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Sulfur isotope characteristics of the Permian VHMS deposits in Tasik Chini district, Central Belt of Peninsular Malaysia

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Abstract: Sulfur isotope data from sulfide and sulfate minerals have been measured from the two typical examples of the Permian volcanic-hosted massive sulfide (VHMS) deposits at the Tasik Chini district in the Central Belt of Peninsular Malaysia. In this study, we present the sulfur isotope data for 33 sulfide minerals and 23 barite samples from two VHMS deposits in the Tasik Chini district. Sulfides show a narrow range of sulfur values from -2.9% to +8.30%, which can be interpreted to be derived from a mixed sulfur source of reduced seawater sulfate with the possible addition of magmatic sulfur. Sulfate sulfur in barites yields a δ^{34} S range between 11‰ and 22‰, which is comparable to that of Permian seawater sulfate. Sulfur isotope results obtained for the VHMS deposits in the Tasik Chini district suggest that the source of ore fluids during the formation of the Tasik Chini VHMS deposit is a seawater-dominated fluid with probably minor magmatic fluid input. This is similar to VHMS associated with ancient and modern submarine hydrothermal systems.

Key words: Tasik Chini, VHMS, sulfur isotope, Peninsular Malaysia

1. Introduction

The sulfur isotope studies of hydrothermal ore deposits define information regarding the origin of the sulfur present in the orebody in the form of sulfides and sulfates (Ohmoto, 1972). Hence, the source of sulfur can be traced on the basis of the total sulfur isotope compositions in an ore deposit (Hoefs, 1997, 2004). Comprehensive studies of sulfur isotope characteristics in ancient VHMS deposits have been produced by Ohmoto (1986), Huston (1999), and Huston et al. (2010) and in modern VHMS deposits by Shanks (2001) and Rouxel et al. (2004).

Sangster (1968) was the first researcher to recognize that the trend of δ^{34} S variation in Proterozoic and Phanerozoic VHMS deposits closely parallels the ancient seawater curve, but is offset to lighter δ^{34} S values by about 18‰ or ~16‰ (Huston, 1999; Huston et al., 2010). Subsequent studies have confirmed the general trend that seawater sulfate provides a source of reduced sulfur for many VHMS deposits (e.g., Large, 1992; Downes and Seccombe, 2004; Scotney et al., 2005; Inverno et al., 2008). More recent works on modern seafloor hydrothermal sulfide systems also indicate a consistent role of reduced sulfur in addition to seawater δ^{34} S source (e.g., Shanks, 2001; Rouxel et al., 2004). Ohmoto and Skinner (1983) and Solomon et al. (1988) suggested that the reduced sulfur in VHMS ores was derived from the partial inorganic reduction of marine sulfate as seawater convected through the volcanic pile underlying VHMS deposits and rock sulfur dissolved from the volcanic pile.

The Tasik Chini district is located within the Central Belt of Peninsular Malaysia, the important metallogenic belt in Peninsular Malaysia (Figure 1). Deposits of barite, iron-manganese, base metals, and precious metals in the Tasik Chini district have a long mining history. The larger mineral deposits of the district are cited as examples of the Kuroko-type massive sulfide deposit (Hutchinson, 1986) but have received little attention in this context in the literature. The Bukit Botol and Bukit Ketaya deposits are two representative polymetallic deposits in the Tasik Chini district. However, prior to this study, no isotopic data for sulfur from sulfides and sulfates from these deposits have been reported. Herein, we provide the first comprehensive study of sulfur isotope data for the VHMS deposits in the Tasik Chini district. The research was carried out to (1) determine the sulfur isotope characteristics for the massive sulfide mineralization; (2) characterize the sources of mineralizing fluids at Tasik Chini; and (3) determine whether a similar distribution of the sulfur isotopes is shown by the VHMS deposits in Tasik Chini.

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Figure 1. Geological map of Peninsular Malaysia showing the metallogenic belts and location of the VHMS deposits in the Central Belt of Peninsular Malaysia (modified from Mohd Basril Iswadi, 2014).

2. Geological settings

Massive sulfide, barite, and Fe–Mn–Si layers, and zones of intense hydrothermal alteration are exposed at numerous localities throughout the Tasik Chini district. As a result, many prospecting, mining, and exploration activities have been undertaken at different localities/prospects in the area, from geochemical grab sampling to diamond drilling, extensive mapping, and even several small local operations (Mohd Basril Iswadi, 2014).

