Physicochemical controls on bismuth mineralization: An example from Moutoulas, Serifos Island, Cyclades, Greece

MICHALIS FITROS1,*, STYLIANOS F. TOMBROS1, ANTHONY E. WILLIAMS-JONES2, BASILIOS TSIKOURAS1,3, ELENI KOUTSOPOULOU1, and KONSTANTIN HATZIPANAGIOTOU1

1Department of Geology, Section of Earth Materials, University of Patras, Rion, 26500, Patras, Greece
2Department of Earth and Planetary Sciences, 3450 University Street, Montreal, Quebec H3A 2A7, Canada
3Faculty of Science, Physical and Geological Sciences, Universiti Brunei Darussalam, Jalan Tunung Link, BE1410 Gadong, Bandar Seri Begawan, Brunei Darussalam

ABSTRACT

The 11.6 to 9.5 Ma Serifos pluton intruded schists and marbles of the Cycladic Blueschist unit, causing thermal metamorphism, the development of magnetite Ca-exo- and endo-skarns and the formation of low-temperature vein and carbonate-replacement ores. Potentially, the most important ores occur in the Moutoulas prospect where the mineralization in retrograde skarn and quartz veins culminated with the deposition of native bismuth. A combination of fluid inclusion microthermometry and isotopic geothermometry suggests that the Moutoulas mineralization formed at a hydrostatic pressure of ~100 bars, from moderate-to-low temperature (~190–250 °C), and low-salinity (1.3–5.6 wt% NaCl equivalent) fluids. The calculated δ34S compositions are consistent with the ore fluids having been derived from the Serifos pluton. Bismuth mineralization is interpreted to have occurred as a result of wall-rock interaction and mixing of a Bi-bearing ore fluid with meteoric waters. Native bismuth and bismuthinite deposited at ~200 °C, near neutral pH (6.5), low fO2 (−16.5), and low fS2 (−44). Supergene alteration in Serifos led to the oxidation of native bismuth to bismite and bismutite.

Keywords: Native bismuth, retrograde skarn, supergene alteration, Moutoulas, Serifos

INTRODUCTION

Knowledge of the aqueous geochemistry of bismuth is still incomplete, in particular, the physicochemical controls of its transportation and deposition. Experimental and theoretical studies (e.g., Skirrow and Walshe 2002; Tooth et al. 2008; Mavrogenes et al. 2010; Henley et al. 2012; Etschmann et al. 2016) suggest that Bi can be mobile either in vapors at high temperature or in the liquid as complexes of Bi3+ ions with hydroxyl and chloride ions, e.g., Bi3+(OH)3n+ (x = 1, 2; n = 1, 6, 9; m = 12, 20, 21), Bi(OH)3n+, BiCl3n+ (x = 1, 2; n = 1, 2), BiCl3 (x = 1, 2, 3; n = 4, 5, 6) and BiCl3.

Occurrences of native bismuth in Greece are found mainly in the Serbomacedonian, Rhodope, and Attico-cycladic massifs in Cu-Mo porphyries, skarns, carbonate replacement deposits and related vein stockworks, volcanic-hosted epithermal deposits, and in shear-zone deposits (e.g., Plaka skarn, Lavrion, Greece, Voudouris et al. 2007 and references therein; Cook et al. 2009). In these deposits, the native bismuth is intergrown with bismuthinite, galena, Bi-sulfosalts (gustavite, lillianite, aikinite, and cosalite), Bi-tellurides and electrum or occurs as inclusions in galena (Voudouris et al. 2007). Supergene alteration of native bismuth led to the formation of bismite and bismutite.

This study focuses on the Moutoulas deposit, an unexploited prospect, on Serifos Island, where native bismuth precipitated in clear quartz veins. In it, we investigate the physicochemical controls on the precipitation of native bismuth as a retrograde skarn mineral and its subsequent supergene alteration. We introduce a new approach for the calculation of Bi(OH)3 contours over temperature with the aim to predict the favorable conditions in which native bismuth precipitates. It is proposed that bismuth was transported as complexes involving hydroxyl and bicarbonate ions, e.g., Bi(OH)3(HCO3)3 and that it deposited as native bismuth during mixing of the ore fluid with meteoric water.

