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Tracing back sulfur isotope reequilibration due to contact metamorphism: A Case study from the Perubar VMS deposit, Central Peru

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ABSTRACT: The mid-Cretaceous Perubar VMS deposit, Central Peru, affected by contact metamorphism, has been the subject of a sulfur isotope investigation. The measured $\delta^{34}S$ values for sulfate-sulfide pairs from the deposit indicate that close to equilibrium isotopic reequilibration occurred during metamorphism. After "filtering" the contact metamorphism effect, sulfur isotope desiquilibrium trends for coexisting sulfate-sulfide pairs were obtained on the $\delta^{34}S$ versus $\Delta^{34}S$ diagram, indicating a mixing between seawater sulfate and hydrothermal H_2S. It suggests that contact metamorphism occurred in a closed system and that the original bulk sulfur isotope composition of the Perubar deposit was mostly preserved. Sulfur reequilibrated only locally, by isotope exchanges between adjacent sulfate and sulfide minerals.

1 INTRODUCTION

The mid-Cretaceous volcano-sedimentary sequences of the Casma Group in Central Peru host several volcanogenic massive sulfide deposits. A major deposit, consisitng of the Graciela, Juanita, Cecilia North and Cecilia South orebodies, was discovered in the Cocachacra mining district, 50 km to the east of Lima, owned by the company Perubar, S.A. (Vidal, 1987). These VMS orebodies were subject to Upper Cretaceous contact metamorphism.

Metamorphosed VMS deposits have been the subject of numerous sulfur isotope investigations (e.g., Lusk and Krouse, 1997; Cook and Hoefs, 1997). In this communication, we present an application of the use of sulfur isotope fractionation between sulfate-sulfide pairs, as developped by Zheng (1991), to trace the pre-metamorphic sulfur isotope signature of VMS deposits. The present case study is based on sulfur isotope data for sulfate-sulfide pairs from the four volcanogenic massive sulfide-barite orebodies of the Perubar deposit.

2 GEOLOGICAL CONTEXT

The Perubar VMS deposit occurs in a sequence of submarine volcanic and associated sedimentary rocks of mid-Cretaceous age, deposited in or at the margins of rapidly subsiding sub-basins, part of a back-arc pull-apart system controlled by transform faults. The VMS orebodies are spatially associated with intensively silicified (±sericitized) volcanic rocks, ranging from basaltic andesite to dacite. The different features of these ore occurrences present several analogies with the present-day Eastern Manus back-arc basin, where hydrothermal activity and extensive sulfide deposits are associated with basaltic to dacitic submarine volcanism (Binns and Scott, 1993).

During the Upper Cretaceous, the Cocachacra district underwent contact metamorphism associated with the intrusion of the Peruvian coastal batholith, with subsequent formation of biotite-sillimanite hornfels in the host-rocks and pyrite-pyrrhotite-magnetite assemblages within the VMS orebodies. The metamorphism effects were more pronounced in the Graciela and Juanita orebodies compared to the Cecilia North and South occurrences.

The Perubar orebodies present a typical proximal-to-distal zonation, from: (i) stockwork, (ii) massive pyrite-pyrrhotite-magnetite, (iii) massive Zn, (Fe>Pb) sulfides (±barite), (iv) banded barite and Zn, (Fe>Pb) sulfides, and (v) banded barite-pyrite.

3 METHODOLOGY

Samples of barite (20), pyrite (23), sphalerite (20) and pyrrhotite (4) were selected for sulfur isotope analyses. The analyses were performed at the University of Lausanne stable isotope laboratory, using a Fisons EA 1108 elemental analyser coupled to a Finnigan MAT Delta S isotope ratio mass spectrometer. The analytical uncertainty (2σ) was ±0.2‰. The data are reported as per mil (‰) deviations relative to the Canyon Diablo Troilite (CDT) standard.

4 RESULTS

The δ^{34}S values of barite, pyrite, sphalerite and pyrrhotite range from 8.1 to 17.1, –3.4 to 5.9‰, –3.3 to 2.9‰, –2.3 to 4.1‰, respectively (Table 1). Barite δ^{34}S signatures, as well as sulfides δ^{34}S signatures fall within very similar ranges for each of the four studied VMS orebodies.

