

Sulfur isotope geochemistry and mineralogy of Balcılar vein type barite-sulphide mineralization, Biga peninsula, NW Turkey

Balcılar damar tipi barit-galenit cevherleşmesinin maden jeolojisi ve sülfür izotop jeokimyası, Biga yarımadası, Türkiye

Gülcan BOZKAYA^{1*}, David A. BANKS²

¹Department of Geological Engineering, Engineering Faculty, Pamukkale University, Denizli, Turkey.
gbozkaya@pau.edu.tr

²School of Earth and Environment, University of Leeds, Leeds, UK.
D.A.Banks@leeds.ac.uk

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* Corresponding author/Yazışılan Yazar

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Abstract

The Balcılar (Çanakkale) barite-galena mineralization is a typical example of the vein type barite-lead-zinc deposits in the Biga Peninsula. The lithologic units in the study area are Akçaalan andesite, Eocene, Adadağı pyroclastics, Oligocene, Dededağ dacite, Miocene, Karaömerler basalt, Plio-Quaternary and alluvium Quaternary. Barite-galena veins occurred along the faults developed within the andesites. Barite, quartz and galena are main minerals and are accompanied by minor amounts of sphalerite, pyrite, chalcopyrite, covellite and marcasite. The earliest barite (barite I) occurs as coarse-grained subhedral-euhedral crystals and the later (barite II) as small tabular crystals in between the earlier coarse crystals. Quartz occurs as fine-grained crystals with the later small barite crystals. Galena, sphalerite, chalcopyrite, pyrite, marcasite and covellite occur open spaces within the earlier barite (barite I) crystals. Sulfur isotopes indicate that in galena the reduced sulfur from bacterially or inorganically reduced sulphate, or from an isotopically light reduced S-source. The $\delta^{34}S_{H2S}$ values calculated from the barite-H₂S and galena-H₂S fractionation factors, in the same samples, indicate a temperature of between 200 and 300 °C. Relatively lower $\delta^{34}S$ values of barites than dissolved sulphate in modern oceans or Eocene sea waters have been evaluated as the ore forming hydrothermal fluids were derived from interacting throughout the magmatic host-rocks.

Keywords: Barite-galena, Ore geology, Sulfur isotope, Çanakkale, Turkey

Öz

Balcılar (Çanakkale) barit-galenit cevherleşmesi, Biga yarımadasındaki damar tipi kurşun-çinko-barit yataklarının tipik örneklerinden birisidir. İnceleme alanındaki litolojik birimler; Eosen Akçaalan andeziti, Oligosen Adadağı piroklastikleri, Miyosen Dededağ dasiti, Pliyo-kuvaterner Karaömerler bazaltı ve Kuvaterner alüvyonlar olarak ayrırtlanmıştır. Barit-galenit damarları andezitler içerisindeki faylar boyunca oluşmuşlardır. Barit, kuvars ve galenit ana mineraller olup, bu minerallere az miktarda sfalerit, pirit, kalkopirit, kovellin ve markazit eşlik etmektedir. Baritler erken evrede iri-taneli yarı özsekilli-özsekilli kristaller (barit I) ve geç evrede kaba kristallerle girift küçük çubuksu kristaller (barit II) biçiminde iki-evreli mineralizasyonla gelişmiştir. Kuvars küçük barit kristalleriyle birlikte geç evrede oluşmuştur. Galenit, sfalerit, kalkopirit, pirit, markazit ve kovellin geç evre ürünleri olup, önceki oluşan barit kristalleri içerisindeki boşluk zonları boyunca oluşmuşlardır. Sülfür izotop bulguları galenitteki sülfürün bakteriyel veya inorganik sülfattan (SO_4^{2-}) indirgenmiş veya izotopik olarak hafif S-kökenle etkileşimi göstermektedir. Barit-H₂S ve galenit-H₂S ayrılma faktörlerinden itibaren hesaplanan $\delta^{34}S_{H2S}$ değerleri, sıcaklık koşullarının 200-300 °C arasında olduğunu göstermiştir. Baritlerin güncel okyanus veya Eosen deniz suyu bileşiminden daha düşük $\delta^{34}S$ değerleri, hidrotermal sıvıların magmatik yan kayalarla etkileşiminden kaynaklandığı biçiminde değerlendirilmiştir.

Anahtar kelimeler: Barit-galenit, Maden jeolojisi, Sülfür izotopu, Çanakkale, Türkiye

1 Introduction

The Biga region is located within the "Tethyan Eurasian Orogenic Belt" [1] or "Tethyan Eurasian Metallogenic Belt" [2], extending from Western Europe through Anatolia to Iran (Figure 1a). It is intensely mineralized, actively explored and mined and is one of the economically important areas of Turkey. There are numerous vein type Cu-Pb-Zn deposits hosted by metamorphic, sedimentary and volcanic rocks (e.g., Koru, Tesbihdere, Balcılar, Kumarlar, Arapuçandere, Bağırkaçdere). The Balcılar Ba-Pb vein-mineralization is a typical example of the volcanic-hosted vein type mineralization, located near the village of Balcılar in the Lapseki district (Figure 1b).

The geological characteristics and genesis of the deposits was reported by various authors [3]-[7], whose opinion was that mineralization is vein type, from hydrothermal fluids related to local volcanic activity. Additionally, Yanagiya and Sato [8]

identified the alteration zones using Landsat TM images. Despite previous studies of the Balcılar mineralization [4],[5], [9], the origin of the oxidised and reduced sulfur in barite and galena is still unknown. This study's aim is to detail the mineralogy, paragenesis and sulfur-isotope geochemistry which will be combined with fluid inclusion data [10] to better understand the source and role of the mineralizing fluid.

2 Geological background and lithology

The barite-galena mineralization at Balcılar is located in the northeastern part of the Biga Peninsula which comprises metamorphic, igneous and sedimentary units of Permian to Quaternary age. Tertiary volcanic and volcano-sedimentary units outcrop in vicinity of the mineralization. These are the Akçaalan andesite (or Balıklıcesme volcanics, Middle Eocene), Adadağı pyroclastics (or Çan volcanics, Oligocene) and Dededağı dacite (or Doyran volcanics, Miocene) and Quaternary alluvium ([11], Figure 2).

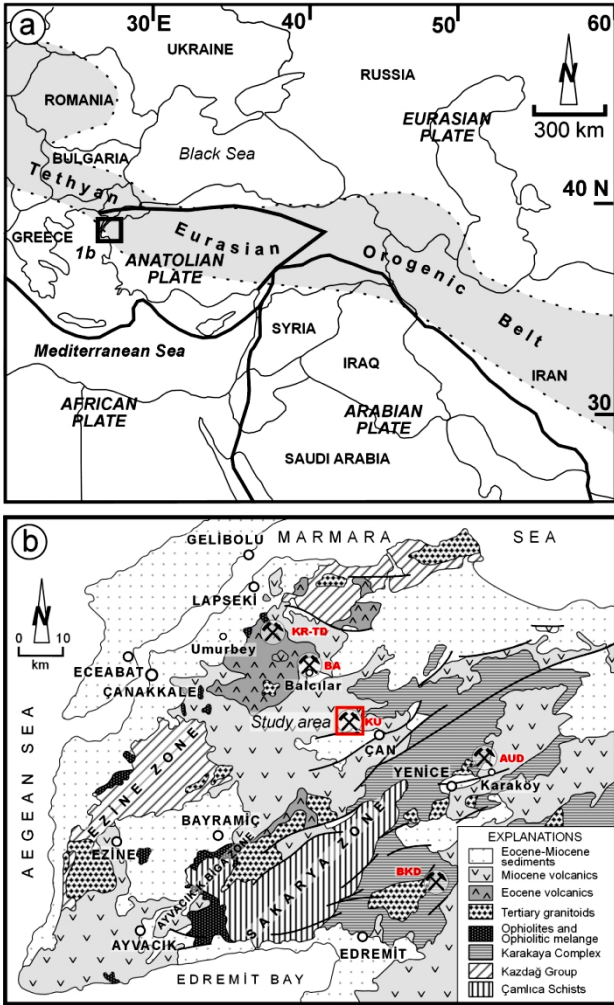


Figure 1: a): Location of the Biga Peninsula in relation to the boundaries of the major tectonic plates and Tethyan Eurasian Orogenic Metallogenic Belt (simplified after [2]). b): Simplified geological map of the Biga Peninsula and distribution of the main Pb-Zn deposits (KR-TD: Koru-Tesbihdere, BA: Balçılar, KU: Kumarlar, AUD: Arapucandere, BKD: Bağırkaçdere).