The VHMS deposits of the present study are the two most extensively explored deposits in the Tasik Chini district: the Bukit Botol and Bukit Ketaya deposits. Both of the deposits occur in a similar package of Permian age coherent felsic volcanic and volcaniclastic rocks within the Permo-Triassic volcano-sedimentary succession (Figure 2). Lithogeochemical data indicate that the footwalls of both deposits contain rhyodacite rocks, but the ore horizon units at both deposits are significantly different. The ore horizon unit at Bukit Botol contains felsic volcanic and rhyodacitic volcaniclastic rocks, but the ore horizon succession to Bukit Ketaya consists of volcanic breccia of rhyolitic composition (Figure 3). The hanging-wall unit consists of similar sedimentary rocks of Permo-Triassic age that unconformable underlie Jurassic-Cretaceous sedimentary formations. The presence and deposition of this sedimentary succession and volcaniclastic rocks are interpreted to cause the termination of the mineralizing process due to rapid sedimentation of the volcanosedimentary sequence within the Tasik Chini area (Mohd Basril Iswadi, 2014).

At each deposit, the mineralization shows distinct ore zonation forming stringer to massive sulfides at the footwall followed by barite and Fe+Mn±Si layers at the stratigraphic top, and exhibits conformable bedding or banding within felsic volcanic host rocks (Figure 3). These forms are consistent with a VHMS deposit formed on the seafloor because the presence of Fe+Mn±Si layers, "exhalites", is the diagnostic criterion of seafloor VHMS formation (e.g., Doyle and Allen, 2003), although this definition is intended to include subseafloor replacement immediately below the seafloor (e.g., Kalogeropoulus and Scott, 1983).

The sulfide mineral assemblages are largely pyrite as the major mineral, with subordinate chalcopyrite, sphalerite, and rare galena. Additionally, traces of Snand Ag-bearing minerals, with gold, are also present in the massive sulfide and barite layers. Chalcopyrite, Agbearing minerals and gold are locally abundant at the Bukit Botol deposit, but were not observed at the Bukit Ketaya deposit (Mohd Basril Iswadi, 2014). In general, the sulfide assemblages of both Bukit Botol and Bukit Ketaya are comparable in terms of lithologic association with descriptions of the bimodal-felsic VHMS type as summarized by many workers including Barrie and Hannington (1999), Franklin et al. (2005), and Galley et al. (2007). The association of Sn-bearing minerals with sphalerite indicates cogenetic formation similar to other VHMS deposits (e.g., Kidd Creek, Neves-Corvo; Hannington et al., 1999a, 1999b). With the exception of later stage barite and iron oxide precipitation during barite and Fe+Mn±Si layer formations, the local distribution of barite in the stockwork and massive sulfides in both the Bukit Botol and Bukit Ketaya deposits suggests that this barite developed as a result of hydrothermal and seawater fluid mixing similar to the formation of barite recognized from the JADE active hydrothermal field in the Central Okinawa Trough by Luders et al. (2001).

In the framework of the tectonic model for the Central Belt of Peninsular Malaysia, both deposits display a range of lead isotopic compositions originated from mixing of bulk crust/juvenile arc and minor mantle sources, which are typical for VHMS deposits in island-arc—back-arc setting (Mohd Basril Iswadi, 2014). The detailed studies on geochemical and geochronological data of VHMS deposits in the Tasik Chini area also support this current view (Mohd Basril Iswadi, 2014; Mohd Basril Iswadi et al., 2016).

3. Methodology

Samples for sulfur isotope analyses were determined in sulfide minerals within the different styles of mineralization (massive, disseminated, and stringer sulfide ore zones) and in barite samples from exposures at both the Bukit Botol and Bukit Ketaya deposits. The sulfur isotope analyses were carried out via two methods at CODES and the CSL, UTAS: (1) conventional and (2) laser ablation technique.