Table 1. δ^{34}S values (‰CDT) of barite (ba), pyrite (py), sphalerite (sl) and pyrrhotite (po) from the Perubar VMS orebodies.

sample	**orebody**	$\delta^{34}S_{ba}$	$\delta^{34}S_{py}$	$\delta^{34}S_{sl}$	$\delta^{34}S_{po}$
MPP317	Juanita	10.8	-1.2	1.9	-
MPP318	Juanita	-	-1.3	-1	-
MPP413	Juanita	8.7	-	-1.1	-
MPP414	Juanita	14.6	-	-	-
MPP670	Juanita	-	-	1.2	-
MPP672	Juanita	-	-1.2	0.6	-
MPP673	Juanita	-	-	0.1	-
MPP680	Juanita	-	-0.3	-0.6	-0.9
MPP332-2	Graciela	13.4	3.5		4.1
MPP333	Graciela	8.1	-2.3	-	-1.3
MPP612	Graciela	-	0.1	-0.4	-
MPP614	Graciela	16.6	5.9	-	-
MPP615	Graciela	-	1.2	-	-
MPP617	Graciela	16.2	-	-	-
MPP304	Cecilia South	-	-	2.1	-
MPP517	Cecilia South	15	2.1	2.6	-
MPP518	Cecilia South	13.7	-	-	-
MPP520	Cecilia South	11.8	-1.8	-	-
MPP529	Cecilia South	-	0.3	-	-
MPP531	Cecilia South	13.4	-1.3	0.5	-
MPP535	Cecilia South	14	0	0.3	
MPP536	Cecilia South	12.5	-	-	-2.3
MPP537	Cecilia South	12.8	0.7	-	-
MPP557c	Cecilia North	-	-2.1	-1.3	-
MPP558	Cecilia North	-	-	1.6	-
MPP569	Cecilia North	13.2	-3.4	-3.3	-
MPP570	Cecilia North	15.7	3.7	4.5	-
MPP571	Cecilia North	17.1	3.6	-0.9	-
MPP572	Cecilia North	16.1	1.7	2.9	-
MPP576	Cecilia North	10.3	-1.9	-2.6	-
MPP578	Cecilia North	13.6	-0.3	-0.4	-

5 DISCUSSION

5.1 *Equilibrium versus desiquilibrium process*

The covariation of the sulfur isotope composition of both sulfate and sulfide in a four sulfur species (H_2S, SO_4^{2-}, sulfate and sulfide minerals) close system is ascribed to isotope exchange between oxidized and reduced sulfur species during mineral precipitation (Zheng, 1991). Isotopic exchange could be a thermodynamic process due to simple cooling of a single hydrothermal fluid, which results in an equilibrium fractionation, or a kinetic process due to mixing of two sulfur reservoirs, which leads to a disequilibrium fractionation (Fig. 1, Zheng, 1991).

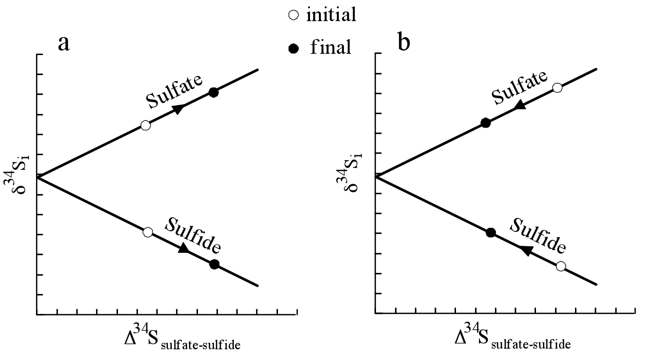

Fig. 1. Schematic δ^{34}S vs Δ^{34}S diagram for coexisting sulfate-sulfide pairs, showing equilibrium (a) vs disequilibrium (b) process (adapted from Zheng, 1991).