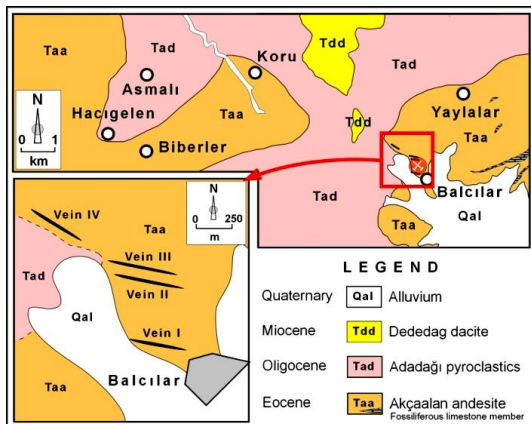


Figure 2: Geological map of the Balçılar barite-lead mineralized area and locations of the barite-galena veins.

The Akçaalan andesite unit includes andesite, basaltic andesite, lesser rhyodacite and dacite, but rarely their pyroclastic equivalents, with intercalations of limestone towards the top of the sequence. Andesites have a hypohyaline

porphyritic texture, consisting of phenocrysts of plagioclase, pyroxene (augite and aegirine-augite), with rare hornblende and biotite in a matrix of volcanic glass and microcrystals. The fossil assemblages within the limestone lenses are consistent with a Middle Eocene age [11],[12]. This unit is discordantly overlain by the Adadağı pyroclastics which contain tuffs, agglomerates and lavas of andesitic and dacitic composition. An Oligocene age was suggested for this unit based on its stratigraphic position as suggested by Sümengen et al. [13] and Ercan et al. [14]. The Dededağ dacite unit is primarily dacitic with rare rhyodacitic lavas which have a hypohyaline porphyritic texture. The matrix is extensively silicified and argillized with widespread phenocrysts of plagioclase, hornblende, biotite, sanidine and quartz [11]. The mineralogy and texture of this unit is very similar to that of the Adadağı pyroclastics, but is distinct in terms of the stratigraphic position. All of these units are overlain by Quaternary unconsolidated detrital alluvium.

3 Ore Geology and mineralization

The mineralization is located along a river channel in the northwest part of the village of Balçılar. Four parallel veins within the andesite, identified as vein I to vein IV, according to their distance from the village (Figure 2), are typically 40 to 100 cm thick, and occur along fault zones in a N 55-80 W/55-65 NE direction (Figure 2, 3). The veins consist mainly of barite (~95%) and lesser amounts of galena (~5%). Petrographic observations of thin sections and polished blocks show barite and galena are accompanied by small amounts of quartz, sphalerite, pyrite, chalcopyrite, marcasite, and covellite. Two morphologies of barite are present, the early (bt I) barite is coarse grained with subhedral to euhedral crystals, whereas later stage barite (bt II) occurs as small tabular crystals which intersperse the larger coarse crystals (Figure 4). Quartz was formed during the later stage together with the small barite (bt II) crystals.

Galena crystals have anhedral morphologies and are surrounded by euhedral barite I crystals (Figure 5). Greenish-grey colored fahlore inclusions, occurring as roundish and rod-shaped crystals, were also found in galena. Chalcopyrite, pyrite and covellite are developed on the border between galena and barite crystals. Anhedral sphalerite is shown enclosing galena crystals, filling the open spaces within the early barite crystals and also replacing the early barite. Chalcopyrite is found either along sphalerite boundaries or on the boundaries between the galena and barite crystals. Chalcopyrite occurring as disseminated and capillary veinlets along the boundaries of sphalerite is considered to represent "chalcopyrite disease" [15] or alternatively replacement and co-precipitation resulting from the interaction of sphalerite with hydrothermal fluids [16],[17]. Pyrite is mostly observed as disseminated euhedral crystals within the gangue minerals and along the boundaries of galena and barite crystals. Marcasite is rare in the gangue minerals, whereas covellite co-exists with chalcopyrite and pyrite on the boundaries of galena and barite.