The conventional technique involves sulfides and sulfates extracted by hand drilling of hand samples. Measurements of sulfur isotopes were performed using conventional procedures of Robinson and Kusakabe (1975) for sulfides, and methods of Yanagisawa and Sakai (1983) for sulfates on a VG Sira Series II mass spectrometer. By contrast, the laser ablation analyses of sulfur isotopes were determined on fine-grained intergrowth and coarsegrained crystals sulfides on ~200-µm-thick polished sections using the laser ablation methods of Huston et al. (1995). Determinations were made on an 18W Quantronix 117 Nd:YAG model laser in an oxidizing atmosphere (at 25 torr oxygen pressure) and a ~35 mA current for 2 s on single or multiple sites (up to 5) to yield sufficient SO, for analysis. All results are reported as permil (‰) variations from the Canon Diablo Troilite (CDT). The analytical precision (1δ) of sulfur based on repeated analyses of an internal standard for both sulfides and sulfates is 0.2‰ from both techniques.

4. Sulfur isotope results

The δ^{34} S values for sulfide minerals of the VHMS deposits of the Tasik Chini district are uniform, ranging from –2.9 to 4.1 permil. Data for Bukit Botol (n = 22) and Bukit Ketaya (n = 11) show very similar ranges (Table). With the exception of one sample having an 8.3 permil sulfur value, the sulfide δ^{34} S values from the Bukit Botol deposit range from –0.8 to 4.1 permil. These values are also indistinguishable based on types of mineral and the style of mineralization, suggesting a homogeneous source. The sulfur isotope values for pyrites from the massive sulfide ore range from 0.5‰ to 8.3‰, and analyses of mixed



Figure 2. Map showing regional geology of the Tasik Chini district and the location of the Bukit Botol and Bukit Ketaya VHMS deposits (modified from Mineral and Geoscience Department of Malaysia, 2004).



Figure 3. (a) Schematic cross-section of the Bukit Botol deposit showing the stratigraphic sequence and mineralization styles (modified from Mohd Basril Iswadi et al., 2016). (b) Schematic cross-section of the Bukit Ketaya deposit showing the stratigraphic sequence and mineralization styles (modified from Mohd Basril Iswadi et al., 2016).

pyrite-chalcopyrite yielded δ^{34} S content range between 1.4 and 4.1 permil. Mixed pyrite-chalcopyrite from a stringer zone mineralization has low δ^{34} S values of -0.8% to 1.4‰. A single analysis of chalcopyrite yielded a δ^{34} S content of 0.5 permil. Three analyses of disseminated pyrite in altered host felsic volcanic host rocks gave a value of 2.1‰ to 4.1‰ (Figure 4).

The Bukit Ketaya sulfides have a narrow range of δ^{34} S values, from -2.9 to 3.6 permil, relative to those of the Bukit Botol deposit, also indicating a homogeneous source. Based on the classified mineral and ore types, the sulfur isotope values for pyrite from the thin sheet massive sulfides have higher sulfur isotope values, ranging from 2.2‰ to 3.6‰.

The disseminated and feeder zone mineralizations have a lower range of δ^{34} S values, with a pyrite value of between -2.9% and 0.2% (Figure 5). Based on the δ^{34} S data obtained, the values for the thin sheet massive sulfide and feeder zone mineralization at the Bukit Ketaya deposit are almost identical, suggesting that they have a common sulfur source.

Isotope sulfur ratios for twelve barites from the Bukit Botol deposit yielded a range varying from 11‰ to 18‰ (Figure 4; Table). This is similar to that for barite from the barite-bearing layer and lens of the Bukit Ketaya deposit (n = 11), which display δ^{34} S values of 15 to 19 permil with two exceptional heavier (+22‰) and lighter (+11‰) values (Figure 5; Table).

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Table. Sulfur isotope data for sulfides and sulfates from the studied Tasik Chini VHMS deposits. Annotation: py = pyrite, cpy = chalcopyrite, ba = barite, C = conventional analysis, and LA = laser ablation.