GEOLOGICAL SETTING

Serifos Island is part of the Attico-Cycladic massif of Greece, which includes three nappes: the lower Cycladic Basement Unit consisting of gneisses of Variscian ages (CB), the Cycladic Blue- schist Unit (CBU), and the Upper Cycladic Unit (UCU) (Rabillard et al. 2015). The CB in Serifos comprises alternating hornblendebiotite and quartz-feldspathic gneisses, intercalated with quartzites and marbles, and the CBU, amphibolites intercalated with gneisses and greenschists containing thinly bedded dolomitic marbles. The latter unit represents a metamorphosed volcanosedimentary sequence developed along a Mesozoic continental margin. At least two Tertiary metamorphic events affected the CBU. The first event occurred between 53 and 40 Ma and was characterized by eclogite to blueschist facies conditions (T = 450–500 °C, P = 1.5 ± 0.3 GPa, Brichau et al. 2010). This event was followed by a greenschist to amphibolite facies event (T = 670–700 °C and P = 0.4–0.7 GPa, Xypolias et al. 2012) that occurred between ≥25 and ~12 Ma (Bolhar et al. 2010). The UCU comprises an ophiolite nappe that was obducted in the Late Jurassic, and is overlain by unmetamorphosed sedimentary rocks (Bröcker and Franz 2005;
Rabillard et al. 2015). The following lithotypes of UCU occur in Serifos (Fig. 1): calcite marbles, ankerite-dolomite-talc-goethite carbonate-replacement orebodies, meta-basites, and serpentinites (Grasemann and Petrakakis 2007; Petrakakis et al. 2007). The lower Megalo Livadi detachment (ML) separates the CB from the CBU, and the upper Kavos Kiklopas detachment (KK) separates the CBU from the UCU (Grasemann et al. 2012; Ducoux et al. 2017; Fig. 1).

The Serifos pluton was emplaced at ~11.6 to 9.5 Ma in the CB and CBU rocks along the NE-SW trending ML detachment, creating a contact metamorphic aureole, 0.5 to 1 km in width (Fig. 1, Rabillard et al. 2015). L-type, hornblende-biotite granodiorite with subordinate tonalite intruded at its center, and granodiorite to S-type hornblende-biotite-allonite-zinnwaldite granite at its margins (Stouraiti and Mitropoulos 1999; Grasemann and Petrakakis 2007; Seymour et al. 2009). The pluton crystallized at a temperature of ~700 to 750 °C and was emplaced at a pressure of 0.15 to 0.35 GPa (Seymour et al. 2009). Granodioritic to granitic apophyses, zoned pegmatites, aplites, and dactite dikes intruded the CBU rocks along NW-SE trending, counterclockwise reverse faults (Fig. 1). Their ages range from 8.2 to 8.7 Ma (Altherr et al. 1982), and they formed at T ≤ 650 °C and P = 0.1–0.2 GPa (Stouraiti and Mitropoulos 1999; Seymour et al. 2009).

Pyroxene-garnet exoskarns occur in the CBU marbles and garnet- and pyroxene-garnet endoskarns in the pluton (Ducoux et al. 2017; Fig. 1). The exoskarns comprise diopside-hedenbergite, andradite, wollastonite, and magnetite and minor sanuitite (Mgb2O3) (Salemkir 1985; Seymour et al. 2009; Fig. 1). Formation of ore minerals in the Serifos exoskarn began with the deposition of high-temperature magnetite at the contact of the pluton with the CBU (Fig. 1). Subsequent retrograde skarn formation at Moutoulas (~1 km from the pluton contact, Fig. 1) resulted in the precipitation of pyrite, sphalerite, chalcopyrite, galena, and native bismuth. The mineralization takes the form of lenses up to 0.5 × 40 × 25 m in size that mainly replaced the CBU marbles, and it is interpreted to represent an early carbonate replacement event (Seymour et al. 2009). Four major syntaxial quartz veins trending NNW-SSE (up to 100 m long and 0.5 m wide) cross-cut the CBU schists and marbles and are surrounded by alteration halos comprising an inner silica + sericite + pyrite + calcite zone (replacing orthoclase and albite of the CBU schists) and an outer epidote ± chlorite, barite, pyrite, and galena zone (Fig. 2a). The magnetite and sulfide ores underwent later supergene oxidation.