5.2 *VMS deposits: precipitation under isotope desiquilibrium process*

Most of the models explaining the precipitation ofsulfate and sulfide minerals in VMS deposits (e.g., Ohmoto, 1996; Velasco et al., 1998) invoke the mixing of a warm, reduced and metal-bearing hydrothermal fluid with seawater. Sulfate minerals would precipitate preferentially from the seawater sulfate (Kalogeropoulos and Scott, 1986) and sulfide minerals from hydrothermal H_2S. Furthermore, the fractionation between sulfate and sulfide would progressively decline between the δ^{34}S values of the two end-member reservoirs, so that disequilibrium fractionation is produced between the coexisting sulfate-sulfide pairs (Fig. 1b) to yield unreasonably high-temperature estimates (Zheng, 1991).

5.3 *Contact metamorphism effect*

With increasing metamorphic temperature (e.g., contact metamorphism), sulfate-sulfide pairs precipitated from a 4-species closed system (see above) will tend to follow one of the six sulfur isotope reequilibration paths described in Figure 2. Assuming that metamorphism occurred in a closed system, with preservation of the original bulk sulfur isotope composition, these paths will depend on the original sulfate/sulfide ratio. In this context, as described by Zheng (1990), a close to equilibrium fractionation is advocated to generalize the coupled fractionation relationships on the δ-Δ diagram (Fig. 2) and therefore to embrace both equilibrium and disequilibrium processes.

The barite-pyrite and barite-sphalerite (or barite-pyrrhotite) pairs from the four studied VMS orebodies of Graciela, Juanita, Cecilia North and Cecilia South are shown in Figure 3. Temperatures calculated from barite-pyrite and barite-sphalerite (or pyrrhotite) geothermometers range between 331° and 600°C. These temperarures are unreasonably high estimates for VMS deposits and suggest disequilibrium isotopic fractionation. Moreover, the Graciela and Juanita orebodies yield high-

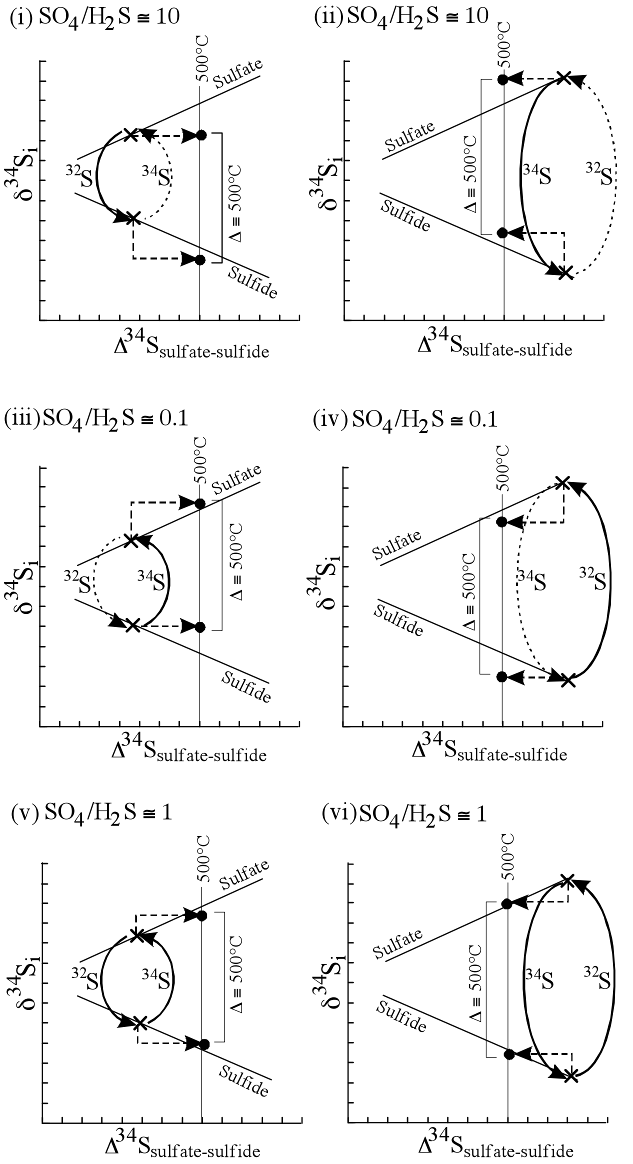

Fig. 2. Reequilibration paths for a sulfate-sulfide system, represented in the $\delta^{34}S$ vs $\Delta^{34}S$ diagram for coexisting sulfate-sulfide mineral pairs. Pre-metamorphic values are represented by the crosses, and metamorphic values by the dots. The selected 6 different paths depend mainly on: (a) the sulfate/sulfide initial ratio (SO_4/H_2S); (b) the pre-metamorphic "initial" or "final" character (see Fig. 1) of the mineral pair (^{34}S-rich sulfate/^{32}S-rich sulfide vs. ^{32}S-rich sulfate/^{34}S-rich sulfide), either for an equilibrium or a desiquilibrium process. Examples are given assuming a complete sulfur isotope reequilibration at 500°C.

temperature estimates within a quite narrow range (between 500° and 579°C for Graciela and between 455° and 600°C for Juanita) whereas the Cecilia North and South occurrences yield lower temperature estimates within a much wider range (between 331° and 500°C for Cecilia North, and between 381° and 459°C for Cecilia South (Fig. 3). These differences reflect the distance of the respective orebodies from the coastal batholith intrusion. As the Graciela and Juanita orebodies lie only a few decameters away from the intrusive contact, most of the primary sulfur isotope were reequilibrated during contact metamorphism to a close to equilibrium temperature of 500°C (Fig. 3). By contrast, in the-Cecilia North and South orebodies, the original sulfur isotope composition has been partly preserved, although the Δ suggest a reequilibration tendency around 400°C (Fig. 3).

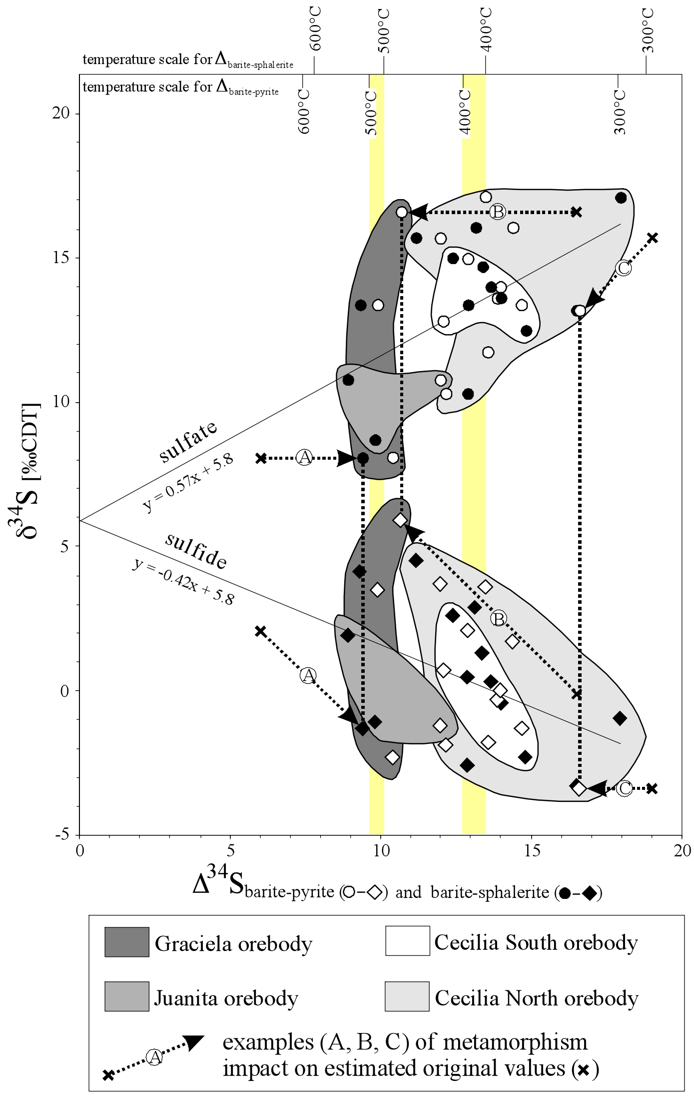

Fig. 3. $\delta^{34}S$ vs $\Delta^{34}S$ diagram for coexisting sulfate-sulfide mineral pairs from the four orebodies of the Perubar VMS deposit.

5.4 *"Filtering" the contact metamorphism effect*

Assuming a limited fluid-rock interaction during metamorphism, we trace back the effect of contact metamorphism on the sulfur isotope composition of the sulfur species in the Perubar VMS orebodies. Within the frame of the theoretical reequilibration paths presented in Figure 2, we discuss here 3 contact metamorphism "filtering" examples (Fig. 3):

1. The measured barite-sphalerite pair A from the Graciela orebody (Fig. 3) is part of a sulfate-rich sample ($SO_4/H_2S \cong 10$). The ^{34}S-depleted barite composition remains almost unchanged during contact metamorphism. The $\delta^{34}S$ value of the sphalerite shifts in the negative direction, taking the ^{32}S from the surrounding barite. In this case, the contact

metamorphism effect followed the rules of reequilibration path (i) in Figure 2.

2. The barite-pyrite pair B from the Cecilia North orebody (Fig. 3) comes from a sulfate-rich sample ($SO_4/H_2S \cong 10$). In contrast with pair A, the barite has a ^{34}S-rich composition. Thus, the pyrite shifts its $\delta^{34}S$ value in the positive direction, whereas the barite composition remains almost unchanged. For this example, the contact metamorphism effect followed the rules of reequilibration path (ii) in Figure 2.

3. The barite-pyrite pair C from the Cecilia North orebody (Fig. 3) comes from a sulfide-rich sample ($SO_4/H_2S \cong 0.1$). In this case, the ^{32}S-rich pyrite composition remains almost unchanged with increasing metamorphic temperature, whereas the barite shifts its $\delta^{34}S$ value in the negative direction. Therefore, the contact metamorphism effect respected the rules of reequilibration path (iv) in Figure 2.

Applying these rules of the reequilibration paths on additional sulfate-sulfide mineral pairs from the Perubar VMS orebodies, we were able to trace back the sulfur isotope reequilibration due to contact metamorphism (Fig. 4).

6 CONCLUSIONS

1. After removal of isotope reequilibration due to the contact metamorphism on the most affected sulfate-sulfide pairs, the four studied VMS orebodies yield similar trends for sulfate and sulfide in the δ- Δ diagram (Fig. 4). This indicates that they emplaced under similar physico-chemical conditions. The four studied orebodies probably formed from the same hydrothermal system.

2. The isotopically heaviest barite samples yield $\delta^{34}S$ values between 15 and 17‰, which corresponds to mid-Cretaceous sulfur isotope signature of marine evaporites (Claypool et al., 1980). Moreover, after filtering the effect of metamorphism on the sulfur isotopically heavy barites, a great majority of them plots in the high δ-Δ end-member area (Fig. 4). Thus, seawater was most likely the sulfate end-member reservoir of the system. The most realistic explanation for precipitation of the Cocachacra VMS deposit would then be the mixing of a warm, H_2S-rich, metal-bearing hydrothermal fluid with the mid-Cretaceous seawater.

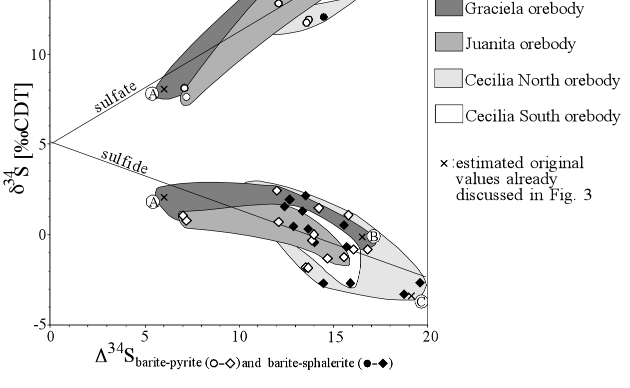

Fig. 4. $\delta^{34}S$ vs $\Delta^{34}S$ diagram for coexisting sulfate-sulfide mineral pairs from the four orebodies of the Perubar VMS deposit after removal of contact metamorphism effect.

3. Sulfur isotope reequilibration due to contact metamorphism in the Perubar VMS orebodies most likely occurred in closed system, as our “metamorphism filtering” method yield coherent results. For that reason, we can rule out any significant input of external sulfur in the system. We conclude that the original bulk sulfur isotope composition of each massive sulfide body was mostly preserved. Sulfur reequilibrated only locally, by isotope exchanges between adjacent sulfate and sulfide minerals.

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