Location	Sample	Minerals	Type of mineralization	δ ³⁴ S (‰)	Method
Within Bukit Botol deposit area (102.9410 mE, 3.3664 mN)					
1	BB1	ру-сру	massive ore	1.88	С
2	BB1a	ру-сру	massive ore	4.12	С
3	BB1b	ру-сру	massive ore	1.54	С
4	BB2	ру	massive ore	8.30	С
5	BB2a	ру-сру	massive ore	1.57	С
6	BB2b	ру-сру	massive ore	1.38	С
7	BB2c	ру-сру	massive ore	2.25	С
8	BB2d	ру	massive ore	1.37	С
9	BB2f	сру	stringer zone	0.48	С
10	T5-1	ру	massive ore	2.58	LA
11	T5-2	ру	massive ore	1.57	LA
12	T6-1	ру	massive ore	3.15	LA
13	T6-2	ру	massive ore	1.57	LA
14	T7-1	ру	disseminated	2.08	LA
15	T7-2	ру	disseminated	2.47	LA
16	T8-1	ру	massive ore	3.99	LA
17	T8-2	ру	massive ore	2.30	LA
18	T10-1	ру	massive ore	2.57	LA
19	T10-2	ру	massive ore	0.58	LA
20	BB10	ру	disseminated	4.13	С
21	BB10c-1	ру-сру	stringer zone	1.36	С
22	BB10c-2	ру-сру	stringer zone	-0.80	С
23	Tasik 1	ba	barite ore	16.15	С
24	Tasik 2	ba	barite ore	11.60	С
25	Tasik 3	ba	barite ore	17.66	С
26	Barite	ba	barite ore	17.42	С
27	MBTC-S3	ba	barite ore	18.15	С
28	BB1 (barite)	ba	barite ore	15.95	С
29	BB2 (barite)	ba	barite ore	16.24	С
30	B1	ba	barite ore	13.65	С
31	B2	ba	barite ore	14.85	С
32	BB2-X	ba	barite ore	11.82	С
Within Bukit Ketaya deposit area (102.9215 mE, 3.4091 mN)					
1	BK12a	ру	stringer zone	-2.87	С
2	BK12a-lower	ру	stringer zone	-2.56	С
3	BK12a-upper	ру	stringer zone	-2.35	C

Table. (Continued).

4	KZMA-1	ру	stringer zone	-0.77	С
5	KZMA-2	ру	stringer zone	-0.36	С
6	KZMA-3	ру	stringer zone	-0.66	С
7	BKCL-1	ру	disseminated	0.15	С
8	BKCL-2	ру	disseminated	-1.66	С
9	BMSE1	ру	massive ore	2.19	С
10	BMSE1-1	ру	massive ore	3.28	С
11	BMSE1-2	ру	massive ore	3.51	С
12	BK06	ba	barite ore	22.61	С
13	BK08	ba	barite ore	18.54	С
14	BK08a	ba	barite ore	16.86	С
15	BK09	ba	barite ore	18.46	С
16	14AR	ba	barite ore	11.58	С
17	S 6/7a12	ba	barite ore	20.66	С
18	S 6/7a13	ba	barite ore	20.39	С
19	BK01 (ba)	ba	barite ore	16.02	С
20	BK02 (ba)	ba	barite ore	15.68	С
21	BKX	ba	barite ore	17.00	С
22	S 5/6a4	ba	barite ore	18.87	С



Figure 4. Histogram of δ^{34} S values for sulfides and sulfates from the Bukit Botol deposit, Central Belt of Peninsular Malaysia.



Figure 5. Frequency distribution of δ^{34} S values of sulfides and sulfates for Bukit Botol deposit, Central Belt of Peninsular Malaysia.

5. Discussion

5.1. Significance of sulfur isotopes

The sulfur isotope data of sulfides from the Bukit Botol deposit exhibit a uniform range of δ^{34} S values between -0.8% and + 4.1%, and one sample displays a higher δ^{34} S value of +8.3%. Meanwhile, the δ^{34} S values for sulfides from the Bukit Ketaya deposit are characterized by a narrow and restricted range of δ^{34} S between -2.9% and +3.6%. The δ^{34} S values of barite minerals of both deposits are very uniform, which indicates they were derived from the same sulfur source. In general, the range of sulfur values obtained from the VHMS deposits of the Tasik Chini district are comparable and within the typical δ^{34} S values range from -20% to 27% in sulfides and 10% to 40% in sulfates variability of global VHMS deposits (Ohmoto and Rye, 1979; Huston, 1999).

In comparison, the significantly narrow ranges of sulfides with a cluster toward positive δ^{34} S values in both deposits are similar to those of several ancient VHMS deposits, including the Osborne Lake deposit in the Snow Lake area, Canada (-1.1‰ to +6.0‰; Sangameshwar, 1972), the El Cobre deposit, Cuba (-1.4‰ to +7.3‰; Cazañas et al., 2003), the Mount Morgan deposit, Australia (-1.6‰ to +5.3‰; Ulrich et al., 2002), the Lewis Ponds, Mount Bulga, Belara and Accost deposits in the Lachlan Fold Belt, New South Wales (range of -1.7‰ to +5.9‰; Downes and Seccombe, 2004). However, the abundance of

significant low δ^{34} S values in sulfides at the Bukit Ketaya deposit is also probably comparable with a δ^{34} S signature exhibited by the Mount Lyell deposits, Tasmania (–10‰ to +10‰; Huston et al., 2011). Moreover, most sulfates (barites) from both deposits have δ^{34} S values (11‰ to 18‰, Bukit Botol; 11‰ to 22‰; Bukit Ketaya). As the host volcanic rocks of both deposits are of Early Permian ages (Mohd Basril Iswadi, 2014), this sulfur isotope's value ranges are similar to or slightly higher than those of Permian seawater sulfate (+10‰ to +12‰; Claypool et al., 1980; Kampschulte and Strauss, 2004), indicating a large component of marine sulfate in this mineral.

5.2. Source of sulfur

Sulfur in VHMS deposits usually comes from: (1) a magmatic source (Ohmoto, 1996) through a direct contribution from a vapor-rich magmatic fluid (Ohmoto, 1986; Stanton, 1990; Gemmell and Large, 1992; Sillitoe et al., 1996; Herzig et al., 1998, Galley et al., 2000; Solomon et al., 2004) or leaching from subsurface magmatic rocks (Ohmoto and Goldhaber, 1997); (2) an inorganic reduction of seawater sulfate during a deep circulation process (Ohmoto et al., 1983; Solomon et al., 1988); and (3) a bacterial reduction of seawater sulfate (Sangster, 1976; Cagatay and Eastoe, 1995).

The ranges of sulfur isotope values of the Bukit Botol and Bukit Ketaya deposits in the Tasik Chini district are plotted with a sulfur value range from various rocks and shown in Figure 6. The uniform and almost identical δ^{34} S values of sulfides from both deposits suggest a homogeneous hydrothermal system, and the closeness to

0% is consistent with a magmatic source (e.g., $0 \pm 2\%$; Ohmoto and Rye, 1979). Thus, the data suggest a probable source of sulfur in the sulfides was leached from the



Figure 6. Comparison of 8³⁴S values for Bukit Botol and Bukit Ketaya deposits with selected Permian VHMS deposits, modern seafloor VHMS deposits from various tectonic settings and natural geological settings. Source of data: Permian VHMS deposits; Afterthought and Bully Hill, California-Gustin (1990), and Eastoe and Gustin (1996); Yanahara, Japan-Yamamoto et al. (1968), and Kajiwara and Date (1971); Red Ledge, Idaho-Fifarek et al. (1984), and Fifarek (1985); Mount Chalmers, Queensland-Huston (1999), and Hunns (2001); Permian seawater-Claypool et al. (1980), and Kampschulte and Strauss (2004). Modern VHMS deposits; back-arc/arc-hosted deposits; Okinawa Trough, Japan-Halbach et al. (1989); Manus Basin-Lein et al. (1993); Mariana Trough-Kusakabe et al. (1990); Brothers Volcano, Kermadec Tonga-de Ronde et al. (2005); MORB-hosted deposits (unsedimented ridges); Southern Juan de Fuca Ridge (SJFR)-Shanks and Seyfried (1987); Galapagos Rift-Skirrow and Coleman (1982), and Knott et al. (1995); Axial Seamount-Hannington and Scott (1988); Broken Spur-Duckworth et al. (1995); Snakepit-Kase et al. (1990); TAG-Herzig et al. (1998), Chiba et al. (1998), and Gemmell and Sharpe (1998); East Pacific Rise (EPR)-McConachy (1988), Bluth and Ohmoto (1988), Stuart et al. (1994), Hekinian et al. (1980), Arnold and Sheppard (1981), Styrt et al. (1981), Kerridge et al. (1983), Zierenberg et al. (1984), Woodruff and Shanks (1988), and Marchig et al. (1990); MORB-hosted deposits (sedimented ridges); Escanaba Trough-Koski et al. (1988), Zierenberg et al. (1993), and Böhlke and Shanks (1994); Guayamas Basin-Peter and Shanks (1992), and Shanks et al. (1995); Middle Valley-Goodfellow and Blaise (1988), Duckworth et al. (1994), Zierenberg (1994), and Stuart et al. (1994); modern seawater-Rees et al. (1978). Natural geological settings: metamorphic rocks, sedimentary rocks, volcanic H₂S, volcanic SO₂ and granites-Hoefs (2004).

igneous rocks most likely the volcanic host rocks at both deposits. Nevertheless, a direct magmatic source seems unlikely because a direct magmatic contribution would be more effective in supplying metals, in particular the Cu, Au, Bi, and Te, to VHMS deposits (Large, 1992), and is significant in the formation of giant VHMS deposits (Ulrich et al., 2002).

Furthermore, the relatively narrow range and nearly positive $\delta^{34}S$ values of sulfides from both deposits also rule out a bacterial sulfate source for the sulfur, such as in many VHMS deposits of the Iberian Pyrite Belt, Portugal (e.g., Velasco et al., 1998). However, these characteristics are an indicator of an inorganic reduction process of seawater sulfate in many other VHMS deposits of high temperature formation (Sasaki and Kajiwara, 1971) with the presence of ferrous iron as a reduction agent (Ripley and Ohmoto, 1977; Mottl et al., 1979; Shanks et al., 1981; Kerridge et al., 1983; Shanks and Seyfried, 1987). This similar interpretation is suggested for the δ^{34} S of sulfide characteristics at both the Bukit Botol and Bukit Ketava deposits because there are occurrences of the Fe-Mn±Si layers at the top of the mineralized systems. In addition, inorganic reduction processes usually reach metastability and less or no isotopic fractionation occurs between sulfur species (Cross and Bottrell, 2000).

As discussed above, the similarity of δ^{34} S values of sulfates also indicates a contribution from seawater sulfate during Permian time. The close association of $\delta^{34}S$ for sulfate with Permian seawater is clearly shown in Figure 6 by several VHMS deposits from the Permian time interval, including the Tasik Chini deposit systems (both Bukit Botol and Bukit Ketaya). Thus, it is inferred that Permian seawater is the primary source of sulfate for sulfate minerals precipitation. However, the higher $\delta^{34}S$ values of sulfates present in the Tasik Chini deposit and other VHMS deposits could be due to the contribution of hydrothermal sulfate (Ohmoto, 1996; Solomon et al., 2004a; Scotney et al., 2005). This interpretation is consistent with the experimental evidence, which indicates that sulfate is reduced in high temperature hydrothermal systems interacting with volcanic rocks by oxidation of Fe²⁺ (Ohmoto and Rye, 1979). This results in fractionation between 0 and 25 permil lower than the starting sulfate (Rye and Ohmoto, 1974), depending on the relative

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fraction of sulfur of hydrothermal origin (H₂S oxidation) in the mixture sources (Hannington and Scott, 1988).

Additionally, the highly variable $\delta^{34}S$ and low to negative values for sulfide within the Permian deposits in Figure 6, including the Tasik Chini deposits, are consistent with the relationship between the deposits and seawater (Sangster, 1968). The values on average are ~16 permil more depleted than that of the co-existing seawater (Huston, 1999; Huston et al., 2010), and the $\delta^{34}S$ of precipitated sulfide minerals closely reflects the $\delta^{34}S$ of the hydrothermal solutions (Ohmoto and Rye, 1979).

6. Conclusions

1. The sulfur isotope ratios of the sulfides at both the Bukit Botol and Bukit Ketaya deposits are distributed in a narrow range, close to the average ratio in magmatic sulfur, whereas the δ^{34} S composition of sulfates is similar to or slightly higher than that of Permian seawater sulfate.

2. These features demonstrate that the derivation of hydrothermal sulfide sulfur from the seawater involved inorganic or chemical reduction of seawater sulfate.

3. A magmatic source contribution is also significant when considering the presence of a narrow range of δ^{34} S values and near to 0‰ for sulfides. This sulfur was most likely derived from the volcanic rocks that hosted the mineralization at both deposits.

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