ANALYTICAL METHODS

The ore minerals were identified using a combination of reflected light microscopy and X-ray diffraction (XRD) on a D8 Advance diffractometer (Bruker AXS) equipped with a LynxEye strip silicon detector. The X-ray diffractometer employed Ni-filtered CuKα radiation, a voltage of 35 kV, a 35 mA current, and 0.298° divergence and anticounter slits. Random powder mounts of samples were scanned from 2 to 70° 2θ with a scanning step of 0.015° 2θ, and with 18.7 s count time per step, using the LabSpec software. Liquid composition analysis was carried out with a Shimadzu HPLC-SP Super ion chromatograph on double distilled water leaches using the method of Yardley et al. (1993). The analytical precision for all gases analyzed was ±1%, whereas for the cations and anions ±0.1 ppm.

Fifteen sulfide mineral samples were analyzed for their sulfur isotope compositions. Only crystals of a given sulfide in textural equilibrium with contiguous crystals were selected for analysis to be used for geothermometry. These crystals were handpicked after examination under a binocular microscope to ensure textural equilibrium and were repeated measurements of lead isotope ratios of standard NBS981 yielded 204Pb/206Pb = 16.9397 ± 0.001 and 238U/206Pb = 15.4974 ± 0.001 (all errors are reported at ±2σ). The sulfur isotopic ratios are reported in standard δ notation per mil relative to V-CDT. Analytical precision was better than ±0.2‰ for δ34S. We used the AlphaDelta software (Beaudoin and Thirrien 2009) to compute the isotopic fractionation factors and temperatures for mineral pairs in isotopic equilibrium. In addition, we analyzed pyrite and galena for their lead isotope compositions. Lead isotopic compositions were determined using an in-house Finnigan MAT 262 mass spectrometer at the Nanosctructure and Materials Science Laboratory, the Chinese Academy of Sciences, Beijing, China. The inclusions were analyzed for the common gases, mono- and poly-atomic ions and molecules via gas and ion chromatography. Gaseous composition was measured via a LabRAM HR800 Raman spectroscopic microscope, with a laser beam spot size of ~1 μm. The instrument recorded peaks ranging from 100–4000 cm−1 with a spectral resolution of 1–2 cm−1, and their peaks identified using the reference catalog of Drexel et al. (2012). The relative concentrations (in mol%) of these species were calculated from the equations of Drexel et al. (2012) and the cross-sectional scattering coefficients of Drexel et al. (1979), using the LabSpec software. Liquid composition analysis was carried out with a Shimadzu HPLC-SP Super ion chromatograph on double distilled water leaches using the method of Yardley et al. (1993). The analytical precision for all gases analyzed was ±1%, whereas for the cations and anions ±0.1 ppm.

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THE MOUTOULAS MINERALIZATION

Examination of the quartz veins reveals four distinct paragenetic stages of hydrothermal mineralization that can be recognized on the basis of mineralogical and textural relations (Fig. 2b, Table 1). The stage I assemblage occupies the margins of the veins and is characterized by massive, brecciated aggregates of subhedral pyrite with intergrowths of minor arsenopyrite, sphalerite (XFe0.5Sb0.5 = 20.7–25.8), chalcopyrite, and pyrrhotite (Figs. 2b, 3a, and 3b). Pyrite crystals incorporate ap

1Deposit item AM-17-86125, Supplemental Material. Deposit items are free to all readers and found on the MSA web site, via the specific issue’s Table of Contents (go to http://www.minsocam.org/msa/ammin/toc/2017/Aug2017/data/ Aug2017_data.html).
to have replaced pyrite from stage I (Fig. 3c). Stage III occurs toward the vein center and consists of Bi-bearing galena, which intergrows with fluorite and calcite and replaces stage I and II minerals (Fig. 3d, Supplemental Table 1).

The stage IV assemblage develops in three sub-stages, as disseminations replacing stage III galena in the central parts of the veins (Figs. 2c, 3e, and 3f; Table 1; Supplemental Table 1). Calcite, fluorite, and barite also represent this stage. The early sub-stage includes euhedral acicular bismuthinite (Fig. 3e). The middle sub-stage comprises tellurides, including tetradymite, hessite, and melonite, and is succeeded by the late sub-stage that is dominated by native bismuth (Figs. 3e and 3f). In places, native bismuth replaced bismuthinite (Fig. 3f). During subsequent supergene alteration, mixtures of beyerite, bismutite, and bismite replaced native bismuth (Figs. 2c, 3e, 3f, and 4; Supplemental Table 1). Covellite, cerussite, anglesite, chalcocite, goethite, azurite, and malachite also are products of this supergene stage (Table 1, data not shown).

**Results**

**Fluid inclusion studies**

Fluid inclusion data were obtained for two undeformed samples containing clear quartz and sphalerite; the data are for stages I and IV. The analyzed fluid inclusions assemblages (FIAs) occur individually or as small randomly oriented clusters (4–10 μm in diameter). These inclusions are considered as primary in origin following the criteria of Roedder (1984). Their shapes include elliptical, negative crystal, and irregular forms without signs of necking down (Figs. 4a and 4b).
sions were considered to be secondary if they occur in planar arrays interpreted to be healed fractures that do not terminate at growth zones or grain boundaries (Figs. 4a and 4b).

At room temperature, only one type of fluid inclusions was recognized, namely L-V inclusions, consisting of aqueous liquid and vapor, with the liquid being dominant (accounting for ~90 vol% of the total fluid inclusion volume; Supplemental Table 2, Fig. 4b). Neither daughter crystals, trapped solids nor clathrates were observed. The temperature of initial melting of ice ranged from –23.8 to –21.1 °C and the temperature of last melting of ice from –3.7 to –2.1 °C (Supplemental Table 2). Using the software FLINCOR (Brown 1989) for the system H₂O-NaCl (their initial melting temperatures are similar to the eutectic temperature of the system NaCl-H₂O), the corresponding salinities are 1.3 to 5.6 wt% NaCl equivalent (Supplemental Table 2, Fig. 5). The inclusions homogenize to liquid between 190 and ~250 °C (Supplemental Table 2, Fig. 5). As the pressure corresponding to the interpreted depth of emplacement of the Serifos pluton is interpreted to have been 3 to 12 km (Seymour et al. 2009), the trapping temperature of the inclusions was estimated to be ~5 °C higher than the homogenization temperature (corrected by the FLINCOR software). To fully constrain the density and pressure of entrapment (hydrostatic) of the fluid we made use of the Package FLUIDS (Bakker 2012). The calculated hydrothermal trapping pressures for the L-V inclusions vary from 80 to 140 bars, and average 105 bars (s.d. = 10 bars). The fluid densities range from 0.84 to 0.90 g/mL.

Raman spectroscopy and gas chromatography

Laser Raman and bulk composition chromatographic analyses were conducted on four L-V fluid inclusions hosted by stage I
and IV clear quartz that had been analyzed microthermometrically (Supplemental Tables 3 and 4, Fig. 4b). Raman analyses reveal that the gaseous fluid phase is composed of H₂O, CO₂, O₂, H₂, and H₂S. The log(X₁₈O₂H₂O₄) log(X₁₈O₂H₂O₃) and log(X₁₈H₂S₃O₂) ratios range from of –1.0 to –0.8, –2.4 to –1.8, and –3.5 to –1.7, respectively. Also, to estimate temperature we have used the CO₂- and CO₂/H₂S-geothermometers of Arnórsson and Gunnlaugsson (1985) and Nehring and D’Amore (1984). The calculated temperatures for stages I and IV are 235–248 and 190–197 °C, respectively.

Bulk analyses of the liquid phase showed that it contained the cations Na⁺, K⁺, Mg²⁺, Ca²⁺, Si⁴⁺, and the anions Cl⁻, SO₄²⁻, and HCO₃⁻. Si⁴⁺ and HCO₃⁻ are the dominant ions in solution. These data allowed us to estimate the temperatures for the stages I and IV based on the Na-K-Ca geothermometer of Fournier and Truesdell (1973). The temperatures obtained were ~241 and 191–195 °C.

Isotope geochemistry

Sulfur isotope analyses were conducted on pyrite, sphalerite, chalcopyrite, greenockite, and galena (Table 2). The δ³⁴S_CDT isotopic values of stage I pyrite, sphalerite, and chalcopyrite range from 2.7 to 5.1‰. Values of δ³⁴S_CDT for stage II sphalerite and greenockite and III galena, were generally higher, i.e., 3.5, 5.5, and 5.0 to 5.6‰, respectively (Table 2). Temperatures of 249 ± 2 °C and 226 °C were calculated for stage I and stage II from the pyrite-sphalerite and sphalerite-greenockite isotopic pairs, respectively, utilizing the equations of Ohmoto and Rye (1979), Ohmoto and Lasaga (1982), and Li and Liu (2006). The calculated δ³⁴S_H₂O values of the mineralizing fluid range from 2.3 to 4.9‰ (stage I, pyrite, sphalerite, and chalcopyrite), 3.1 to 4.8‰ (stage II, sphalerite and greenockite), and 2.4 to 2.8‰ (stage III, galena) (Table 2). These δ³⁴S_H₂O values reflect a dominantly magmatic source for sulfur for the ore fluids, i.e., the Serifos granodiorite.

Lead isotope data were obtained for stage I pyrite and stage III galena. Their ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb ratios range from 18.806 to 18.902 ± 0.001 and 15.653 to 15.702 ± 0.001 (Table 2). Our ²⁰⁶Pb/²⁰⁴Pb and ²⁰⁷Pb/²⁰⁴Pb values are very similar to those obtained by Stos-Gale (1992) from the Serifos granodiorite (Kefala site, i.e., 18.882 to 18.870 and 15.636 to 15.699) (Fig. 6).

Discussion

Physicochemical conditions of native bismuth formation

Physicochemical conditions of Moutoulas mineralization were estimated from phase-stability relationships using SUPCRT92 (Johnson et al. 1992) with thermodynamic properties from the 2007 database (slop07.dat; Shock and Helgeson 1998). Reactions used to estimate these conditions and values of physicochemical parameters calculated using them are presented in Table 3. The corresponding phase relationships are illustrated graphically on pH vs. log(α_H₂O) plots calculated for temperatures of 250 and 200 °C (Figs. 7a and 7b). These temperatures represent those estimated previously for stage I and stage IV, respectively (Supplemental Tables 2, 3, and 4; Table 2). All solids and gas species were considered behave ideally. Individual ion activity coefficients of dissolved species were calculated using the B-γ extension of Helgeson et al. (1981) for an ionic strength (I) of 0.2.

The formation of sericite after orthoclase and albite in the inner alteration zone of the CBU schists require weakly acidic conditions during stage I (reactions 1 to 3, Table 3). A log(α_H₂O/α_H₂O) value of 0.73, at 250 °C, was calculated based on the equilibrium between orthoclase and albite (reaction 3). The log(α_H₂O/α_H₂O) and log(α_H₂O/α_H₂O) values obtained from reactions 1 and 2 are 3.7 and 2.4, and so the calculated log(α_H₂O) value is –0.47. The pH of the ore solution obtained from these values is 5.4.

A log(α_H₂O) value of –13.8 ± 0.2 (PP-0.8, where PP is the pyrite-pyrrhotite buffer) was calculated for stage I from the pyrite and pyrrhotite equilibrium (reaction 4, Table 3). The maximum X_Pb of sphalerite coexisting with pyrite, for this stage is 25.8% and the calculated log f₃₂[Pb] value is –14.1 ± 0.2 (PP-1.1) based on the equation of Barton and Skinner (1979). Using compositional data for the gas phase in the fluid inclusions (Supplemental Table 3; reaction 5 in Table 3) and the equations of McCartney and Lanyon (1989), we were able to calculate the corresponding log f₃₂[Pb] (–39.2 or HM-2.1, where HM is the hematite-magnetite buffer) (Fig. 7a).

By stage IV, the temperature had decreased to 200 °C, log(α_H₂O) decreased to –16.5 ± 0.5 (PP-1.4) and log f₃₂ for –43.5 (HM-3.5) (Fig. 7b). The value of log f₃₂ was calculated from thermodynamic data for reaction 6, which describes the replacement of bismuthinite by native Bi, a common occurrence in late sub-stage IV. The value of log f₃₂ was determined from compositional data for the gas phase in fluid inclusions as mentioned above for stage I (Table 3). The pH of the fluid
(6.5) and the \( \log a_{\text{HS}(aq)} \) and \( \log a_{\text{H}_2\text{S}(aq)} \) values (–2.9 and –3.7) were calculated using the equilibrium constants for reactions 7, 8, and 9 for the \( \log f_{O_2} \) and \( \log f_{S_2} \) values referred to above (Table 3). A value of \( \log f_{\text{Te}_2(g)} \) (–17.0) was calculated from a combination of reactions 10, 11, and 12. Increased \( \log f_{\text{Te}_2(g)} \), \( \log a_{\text{H}_2\text{Te}(aq)} \), and \( \log a_{\text{HTe}^-(aq)} \) values is suggested to be responsible for the formation of tellurides (e.g., hessite and tetradymite) via reactions like 10 and 13 (Table 3).

During supergene alteration oxidation of native Bi (reaction 14) produced Bi(OH)\(^{3+} \) ions as the dominant dissolved species in solu-
This reaction is promoted by higher log $f_{O_2}$ values (–32.5 or HM+10) and a further decrease of pH of 7.1 (Table 3). The formation of bismutite [(BiO$_2$)$_2$CO$_3$] and bismite (Bi$_2$O$_3$) was likely promoted by a reaction similar to 15 (Table 3).

**Source of metals and depositional controls**

Skarn formation, at Serifos, evolved from high-temperature magnetite ores to retrograde replacement and vein mineralization that culminated with the deposition of native bismuth. Figure 5 shows that the decrease in temperature from stage I (~250 °C) to stage IV (~190 °C) was accompanied by a roughly linear decrease in salinity from ~5.7 to 1.3 wt% NaCl equivalent. This trend suggests dilution of the ore fluid as a result of mixing with waters of meteoric origin. Mixing of the ore fluid with oxidizing meteoric waters is also suggested by the gas chemistry, i.e., an increase of the log $X_{O_2}/H_2O$ ratios from ~3.4.

**Figure 4.** Photomicrographs of multiple fluid inclusion assemblages: (a) primary two-phase L-V (P) and secondary L-V (S) inclusions. The primary inclusions occur individually or as small, randomly oriented clusters, whereas the secondary fluid inclusions form trails that are aligned along fractures and terminate at crystal growth surfaces (scale bar = 25 μm). (b) Detail of a showing the primary inclusions with low V-L ratios (vapor bubble occupies up to ~20 vol%) used for Raman spectroscopy (scale bar = 100 μm).

**Figure 5.** Liquid-vapor trapping temperature vs. salinity plot in the system NaCl-H$_2$O.

**Figure 6.** A plot of $^{206}$Pb/$^{204}$Pb vs. $^{207}$Pb/$^{204}$Pb using age-corrected data. The galena crystals analyzed in this study plot between the “Orogen” and “Upper Crust” curves. The “Upper Crust,” “Orogen,” and “Mantle” were based on the model of Zartman and Doe (1981). Also shown are samples of galena from the Kefala pluton (Stos-Gale 1992) and the Moutoulas mineralization (Chalkias and Vavelidis 1998).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>$\delta^{34}$S</th>
<th>$T$ (°C)</th>
<th>$\delta^{34}$S$_{H_2S}$</th>
<th>$^{206}$Pb/$^{204}$Pb</th>
<th>$^{207}$Pb/$^{204}$Pb</th>
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</thead>
<tbody>
<tr>
<td>SE1</td>
<td>Pyrite (stage I)$^a$</td>
<td>4.83</td>
<td>249</td>
<td>2.28</td>
<td>18.863</td>
<td>15.653</td>
</tr>
<tr>
<td>SE2</td>
<td>Pyrite (stage I)$^b$</td>
<td>3.78</td>
<td>249</td>
<td>3.33</td>
<td>18.867</td>
<td>15.657</td>
</tr>
<tr>
<td>SE3</td>
<td>Pyrite (stage I)</td>
<td>4.44</td>
<td>249</td>
<td>2.94</td>
<td>18.871</td>
<td>15.661</td>
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<tr>
<td>SE4</td>
<td>Pyrite (stage I)</td>
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<td>2.62</td>
<td>18.868</td>
<td>15.659</td>
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<tr>
<td>SE1</td>
<td>Sphalerite (stage I)$^a$</td>
<td>3.73</td>
<td>249</td>
<td>3.33</td>
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<td>–</td>
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<td>2.69</td>
<td>249</td>
<td>2.29</td>
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<td>–</td>
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<tr>
<td>SE3</td>
<td>Sphalerite (stage II)$^a$</td>
<td>3.54</td>
<td>226</td>
<td>3.14</td>
<td>–</td>
<td>–</td>
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<td>SE2</td>
<td>Chalcopyrite (stage I)</td>
<td>5.08</td>
<td>249</td>
<td>4.88</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SE3</td>
<td>Greenockite (stage II)$^a$</td>
<td>5.49</td>
<td>226</td>
<td>4.79</td>
<td>–</td>
<td>–</td>
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<tr>
<td>SE1</td>
<td>Galena (stage III)</td>
<td>5.62</td>
<td>200</td>
<td>3.02</td>
<td>18.896</td>
<td>15.687</td>
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<tr>
<td>SE2</td>
<td>Galena (stage III)</td>
<td>5.04</td>
<td>200</td>
<td>2.44</td>
<td>18.902</td>
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<tr>
<td>SE3</td>
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<td>5.37</td>
<td>200</td>
<td>2.77</td>
<td>18.797</td>
<td>15.702</td>
</tr>
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</table>

$^a$ Temperatures obtained from fluid inclusion data, the CO$_2$-, CO$_2$/H$_2$S-, and Na-K-Ca geothermometers (Tables 3 and 4) and the pyrite-sphalerite (marked by $^a$) and sphalerite-greenockite (marked by $^b$) pairs; according to the equations of Ohmoto and Rye (1979), Ohmoto and Lasaga (1982), and Li and Liu (2006).

$^b$ Utilizing the H$_2$S-sulfide equations of Ohmoto and Rye (1979), Ohmoto and Lasaga (1982), and Li and Liu (2006).
TABLE 3. Reactions and corresponding values of selected physicochemical parameters applicable to the mineralizing fluid at Moutoulas, for temperatures of 250, 200, and 25 °C and an ionic strength I = 0.20.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T (°C)</th>
<th>Calculated physicochemical parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>250°</td>
<td>log(α_{Bi}/α_{H}_2O) = 3.7, pH = 5.4</td>
</tr>
<tr>
<td>2</td>
<td>250°</td>
<td>log(α_{Bi}/α_{H}_2O) = 2.4, pH = 5.4</td>
</tr>
<tr>
<td>3</td>
<td>250°</td>
<td>log(α_{Bi}/α_{H}_2O) = 0.73, pH = 5.4</td>
</tr>
<tr>
<td>4</td>
<td>250°</td>
<td>log(α_{Bi}/α_{H}_2O) = -13.8</td>
</tr>
<tr>
<td>5</td>
<td>250°</td>
<td>log(α_{Bi}/α_{H}_2O) = -39.2 and -43.5</td>
</tr>
<tr>
<td>6</td>
<td>200°</td>
<td>pH = 6.5</td>
</tr>
<tr>
<td>7</td>
<td>200°</td>
<td>log(α_{Bi}/α_{H}_2O) = -16.5</td>
</tr>
<tr>
<td>8</td>
<td>200°</td>
<td>log(α_{Bi}/α_{H}_2O) = -1.8 and -2.9</td>
</tr>
<tr>
<td>9</td>
<td>200°</td>
<td>log(α_{Bi}/α_{H}_2O) = -1.8 and -2.9</td>
</tr>
<tr>
<td>10</td>
<td>200°</td>
<td>log(α_{Bi}/α_{H}_2O) = -17.0</td>
</tr>
<tr>
<td>11</td>
<td>200°</td>
<td>log(α_{Bi}/α_{H}_2O) = -3.8</td>
</tr>
<tr>
<td>12</td>
<td>200°</td>
<td>log(α_{Bi}/α_{H}_2O) = -3.7</td>
</tr>
<tr>
<td>13</td>
<td>200°</td>
<td>log(α_{Bi}/α_{H}_2O) = -14.0, -11.2, -10.3, pH = 7.1</td>
</tr>
<tr>
<td>14</td>
<td>250°</td>
<td>log(α_{Bi}/α_{H}_2O) = -32.5</td>
</tr>
<tr>
<td>15</td>
<td>250°</td>
<td>log(α_{Bi}/α_{H}_2O) = -32.5</td>
</tr>
</tbody>
</table>

Notes: 250 and 1 200 °C, temperatures based on fluid inclusions, the CO_2, CO_3/H_2O, and Na-K-Ca-geothermometers, and pyrite-sphalerite and sphalerite-greenockite isotopic pairs (Tables 3, 4, and 5). The thermodynamic properties of bismuth complexes were compiled from Skirrow and Walshe (2002), Tooth et al. (2008, 2011), and Stos-Gale (1992). Pyrite, tetrahedrite-tennantite solid solutions, and galena from stages I, II, and III of the Moutoulas mineralization contain Bi, indicating that this element was incorporated during retrograde skarn formation and at early stages of the vein-type mineralization. This is consistent with the fact that the Serifos pluto appears relatively enriched in Bi toward its margins (e.g., up to ~60%, Seymour et al. 2009). The Serifos skarn resembles the Lavrion (Greece), Stan Terg (Kosovo), and Wittichen Schwarzwald (Germany) Bi-bearing skarns. In these skarns, Bi is thought to be related to fluids derived from or equilibrated with a granodiorite during the retrograde skarn phase (Fig. 6, Voudouris et al. 2008a, 2008b; Kolodziejczyk et al. 2015; Staude et al. 2012).

The effects of temperature and pH on the solubility of Bi(OH)_2^+ ions are summarized in a temperature vs. pH plot (Fig. 8). Calculation of the contours of the mass of Bi(OH)_2^+ in solution was based on reaction 14 and the temperature, pH, log f_{H_2O}, log f_{H_2}, and α_{H_2O} values obtained for stages I and IV. Saturation of Bi(OH)_2^+ is evident as the mass of Bi(OH)_2^+ in solution decreases from T = 250 to T = 200 °C (Fig. 8). Here it is suggested that the conditions of stage I (lower pH and higher f_{H_2} and f_{H_2O}) favored the formation of Bi-enriched sulfides rather than the deposition of native bismuth. The proposed conditions for this stage lie within...
the stability fields of bismuthinite and pyrite, which show a broad overlap (Fig. 7a). At these conditions, as the ore solution was undersaturated in Bi (Fig. 8), the available Bi cannot form native bismuth and either is incorporated in the crystal lattice of the precipitated sulfides or forms submicroscopic grains within them (e.g., in pyrite and tetrahedrite, Supplemental Table 1).

During stage IV native bismuth formed via reaction 7 that was controlled by the interplay of six physicochemical parameters. Temperature decrease, pH neutralization, $f_{\text{CO}_2}$ increase coupled with decrease of $f_{\text{O}_2}$, $a_{\text{H}_2\text{S}}$ (X$_{\text{H}_2\text{S}}$ values decrease, Supplemental Table 3), and $f_{\text{O}_2}$ created a favorable environment for the precipitation of bismuthinite, then Bi-bearing tellurides, and native bismuth (Fig. 7b). At these more reducing and less acidic conditions the solubility of bismuth decreased (e.g., the log$a_{\text{Bi(OH)}}^{<3}$ values increased from $-14.0$ to $-11.2$, Table 3, Fig. 8) thus leading to the precipitation of native bismuth.

We propose that variation of temperature, pH, log$f_{\text{CO}_2}$, $a_{\text{H}_2\text{S}}$, log$f_{\text{O}_2}$, and log$f_{\text{H}_2\text{O}}$ was related to fluid-rock interaction and subsequent dilution of the ore fluid (Fig. 6). At Moutoulas open hydrothermal system, interaction of the Bi-bearing fluid with the intensely fractured CBU marbles also led to the enrichment of the mineralizing fluid in HCO$_3$ ions (Supplemental Table 4). Then supergene exposure and oxidation of the mineralization (e.g., HCO$_3$ ions required for reaction 15) may have resulted due to the intense exhumation and uplifting of the hydrothermal system (as it is suggested by Grasemann and Petrakakis 2007).

**IMPLICATIONS**

Herein we examine native bismuth in the Serifos skarn and the conditions under which it may be precipitated. We suggest that proximity to a granodiorite, the development of magnetite ores and subsequent retrograde sulfide mineralization played important role in the precipitation of native bismuth, and we propose that in such a hydrothermal environment ($T \approx 200^\circC$) there are six parameters, i.e., temperature, pH, log$f_{\text{CO}_2}$, $a_{\text{H}_2\text{S}}$, log$f_{\text{O}_2}$, and log$f_{\text{H}_2\text{O}}$ that control native bismuth precipitation. We find that wall-rock interaction and dilution of Bi-bearing magmatic fluids, i.e., containing Bi(OH)$_{\text{aq}}^{<3}$, promoted native Bi saturation (Fig. 8) as these fluids facilitated a decrease in the mass of Bi(OH)$_{\text{aq}}^{<3}$ ions in solution. We also propose that the formation of Bi(OH)$_{\text{aq}}^{<3}$-(HCO$_3$)$_{\text{aq}}^{3-}$ complexes could play an important role on transporting this strategic element during wall-rock interaction. Destabilization of these complexes during dilution of the ore fluid via a probable reaction could be a mechanism controlling native bismuth precipitation:

$$\text{Bi(OH)}_2^{<3} + 2\text{HCO}_3^- + \text{H}_2\text{O} = \text{Bi(OH)}_3^{<3} + 2\text{H}_2\text{O} + 2\text{CO}_2$$

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