Biagioniite, Tl$_2$SbS$_2$, from the Hemlo gold deposit, Marathon, Ontario, Canada: occurrence and crystal structure

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Abstract

Biagioniite, ideally Tl$_2$SbS$_2$, is a new mineral from the Hemlo gold deposit, Marathon, Ontario, Canada. It occurs as very rare anhedral crystals up to 65 μm across associated with aurostibite, stibarsen and native gold in a calcite matrix. Biagioniite is opaque with a metallic lustre and shows a black streak. In reflected light biagioniite is moderately bireflectant and not pleochroic. Under crossed polars it is weakly anisotropic with blueish to light-blue rotation tints. Internal reflections are absent.

Reflectance percentages for the four standard wavelengths (R$_{\text{min}}$ and R$_{\text{max}}$) are 35.9 and 37.5 (471.1 nm); 34.7 and 36.2 (548.3 nm); 33.8 and 35.3 (586.6 nm); and 31.5 and 33.7 (652.3 nm), respectively. A mean of four electron microprobe analyses gave: Tl 65.12(31), Ag 3.52(9), Sb 20.22(12), S 10.80(8), total, 99.66 wt.%, corresponding, on the basis of a total of 5 atoms, to (Tl$_{1.87}$Ag$_{0.19}$)$_{2.06}$Sb$_{0.97}$S$_{1.97}$. Biagioniite is monoclinic, space group $Pc$, with $a = 11.0895(9)$, $b = 14.3124(11)$, $c = 7.9352(6)$ Å, $β = 96.230(8)^{\circ}$, $V = 1252.02(17)$ Å$^3$ and $Z = 8$. The four strongest powder-diffraction lines [$d$ in Å ($hkl$)] are: 3.56 (100) (310); 3.37 (75) (012); 3.79 (60) (012); 3.03 (60) (032). In the crystal structure [$R_I = 0.024$ for 2655 reflections with $I > 2\sigma(I)$], thallium adopts various coordinations extending from quasi-linear to quasi-tetrahedral. Antimony forms Sb–Sb pairs, which lead to the formula [Tl$^{+1}$]$_4$[Sb$_2$]$^{4+}$[S$^2$]$_4$. Biagioniite is isostructural with dervillite, Ag$_2$AsS$_2$. The new mineral has been approved by the International Mineralogical Association Commission on New Minerals, Nomenclature and Classification (IMA2019–120) and named for Cristian Biagioni, Associate Professor of Mineralogy at the Department of Earth Sciences of the University of Pisa, Italy.

Keywords: biagioniite, new mineral, thallium, sulfosalts, Hemlo deposit, Canada

Introduction

Several elements, having economic value or environmental concern, are hosted in sulfosalts, a group of complex minerals typically occurring in hydrothermal settings. Our ongoing effort in the last two decades (Bindi and Biagioni, 2018, and references therein) has been the study of these minerals from a structural point of view to try to: (1) elucidate the role played by minor components, which could give interesting insights into the physico-chemical conditions of the crystallisation environments, and (2) allow the potential description of unpredictable structures, unexpected crystallographic features, and new mineral species. Such a body of knowledge has been critical for assessing both the technological potentialities of sulfosalts as well as their geological significance.

In the course of this research project (i.e. Biagioni et al., 2016; Bindi et al., 2012a,b, 2015a,b), we examined a sample from the Hemlo gold deposit, Marathon, Ontario, Canada (Harris, 1989), belonging to the mineralogical collections of the Museo di Storia Naturale of the University of Florence. The sample consists of tiny criddleite grains associated closely with aurostibite, stibarsen and native gold in a calcite matrix. Among the stibarsen fragments, a small unique grain that turned out to be biagioniite, Tl$_2$SbS$_2$, was found.

Biagioniite was approved as a new mineral by the International Mineralogical Association – Commission on New Minerals, Nomenclature and Classification (IMA2019–120, Bindi and Moelo, 2020). The mineral name honours Cristian Biagioni (b. 1981), Associate Professor of Mineralogy at the Department of Earth Sciences of the University of Pisa, Italy. He is the current Italian Member of the IMA-Commission of New Minerals, Nomenclature and Classification and he is co-author of the description of more than 50 new mineral species. In addition, he contributed to the discovery of the Tl-rich nature of pyrite ores from the Apuan Alps (northern Tuscany, Italy), promoting a new scientific investigations of these ore deposits both from a mineralogical and environmental point of view (e.g. Biagioni et al., 2013, 2017). The holotype material is deposited in the mineralogical collection of the Museo di Storia Naturale of the University of Florence, Italy, under catalogue number 46582/G.

Here we report the description of the new mineral biagioniite, together with the determination of its crystal structure.

Material studied

The Museum sample containing biagioniite comes from the Hemlo gold deposit, which is located near the northeast shore of Lake Superior, 35 km east of Marathon, Ontario (Harris,
Physical and optical properties

Biagioniite occurs as very rare crystals grown on a calcite matrix (Fig. 1). The mineral exhibits a subhedral to anhedral grain morphology, and shows no inclusions of, or intergrowths with, other minerals. The maximum grain size of biagioniite is ~65 μm. It is black in colour and shows a black streak. The mineral is opaque in transmitted light and exhibits a metallic lustre. No cleavage is observed, and the fracture is uneven. The calculated density in transmitted light and exhibits a metallic lustre. No cleavage is observed, and the fracture is uneven. The calculated density is 6.192 g/cm³. Unfortunately, the density could not be measured here because of the small grain size. The Mohs hardness, estimated with respect to the surrounding calcite, is ~3.

In plane-polarised incident light, biagioniite is creamy in colour, moderately bireflectant and not pleochroic. Between crossed polars, biagioniite is weakly anisotropic with blueish to light-blue rotation tints. Internal reflections are absent and there is no optical evidence of growth zonation.

Reflectance measurements were performed in air by means of a MPM-200 Zeiss microphotometer equipped with a MSP-20 system processor on a Zeiss Axioplan ore microscope. The filament temperature was ∼3350 K. An interference filter was adjusted, in turn, to select four wavelengths for measurement (471.1, 548.3, 586.6 and 652.3 nm). Readings were taken for specimen and standard (SiC) maintained under the same focus conditions. The diameter of the circular measuring area was 0.04 mm. Reflectance percentages for Rmin and Rmax are: 35.9 and 37.5 (471.1 nm); 34.7 and 36.2 (548.3 nm); 33.8 and 35.3 (586.6 nm); and 31.5 and 33.7 (652.3 nm), respectively.

Chemical composition

A preliminary chemical analysis using energy-dispersive spectrometry performed on the crystal fragment used for the structural study did not indicate the presence of elements (Z > 9) other than Tl, Sb, S and minor Ag. Analyses were carried out using a JEOL 8200 microprobe (wavelength dispersive

### Table 1. Electron microprobe analysis results (four analytical spots, wt.% of elements) for biagioniite.

|      | Mean   | Range     |
|------|--------|-----------|
| Ag   | 3.52(9) | 3.35–3.77 |
| Tl   | 65.12(31)| 64.58–65.79|
| Sb   | 20.22(12)| 19.65–21.08|
| S    | 10.80(8) | 10.02–11.23|
| Total| 99.66   | 99.09–100.16|

### Table 2. Crystallographic data and experimental details for the selected biagioniite crystal.

| Crystal data |          |
|--------------|----------|
| Formula      | Tl₂Sb₂S₂ |
| Crystal site | MM       |
| Crystal system, space group | Monoclinic, P (m7) |
| Temperature (K) | 293(3) |
| Form         | blocky  |
| Colour       | black   |
| a (Å)        | 11.0895(9) |
| b (Å)        | 14.3124(11) |
| c (Å)        | 7.9352(6)  |
| β (°)        | 96.230(8)  |
| V (Å³)       | 1252.02(17) |
| Z            | 8        |
| Calculated density (g/cm³) | 6.192 |
| μ (mm⁻¹)    | 56.16    |

### Data collection

| Instrument | Bruker D8 Venture |
|------------|-------------------|
| Radiation type, wavelength (Å) | MoKα, λ = 0.71073 |
| Detector-to-sample distance (cm) | 6 |
| Number of frames | 1248 |
| Measuring time (s) | 30 |
| Maximum covered 2θ (°) | 74.98 |
| Absorption correction | Multi-scan |
| Tmin, Tmax | 0.121, 0.155 |
| Collected reflections | 20,833 |
| Unique reflections | 4520 |
| Reflections with Fo > 4σ(Fo) | 2655 |
| Rint | 0.0321 |
| Rexp | 0.0424 |
| Range of h, k, l | –16 ≤ h ≤ 16, –21 ≤ k ≤ 21, –13 ≤ l ≤ 13 |

### Refinement

| Final R1 [Fo > 4σ(Fo)] | 0.0243 |
| Final R1 (all data) | 0.0315 |
| GoF | 0.939 |
| Number refined parameters | 182 |
| Δρmax, Δρmin (e⁻ Å⁻³) | 1.72, –1.57 |
spectrometry mode, 25 kV, 20 nA, in X-ray crystallography and crystal-structure determination.

Data were collected using a Bruker D8 Venture diffractometer equipped with an Photon II CCD detector, with graphite-monochromatised MoKα radiation (λ = 0.71073 Å). Biagiomita was found to be monoclinic, with a = 11.0895(9), b = 14.3124(11), c = 7.9352(6) Å, β = 96.230(8)°, V = 1252.02(17) Å³ and Z = 8. The analysis of the systematic absences (hkl: I = 2n and 00l: I = 2n)

Table 3. Atoms, fractional atom coordinates (Å), and atomic displacement parameters (Å²) for biagiomita.

| Atom | x/a | y/b | z/c | Ueq |
|------|-----|-----|-----|-----|
| Ti1  | 0.2373(3) | 0.5961(8) | 0.4231(14) | 0.0344(3) |
| Ti2  | 0.0541(14) | 0.9136(7) | 0.7263(15) | 0.0437(4) |
| Ti3  | 0.6929(12) | 0.9070(8) | 0.1224(13) | 0.0299(3) |
| Ti4  | 0.3573(16) | 0.8930(9) | 0.6392(17) | 0.0356(3) |
| Ti5  | 0.6551(13) | 0.6061(8) | 0.8956(17) | 0.0355(3) |
| Ti6  | 0.9684(15) | 0.3970(9) | 0.3072(18) | 0.0526(4) |
| Ti7  | 0.1883(2) | 0.4926(9) | 0.6517(2) | 0.0188(7) |
| Ti8  | 0.9602(16) | 0.6861(11) | 0.8476(2) | 0.0713(5) |
| Sb1  | 0.3128(16) | 0.6847(11) | 0.9379(2) | 0.0143(4) |
| Sb2  | 0.6174(17) | 0.6812(12) | 0.3516(2) | 0.0167(4) |
| Sb3  | 0.3062(17) | 0.8307(11) | 0.1799(2) | 0.0155(4) |
| Sb4  | 0.6259(17) | 0.8216(12) | 0.6039(2) | 0.0161(4) |
| Sb5  | 0.1528(7) | 0.5806(4) | 0.0502(9) | 0.0118(15) |
| Sb6  | 0.7909(7) | 0.9183(5) | 0.5002(8) | 0.0177(14) |
| Sb7  | 0.1927(7) | 0.7465(4) | 0.6551(8) | 0.0162(17) |
| Sb8  | 0.7352(8) | 0.7510(5) | 0.8912(8) | 0.0229(17) |
| Sb9  | 0.8479(7) | 0.6293(4) | 0.4144(9) | 0.0191(15) |
| Sb10 | 0.5159(7) | 0.5673(5) | 0.5290(9) | 0.0237(17) |
| Sb11 | 0.0903(7) | 0.8956(5) | 0.1036(8) | 0.0202(15) |
| Sb12 | 0.4270(7) | 0.9350(4) | 0.0130(9) | 0.0179(14) |

Table 4. Selected bond distances (Å) for biagiomita.

| Atom | Bond Distance (Å) |
|------|------------------|
| Ti1  | Sb1  | 2.656(8) |
| Ti2  | Sb2  | 2.638(6) |
| Ti3  | Sb3  | 2.632(6) |
| Ti4  | Sb4  | 2.630(6) |
| Ti5  | Sb5  | 2.630(6) |
| Ti6  | Sb6  | 2.626(6) |
| Ti7  | Sb7  | 2.623(6) |
| Ti8  | Sb8  | 2.620(6) |
| Sb1  | Sb2  | 2.619(6) |
| Sb7  | Sb8  | 2.616(6) |
| Sb2  | Sb3  | 2.615(6) |
| Sb12 | Sb11 | 2.614(6) |
| Sb11 | Sb10 | 2.613(6) |
| Sb10 | Sb9  | 2.612(6) |
| Sb9  | Sb8  | 2.611(6) |
| Sb8  | Sb7  | 2.609(6) |
| Sb7  | Sb6  | 2.607(6) |
| Sb6  | Sb5  | 2.605(6) |
| Sb5  | Sb4  | 2.603(6) |
| Sb4  | Sb3  | 2.599(6) |
| Sb3  | Sb2  | 2.597(6) |
| Sb2  | Sb1  | 2.595(6) |
| Sb1  | Sb  | 2.593(6) |
| Sb  | S  | 2.591(6) |
| S  | Se  | 2.589(6) |
| Se  | Se  | 2.587(6) |
| Se  | Se  | 2.585(6) |

Table 5. Observed and calculated* powder X-ray diffraction data (d in Å) for biagiomita.

- *Calculated diffraction pattern obtained with the atom coordinates and occupancies reported in Table 3 (only reflections with I > 1.0σ(I) are listed).

X-ray crystallography and crystal-structure determination

The same crystal fragment (40 × 50 × 65 μm) used to obtain the chemical data was selected for X-ray single-crystal diffraction.
led to the choice of the space groups $Pc$ and $P2/c$. Although the statistical tests on the distribution of $|E|$ values ($\langle |E|^2 - 1 \rangle = 0.812$) indicated the absence of an inversion centre, suggesting the choice of the space group $Pc$, the structure was preliminarily solved in the $P2/c$ space group. A residual $R_1 = 0.18$ value was achieved quickly. However, the preliminary structural model obtained indicated a large atomic disorder. The structure model was subsequently optimised, and an ordered model was sought, but no improvement in $R$ could be achieved. At this point, a thorough analysis of the structure (essentially based upon the observation of the very large atomic displacement parameters for particular atoms) suggested that some symmetry element of the $P2/c$ space group should be removed. The reflection and atomic position data sets were then adapted to the $Pc$ space group (showing the same reflections conditions) and the structure refined. After several cycles, an ordered solution with full site occupancies was finally determined by carefully removing atoms with low site occupancies and/or non-realistic distances with neighbouring atoms and adding significant positions found in the difference-Fourier syntheses. The structure could be smoothly refined in $Pc$ without any damping factor or restrictions by the program SHELXL (Sheldrick, 2008). The occupancy of all the sites was left free to vary (Tl vs. Sb; Sb vs. S, S vs.□, Tl vs. □).

Fig. 2. The crystal structure of biagioniite down [001]: unit-cell content, atoms labels and Sb–Sb bond lengths (Å). Tl, Sb and S atoms are given as purple, green and yellow circles, respectively.

Fig. 3. Biagioniite: $2a \times 2b$ cell. $\text{Tl}_4\text{(Sb}_2\text{)}_2\text{S}_6$ ribbons parallel to [001], stacked along [010], form undulated layers along [100]. These layers are separated by a one-atom-thick layer of $\text{Tl}_4\text{S}_2$.

Fig. 4. