

## Results

### STRONTIUM ISOTOPE COMPOSITIONS AND CONCENTRATIONS

The data are presented in table 3 and figure 3. The strontium isotope ratios of the barites range from 0.7038 to 0.7066 and the concentrations from

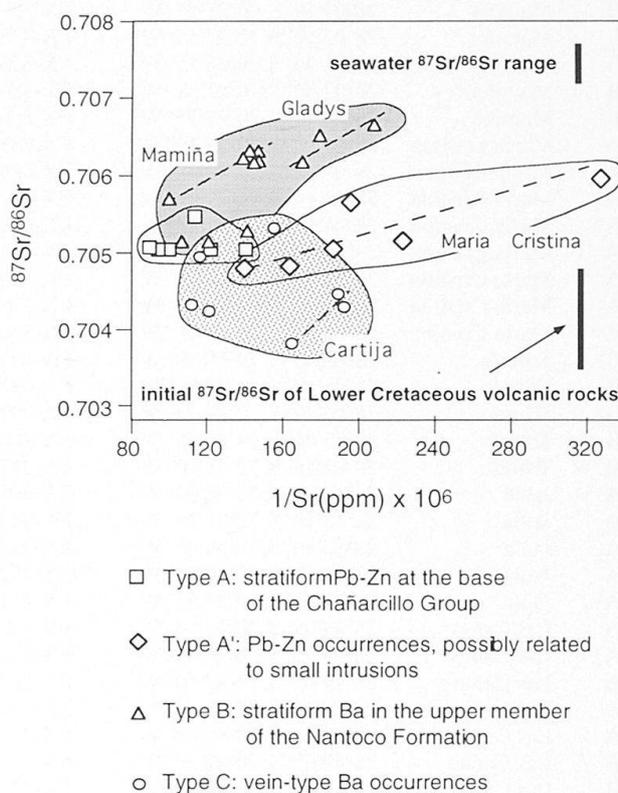


Fig. 3 Covariation plots between  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and strontium concentrations ( $1/\text{Sr}$ ) of the analyzed barite samples. The Lower Cretaceous seawater Sr range is from KOEPNICK et al. (1985). The initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of Lower Cretaceous volcanic rocks are from McNUTT et al. (1975).

Tab. 3 Results of Sr and S isotope data, Sr and Rb concentrations of barite and galena (gn). The Sr isotope, Sr and Rb concentrations have been analyzed at the University of Geneva. The sulfur isotope analyses marked with an asterisk have been made at the SURRC, Glasgow, and the others at the OCGC, Ottawa.

Type	Locality	Coordinates	Sample n°	$\delta^{34}\text{S}_{\text{‰}}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Sr (ppm)	Rb (ppm)
C	Araucana	27°48'20"S, 70°23'50"W	AK-65	13.2*			
C	Chañarcillo	27°48'40"S, 70°25'40"W	Anmar	10.6*			
B	Chañarcillo	27°48'30"S, 70°24'00"W	CRT III	20.3*			
C	Chañarcillo	27°48'30"S, 70°24'00"W	FX-302		0.70498	8549	
C	Chañarcillo	27°48'30"S, 70°24'00"W	FX-303		0.70485	8594	3.0
C	Cartija	27°48'10"S, 70°21'50"W	FX-403-2	11.8	0.70431	5177	3.0
C	Cartija	27°48'10"S, 70°21'50"W	FX-403-4		0.70383	6059	
C	Cartija	27°48'05"S, 70°21'50"W	FX-404	13.6	0.70446	5269	
C	Colorada	27°48'30"S, 70°24'00"W	C244	11.2*			
B	Tocopilla	27°49'05"S, 70°22'10"W	Tocopilla	19.1*			
C	Valenciana	27°48'20"S, 70°23'50"W	Valenciana	12.2*			
A'	Carola	28°03'35"S, 70°28'40"W	FX-092		0.70507		
A'	Carola	28°03'35"S, 70°28'40"W	FX-339-1		0.70513		
A'	Carola NE	28°03'25"S, 70°28'30"W	FX-344-1		0.70519		
B	Gladys	28°05'50"S, 70°29'40"W	FX-322		0.70617	8736	2.1
B	Gladys	28°05'45"S, 70°29'45"W	FX-323-1		0.70572		
B	Gladys	28°05'50"S, 70°29'40"W	FX-397-1	21.1			
B	Gladys	28°05'50"S, 70°29'40"W	FX-397-2	20.5			
B	Gladys E	28°05'55"S, 70°29'05"W	FX-324-2	17.2	0.70648	5565	1.0
B	Gladys E	28°05'55"S, 70°29'05"W	FX-324-7		0.70662	4788	
B	Gladys E	28°05'55"S, 70°29'05"W	FX-325-1		0.70615	5860	5.6
A'	Gladys W	28°05'35"S, 70°30'00"W	FX-328-3		0.70516		
C	Gladys, vein	28°05'50"S, 70°29'20"W	FX-399-1	14.8	0.70530	6335	3.1
B	Mamiña	28°02'50"S, 70°27'55"W	FX-106-I	16.8*	0.70615	6687	
B	Mamiña	28°02'50"S, 70°27'55"W	FX-106-II	17.3*	0.70621	7111	
B	Mamiña	28°02'50"S, 70°27'55"W	FX-319-1	17.4	0.70628	6954	3.3
B	Mamiña	28°02'50"S, 70°27'55"W	FX-329-1	17.3	0.70618	6764	
B	Mamiña	28°02'50"S, 70°27'55"W	FX-335-2		0.70628	6768	
B	Mamiña	28°02'50"S, 70°27'55"W	FX-336	15.1	0.70566	9849	
B	Mamiña	28°02'50"S, 70°27'55"W	FX-386-1	16.8			
B	Mamiña	28°02'50"S, 70°27'55"W	FX-386-6	19.4	0.70535	9902	
A'	Maria Cristina	28°04'40"S, 70°29'10"W	FX-085	17.1*	0.70478	7115	
A'	Maria Cristina	28°04'40"S, 70°29'10"W	FX-086	16.7*			
A'	Maria Cristina	28°04'40"S, 70°29'10"W	FX-087	17.5*			
A'	Maria Cristina	28°04'55"S, 70°29'10"W	FX-088	26.1*	0.70563	5109	
A'	Maria Cristina	28°04'50"S, 70°29'20"W	FX-309	16.4	0.70481	6105	0.5
A'	Maria Cristina	28°04'40"S, 70°29'10"W	FX-326-3		0.70515	4477	
A'	Maria Cristina	28°04'40"S, 70°29'10"W	FX-326-5		0.70499	5331	
A'	Maria Cristina	28°04'40"S, 70°29'10"W	FX-346		0.70594	3047	
B	Triunfo	28°03'40"S, 70°28'10"W	FX-094	16.0	0.70512	8230	
B	Triunfo	28°03'40"S, 70°28'10"W	FX-097-I	17.5*			
B	Triunfo	28°03'40"S, 70°28'10"W	FX-097-II	15.9*			
B	Triunfo	28°03'45"S, 70°28'10"W	FX-100	15.2*	0.70525	6999	
B	Triunfo	28°03'45"S, 70°28'10"W	FX-317-3		0.70511	9225	1.9
A	Jaula	28°12'15"S, 70°38'00"W	FX-301-3	17.2	0.70509	10629	1.3
A	Jaula	28°12'30"S, 70°38'10"W	FX-349-4		0.70510	11135	
A	Jaula	28°12'10"S, 70°38'00"W	FX-351-8	11.8	0.70509	7154	
A	Jaula	28°12'10"S, 70°38'00"W	FX-352-3		0.70508	8189	
A	Jaula	28°12'05"S, 70°37'55"W	FX-353-2		0.70509	9654	2.1
A	Las Cañas	28°49'05"S, 70°42'50"W	FX-70	-26.0 (gn)			
A	Las Cañas	28°49'05"S, 70°42'50"W	FX-070	-7.2	0.70525		
A	Las Cañas	28°49'05"S, 70°42'50"W	FX-308-1	-0.2	0.70548	8795	
A	Las Cañas	28°49'30"S, 70°43'15"W	FX-366-1		0.70517	6611	
A	Las Cañas	28°49'25"S, 70°42'40"W	FX-368	-12.5 (gn)			
A	Las Cañas	28°49'05"S, 70°42'50"W	FX-377-5	-11.3 (gn)			
B	Las Cañas	28°49'45"S, 70°42'50"W	FX-66-1	1.2 (gn)*			
B	Las Cañas	28°49'45"S, 70°42'50"W	FX-66-2	17.4*			
B	Las Cañas	28°49'45"S, 70°42'50"W	FX-406-4	-2.5 (gn)			
B	Las Cañas	28°49'45"S, 70°42'50"W	FX-406-4	15			
B	Las Cañas	28°49'45"S, 70°42'50"W	FX-406-4I		0.70499	5199	
C	Las Tunas	28°52'35"S, 70°43'25"W	FX-365		0.70434	8905	
C	Las Vizcachas	28°51'15"S, 70°44'15"W	FX-364		0.70426	8455	2.7

3'047 to 11'135 ppm. The rubidium content of the barites is in all cases lower than 6 ppm and therefore no correction of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios is required for the decay of  $^{87}\text{Rb}$  to  $^{87}\text{Sr}$ .

The strontium isotope ratios are lower than the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of Lower Cretaceous seawater (0.7072–0.7076; KOEPNICK et al., 1985). The different types of ore yielded different strontium isotopic signatures (Fig. 3). The barites from vein-type occurrences (type C) have the lowest ratios (mean: 0.7045). The barites from stratiform Pb-Zn occurrences next to the volcanic-carbonate rock interface (type A) have relatively low ratios (mean: 0.7052). In contrast, the strontium isotope ratios of the stratiform barites hosted by the upper member of the Nantoco Formation (type B) are relatively high (mean: 0.7060), near a Lower Cretaceous seawater value.

The highest strontium content was observed in the barites from Pb-Zn ore occurrences at the base of the Chañarcillo Group as for example in Jaula (mean of 0.9 wt%). In some occurrences such as Mamiña, Gladys, Maria Cristina and Cartija, there is a trend of increasing  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios with increasing 1/Sr, i.e. decreasing strontium concentrations (Fig. 3). In one vein from the Quebrada Chañarcillo (Cartija), a sample from a lower stratigraphic level (FX-403-4, Tab. 3) yielded a lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio and higher strontium content than a sample from the upper level (FX-403-2) near the upper member of the Nantoco Formation.

#### SULFUR ISOTOPES

The  $\delta^{34}\text{S}$  values of 34 barites from the various occurrences, and 5 galena samples from the Pb-Zn occurrence of Las Cañas are shown in table 3 and figure 4. The data are similar to data obtained by SPIRO and PUIG (1988) for barites of Jaula, Mamiña, Maria Cristina and Gladys (Fig. 4).

Most of the barites from stratiform ore occurrences hosted by the upper member of the Nantoco Formation (type B) have a sulfur isotopic signature of about 16‰ (Fig. 4), which corresponds to the composition of sulfates in equilibrium with Lower Cretaceous seawater (CLAYPOOL et al., 1980). The barites from type C vein occurrences have a slightly lighter sulfur isotopic composition near 12‰.

The barites from Pb-Zn ore occurrences at the base of the Chañarcillo Group (type A) yielded the largest range of sulfur isotopic compositions between -7‰ and 26‰. The lowest values were found in the Pb-Zn deposit of Las Cañas. Here, the  $\delta^{34}\text{S}$  values of barite and galena are lighter in

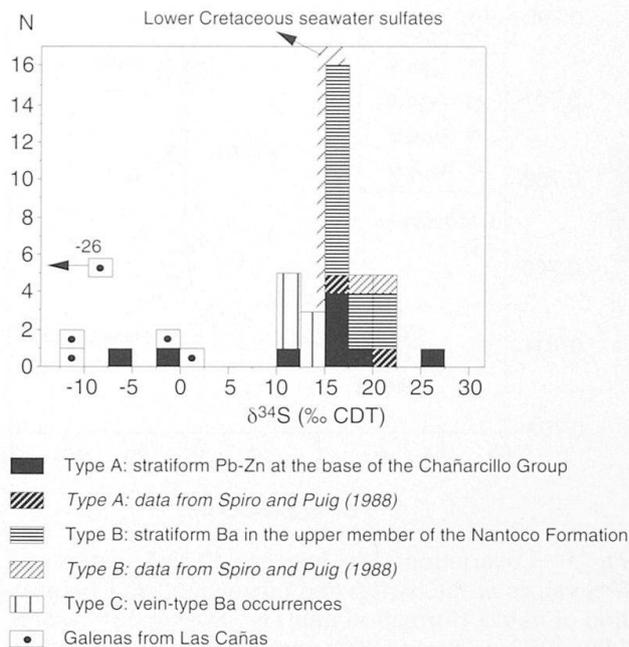


Fig. 4 Sulfur isotopic composition of barites and galenas. Data from SPIRO and PUIG (1988) and this study. The Lower Cretaceous seawater range is from CLAYPOOL et al. (1980).

the stratigraphically lower horizon and in the veins than in the upper barite-quartz lens where the  $\delta^{34}\text{S}$  value of galena is near 0‰ and the  $\delta^{34}\text{S}$  value of barite is near Lower Cretaceous seawater values. In the two ore types, the  $\Delta$  values of the sulfate-sulfide pairs indicate that the two minerals were not in isotopic equilibrium.

#### Discussion

##### STRONTIUM ISOTOPES AND STRONTIUM CONCENTRATIONS

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the barite samples indicate that their strontium is partly derived from an external source to the Chañarcillo Group. The covariation of strontium content (1/Sr) with  $^{87}\text{Sr}/^{86}\text{Sr}$  in various ore occurrences indicates a mixing of strontium between two sources (Fig. 3): (1) a Sr-rich source depleted in  $^{87}\text{Sr}$  and (2) a Sr-poor source with a seawater isotopic signature. In other ore occurrences such as Jaula, the absence of a significant variation of  $^{87}\text{Sr}/^{86}\text{Sr}$  and the relatively high strontium content of the barites suggests that their strontium derived predominantly from the  $^{87}\text{Sr}$ -depleted strontium source.

The Sr-poor sources with a seawater isotopic signature are likely the Lower Cretaceous seawater, or the marine carbonate rocks and presently

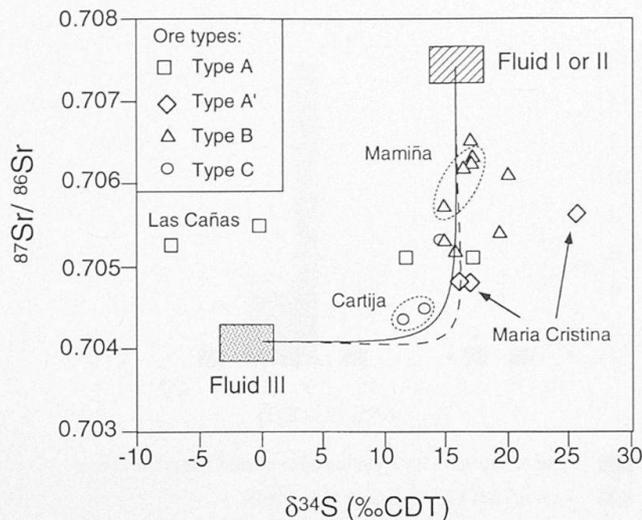


Fig. 5 Covariation plots between  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and  $\delta^{34}\text{S}$  values of the barites and mixing models. Composition of fluid I (formation fluid) is  $^{87}\text{Sr}/^{86}\text{Sr}$ : 0.7074,  $\delta^{34}\text{S}$ : 16‰, 100 ppm Sr, and 2000 ppm S. Composition of fluid II (Lower Cretaceous seawater) is  $^{87}\text{Sr}/^{86}\text{Sr}$ : 0.7074,  $\delta^{34}\text{S}$ : 16‰, 8 ppm Sr, and 2700 ppm S. Composition of fluid III (hydrothermal fluid) is  $^{87}\text{Sr}/^{86}\text{Sr}$ : 0.7040,  $\delta^{34}\text{S}$ : 0‰, 1000 ppm Sr, and 200 ppm S. Mixing trends are between fluids I and III (solid line), and between fluids II and III (dashed line).

dissolved evaporites of the Chañarcillo Group. CISTERNAS (1986) reports a mean strontium content of 117 ppm for the carbonate rocks of the Chañarcillo Group.

The most probable sources of the  $^{87}\text{Sr}$ -depleted strontium are the volcanic and volcanoclastic rocks of the Lower Cretaceous arc, with initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of 0.7035–0.7047 (McNUTT et al., 1975), and the volcanoclastic intercalations in the carbonate rocks of the Chañarcillo Group. Other potential sources are the volcanic rocks of the Cerrillos Formation, that lie unconformably upon the Lower Cretaceous rocks, and intrusive rocks of Cretaceous or younger age, with initial ratios of 0.7022–0.7061 (McNUTT et al., 1975). ZENTILLI (1974) reports a mean strontium content of 425 ppm for the andesites in the Atacama region. The  $^{87}\text{Sr}$ -depleted strontium is most probably derived by leaching of plagioclase from the volcanic rocks. The Paleozoic basement rocks and the Triassic-Liassic clastic rocks of the Canto del Agua Formation can be excluded as significant strontium sources, as they would provide mainly radiogenic strontium. Indeed, calculations based on  $^{87}\text{Sr}/^{86}\text{Sr}$  data of Paleozoic intrusive rocks (McNUTT et al., 1975), show that they would have had a mean  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.7090 at Lower Cretaceous times.

The difference in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between the barites from veins (type C) and those hosted by the upper member of the Nantoco Formation (type B) allows us to rule out that these vein-type barites were remobilized from the stratiform barites.

#### SULFUR ISOTOPES

The  $\delta^{34}\text{S}$  values of the barites hosted by the upper member of the Nantoco Formation (type B) indicate that their sulfur is derived from Lower Cretaceous seawater sulfate, or from sulfate derived by the dissolution of evaporites in the unit. The shift toward  $\delta^{34}\text{S}$  values slightly higher than Lower Cretaceous seawater values is interpreted by SPIRO and PUIG (1988) as resulting from an enrichment in  $^{34}\text{S}$  of the seawater-derived sulfates through bacterial sulfate reduction during their deposition in basins with restricted circulation.

The slightly lower  $\delta^{34}\text{S}$  values of the barites from veins (type C) may reflect the partial involvement of magmatic sulfur derived by hydrothermal leaching of the volcanic rocks. At this stage of the study, the large range of sulfur isotopic compositions in the barites from stratiform Pb–Zn occurrences at the base of the Chañarcillo Group (type A) is not fully understood. It could be attributed to the leaching of bacteriogenic sulfides in the sedimentary rocks or, more likely, to redox processes during hydrothermal leaching of the volcanic rocks, or during transport and ore precipitation (OHMOTO and RYE, 1979).

#### MIXING MODEL

Figure 5 is a binary plot of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and  $\delta^{34}\text{S}$  values of the barites under study. Except for two samples from Las Cañas and one sample from Maria Cristina, there is a large range in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios with little variation in  $\delta^{34}\text{S}$  values. It is only for the barites with the lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios that a slight shift toward lower  $\delta^{34}\text{S}$  values can be observed (Fig. 5). Such a covariation trend can be explained by a mixing model involving reservoirs having different strontium and sulfur concentrations and different  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and  $\delta^{34}\text{S}$  values. Two types of mixing may be distinguished: mixing of fluids and fluid-rock interaction. Therefore, based on the sources of strontium and sulfur characterized above, we have to consider the following four end-members in modelling the mixing processes: (1) sedimentary rocks of the Chañarcillo Group, (2) a local formation fluid in equilibrium with the sedimentary rocks of the Chañarcillo

Group, (3) Lower Cretaceous seawater, and (4) a warm hydrothermal fluid leaching the andesitic volcanic and volcanoclastic rocks of the Bandurrias Formation. The data used for modelling the fluid mixing processes are described below.

For the local formation fluid buffered by the sedimentary rocks of the Chañarcillo Group, we have attributed a concentration of sulfur of 2000 ppm, reflecting mainly an evaporitic parentage, and a concentration of strontium of 100 ppm. No isotopic fractionation has been assumed between this fluid and the rocks.

The Lower Cretaceous seawater has a  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio of 0.7074 (KOEPNICK et al., 1985), a  $\delta^{34}\text{S}$  value of 16‰ (CLAYPOOL et al., 1980), and strontium and sulfur concentrations of 8 ppm and 2700 ppm, respectively.

A  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.704, that is consistent with the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios of the Lower Cretaceous volcanic rocks (MCNUTT et al., 1975), has been selected for the warm hydrothermal fluid leaching the andesitic volcanic and volcanoclastic rocks of the Bandurrias Formation. A  $\delta^{34}\text{S}$  of 0‰ has been taken as a reasonable value for a fluid leaching magmatic rocks (OHMOTO and RYE, 1979). A relatively high strontium concentration is indicated by the  $^{87}\text{Sr}/^{86}\text{Sr}$  vs  $1/\text{Sr}$  diagram (Fig. 3). A value of 1000 ppm has been chosen and is in the range of measured concentrations of basinal brines (e.g. CARPENTER et al., 1974). A sulfur concentration of 200 ppm, also in the range of measured brine concentrations, has been attributed to this fluid.

Simple binary fluid mixing models between the later hydrothermal fluid and the formation fluid or seawater allow us to reproduce the data trend of the barites from the Ba and Pb-Zn occurrences in the  $^{87}\text{Sr}/^{86}\text{Sr} - \delta^{34}\text{S}$  diagram (Fig. 5). The barites from the different ore types would be related to different degrees of mixing between the hydrothermal fluid and the formation fluid, or between the hydrothermal fluid and seawater. In barites from veins and from the Pb-Zn occurrences at the base of the Chañarcillo Group, the hydrothermal fluid that has migrated through the volcanic rocks of the Bandurrias Formation is predominant over the formation fluid or seawater. In the barites hosted by the upper member of the Nantoco Formation, that are higher in the sedimentary sequence, the formation fluid or seawater are dominant over the hydrothermal fluid. However, the data do not allow us to discriminate between a fluid mixing model involving a formation fluid and a fluid mixing model involving the Lower Cretaceous seawater.

In addition, the chemical composition of the hydrothermal fluid migrating from the volcanic

rocks of the Bandurrias Formation into the Chañarcillo Group is likely to be changed due to its interaction with the carbonate rocks. In particular, it will progressively acquire a more radiogenic strontium isotopic signature, and the dissolved sulfur concentration and  $\delta^{34}\text{S}$  values would probably also be affected by this fluid-rock interaction process. Therefore, a realistic mixing model to explain the deposition of barite would have to consider fluid-rock interaction in combination with the fluid mixing discussed above. Further investigations are required to constrain the parameters for modelling adequately the fluid-rock interaction processes.

#### IMPLICATIONS FOR THE GENESIS OF THE Ba AND Pb-Zn OCCURRENCES

Based on geologic evidence and the isotope systematics we favor an epigenetic origin of the Ba and Pb-Zn ore occurrences in the Chañarcillo Group. Stratiform and vein-type mineralizations are locally in close spatial association. The strontium and sulfur isotope data suggest that the vein-type barites are not remobilized stratiform barites. On the contrary, the veins which occur mainly along steeply dipping faults most likely represent major channelways for fluids migrating from the volcanic rocks of the Bandurrias Formation into the carbonate rocks of the Chañarcillo Group. The non-radiogenic signature of galena from the ore occurrences also supports this interpretation.

An early diagenetic barite formation as suggested by DÍAZ (1990b) for Mamiña on the basis of the strong sedimentary facies control of the stratiform barite occurrences (CISTERNAS and DÍAZ, 1990) is not compatible with the data obtained in the present work. The facies control can be explained in other terms. In the case of the ore occurrences at the base of the Chañarcillo Group, the porosity of the facies most likely facilitated the circulation of the brines. The interaction of the mineralizing fluids with evaporites in the upper member of the Nantoco Formation was a major controlling factor for the barite formation as indicated by the sulfur isotopic composition of the stratiform barites. The characteristic zebra texture of this ore type is generally interpreted as indicating a deep subsurface environment (FONTBOTÉ, 1993; TOMPKINS et al., 1994; WALLACE et al., 1994).

In such a scenario the most likely source of barium is the volcanic rocks of the Bandurrias Formation. Fluid mixing is generally considered as an appropriate mechanism to form barite (BLOUNT, 1977; KESLER et al., 1988). The barite oc-

currences probably formed as a result of mixing between a barium-rich brine coming from the volcanic rocks and a locally derived sulfate-bearing fluid, possibly with some concomitant fluid-rock interaction.

### Conclusions

The strontium and sulfur isotopic composition of barites from Ba and Pb-Zn occurrences in the Chañarcillo Group allow us to constrain the source of the ore-forming fluids, and support a genetic model based on mixing between two end-members having different strontium and sulfur concentrations and different  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and  $\delta^{34}\text{S}$  values. The isotopic composition of sulfur in the barites is dominated by the immediate host rock reservoir, that comprises evaporites. By contrast, the strontium isotopic composition and the strontium content of the barites reflect a mixture between a proximal source that is the sedimentary host rocks and a distal source that is the volcanic rocks of the underlying Bandurrias Formation. The barites from the lowermost part of the Chañarcillo Group and from the veins are dominated by the latter source, while barites higher in the sedimentary sequence are dominated by strontium of the immediate host rock.

A two component mixing model between a hydrothermal fluid coming from the volcanic rocks of the Bandurrias Formation and a formation fluid that has leached the carbonate and evaporite host rocks of the Chañarcillo Group can account for the trends in  $^{87}\text{Sr}/^{86}\text{Sr}$  vs  $1/\text{Sr}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  vs  $\delta^{34}\text{S}$  of the barite samples (Fig. 5). Interaction between the hydrothermal fluid and the host rocks probably also occurred. However, data are still lacking to evaluate the relative importance of fluid-rock interaction and fluid mixing. The data support an epigenetic model in which steeply dipping faults and porous carbonate facies acted as major channelways for the mineralizing fluids.

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