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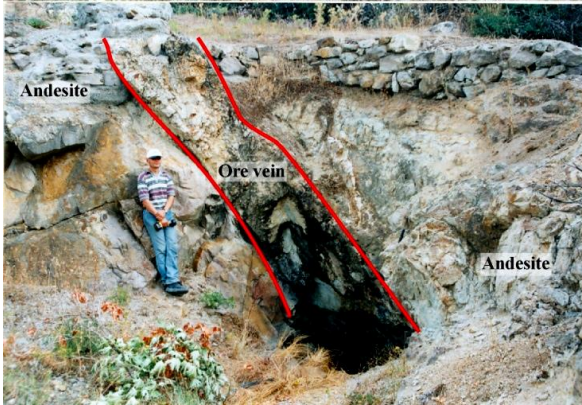


Figure 3: Andesite-hosted barite-galena vein (Vein I) at an old mine entrance near the village of Balçılar.

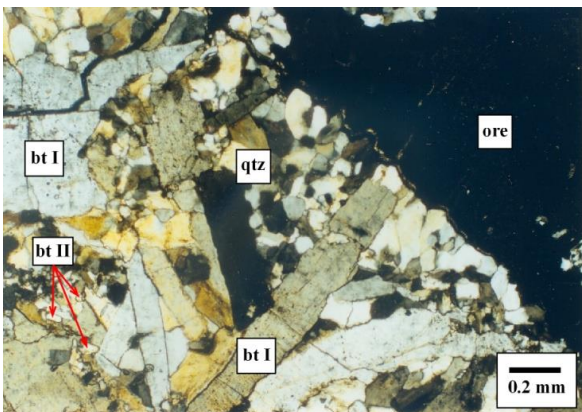


Figure 4: Photomicrograph of barite, quartz and ore minerals (crossed nicols). qtz: quartz, bt I: early stage barite, bt II: late stage barite.

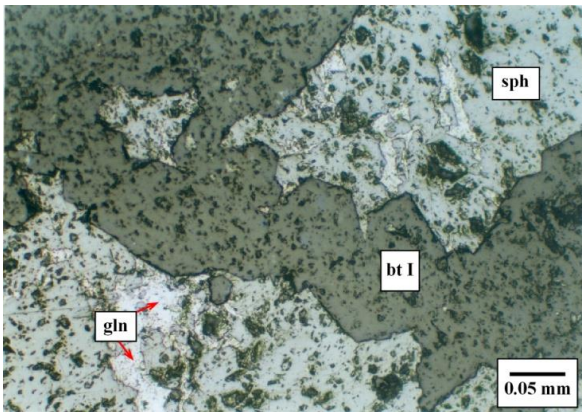


Figure 5: Polished section showing sphalerite amongst euhedral barite crystals and galena inclusions within the sphalerite. gln: galena, sph: sphalerite, bt: barite I.

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4 Sulfur isotopes

Sulfur-isotope studies (performed at the Activation Laboratory in Canada), were carried out on galena and early and late barite, hand-picked from the ore samples that represent various parts of the stockwork and veins, I to IV. Sulfur isotope results show that the $\delta^{34}\text{S}$ V-CDT values of galena and barite vary from -10.4, to -11.9‰ (avg. -11.2‰) and 13.3 to 19.7‰, respectively (Table 1; Figure 6). As barite is the main mineral in the veins this indicates that the main sulfur source in hydrothermal fluid was SO_4 however, the sulfur isotope $\delta^{34}\text{S}$ values of barite indicates two groups, with $\delta^{34}\text{S}$ values from 13.3 to 14.6‰ and 19.5 to 19.7‰. The two $\delta^{34}\text{S}$ values (19.5 and 19.7‰) are similar to Late Eocene seawater. The lighter $\delta^{34}\text{S}$ values would be consistent with early Cretaceous or older seawater (Figure 7; [20],[21]) but this does not fit with the age of the mineralization or its geological setting. The early formed barite, shown in Figures 4 and 5, are larger elongate crystals, but are cut by later formed quartz, barite-II and sulphides. The galena and sphalerite are clearly present as micron-sized inclusions in the early barite-I and were impossible to remove prior to analysis. Therefore, the low $\delta^{34}\text{S}$ values of the initial barite is probably due to contamination from sulphide inclusions. The second generation of barite is uncontaminated and the heavier $\delta^{34}\text{S}$ values are consistent with seawater SO_4 at the time of mineralization. We therefore exclude a second SO_4 source to account for the different $\delta^{34}\text{S}$ values of barite.

We can exclude oxidised sulphide from hydrothermal fluids as a source of SO_4 $\delta^{34}\text{S}$ as the values of alunite (Table 1) from alteration zones around upwelling magmatic fluids [23],[24] are much less positive. These fluids represent the near surface oxidation of sulphide in magmatic fluids and are quite different from a seawater SO_4 source.

The $\delta^{34}\text{S}$ values of galena are distinctly lower than those normally taken to indicate a magmatic sulphur source in magmatic hydrothermal deposits (-3 to +1‰; [25]). However, the values here are similar to those of the nearby Tesbıhdere deposit [26] and are also anomalously lower than that of the mantle (0 ± 3 ‰), igneous rocks (+1‰ to +3‰) [27], crustal (mean +7‰; [28]) or sulphur derived from seawater (+20‰; [29]). Light $\delta^{34}\text{S}$ values can be the result of biological fractionation, for example of seawater SO_4 , or of leaching of biogenic sulphides, however there is no evidence of sulphides in the immediate country rocks to indicate that the sulfur in galena was derived from an external, isotopically light S-source. The $\delta^{34}\text{S}$ values of sulphides of the galena indicate a significant contribution from a magmatic source to the ore-forming fluids ([30],[18],[19]), but values are more negative than the normal range of $\delta^{34}\text{S}$ values for magmatic hydrothermal deposits (-3 to +1‰; [25]).

Having excluded leaching sedimentary sulphides, the more likely explanation is that the negative $\delta^{34}\text{S}$ values can be explained by boiling of a hydrothermal fluid that was originally derived from a magma. Boiling and negative $\delta^{34}\text{S}$ values have (Table 1) been recognized here and at other deposits in the region ([31],[32],[33],[34]). [35] suggest that fluid boiling will lead to a loss of H_2 and the oxidation of the ore fluid. In the more oxidized ore fluid, the ratio of $\text{H}_2\text{S}/\text{SO}_4^{2-}$ will decrease dramatically, leading more ^{34}S to concentrate in SO_4^{2-} , resulting in the observed more negative $\delta^{34}\text{S}$ values in sulphides (e.g., [36],[37]).

Table 1: Sulfur-isotope compositions of galena and barite crystals separated from the mineralization in veins I to IV, compared with locations in the Biga Peninsula.

Balcilar Veins				Biga Peninsula		
Sample	Location	$\delta^{34}\text{S}$ ‰ barite	$\delta^{34}\text{S}$ ‰ galena	Location	$\delta^{34}\text{S}$ ‰ Sulphate	$\delta^{34}\text{S}$ ‰ Sulphide
BA-203	v-I	14.6	-10.4	Koru ^[11]	14.9/17.2 (barite)	
BA-5	v-II	-	-10.7	Turplu ^[23]	4.8/7.8 (alunite)	0.6/1.8 (py)
BA-6	v-II	-	-11.4	Simav ^[23]	-1.5/6.2 (alunite)	
BA-15	v-III	13.9	-11.9	Tesbihdere ^[33]		-9.8/-2.4 (cpy-gal)
BA-215	v-IV	-	-11.3	Tesbihdere ^[43]		-8.7/-6.1 (gal)
BA-216	v-IV	13.9	-11.1	Arapucandere ^[34]		-5.9/-3.4 (gal)
BA-218	v-IV	13.3	-11.2	Kartaldag ^[31]		-4.8/-2.2 (py)
BA-219	v-IV	19.7	-11.8	Kumarlar ^[10]		-7.0/-3.1 (gal)
BA-220	v-IV	19.5	-	Balya ^[24]		1.8/2.7 (py)
				Ovacik-Narlica ^[44]		-4.6/5.3 (bulk)

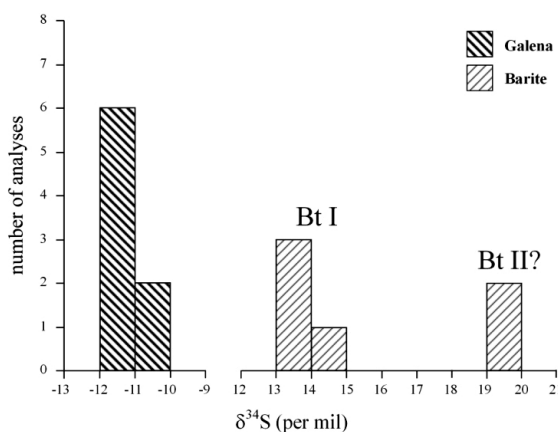


Figure 6: Distribution of sulphur isotope values of barite and galena from the Balcilar barite-lead mineralization.

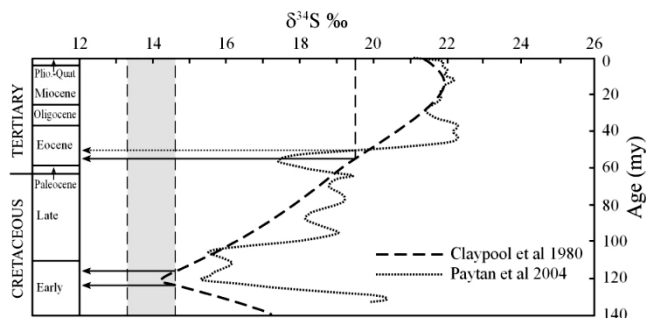


Figure 7: Age and $\delta^{34}\text{S}$ isotope values relations to barites (Sulfur isotope age curves were taken from [20] and [21]).

This process is observed in other deposits worldwide, for example, at the Valles Caldera, Summitville and White Island ([38]-[40]). [41] suggested that fluid boiling will lead to a loss of H_2 which occurs faster than the loss of H_2S from the aqueous fluid into the vapour phase [42]. Oxidation of aqueous H_2S would occur leading to preferential incorporation of ^{34}S into SO_2 or SO_4 , for example, with the H_2S remaining in the fluid becoming lighter as boiling progressed and thereby producing negative $\delta^{34}\text{S}$ values in sulphides (e.g., [36],[37]). Our conclusions are that sulphur was indeed derived from the magmatic fluid and that boiling and flashing resulted in changes to the redox state of the fluid that led to the more negative than normal magmatic $\delta^{34}\text{S}$ values.

Other deposits in the Biga Peninsula (Table 1) have $\delta^{34}\text{S}$ values that are also more negative than expected for magmatic sulphide. Although the values are less extreme than those from this study and from Tesbihdere [33], in the absence of other evidence such negative $\delta^{34}\text{S}$ values may also be indicative of boiling zones and more oxidising conditions in the fluids commensurate with higher grade sulphide-mineralized zones elsewhere in the Biga Peninsula.

5 Conclusions

The mineralization at Balcilar (Çanakkale), is predominantly barite, with lesser amounts of galena and minor amounts of quartz, sphalerite, pyrite, chalcocopyrite, covellite and marcasite. There are two distinct generations of barite, which can be distinguished on the basis of morphology, and where the first generation of barite is volumetrically dominant. Galena, sphalerite and quartz precipitated in the open spaces between the first barite crystals along with the second generation of smaller barite crystals. The heaviest $\delta^{34}\text{S}$ values of the second generation barite are consistent with SO_4 derived from Eocene sea water. The first generation of barite has $\delta^{34}\text{S}$ values which are lower than seawater at the time of mineralization and we suggest this was caused by micron sized sulphides whose very negative $\delta^{34}\text{S}$ values lowered the $\delta^{34}\text{S}$ values of the barite. We proposed that despite the difference in sulphur isotopes both generations of barite derived SO_4 from the same seawater source. The distinctly negative $\delta^{34}\text{S}$ values of galena are lower than those of magmatic sulfur, but would be comparable with sulphide originating from bacterial reduction of seawater SO_4 . However, two distinct surface reservoirs of reduced and oxidised surface seems improbable. Pre-existing sulphides, with negative $\delta^{34}\text{S}$ values, in the country rocks could have been leached by the hydrothermal fluids but there is no evidence of any such sulphides. Therefore, we suggest that the negative $\delta^{34}\text{S}$ values of the galena are due to boiling of the magmatic fluid at depth. Such a process has been shown to produce very negative $\delta^{34}\text{S}$ at the surface such as at White Island, New Zealand [40].

Fluid inclusion evidence shows that in both generations of barite the fluids that were trapped are liquid only, which implies trapping of these fluids at temperatures of less than c. 60 °C and therefore consistent with a surface source of the fluids. In sphalerite, co-precipitated with galena, the fluid inclusions were trapped at c. 150 °C and this would imply a

fluid ascending from depth. Our conclusion is that the barite-sulphide mineralization was emplaced in the uppermost parts of the epithermal system where seawater and the remnants of the magmatic-hydrothermal fluid from depth were present. The volumetric lack of sulphides reflects that most of the metals in the hydrothermal fluid were deposited deeper in the mineralizing system and this fluid reaching the surface was the left-overs after mineralization [10].

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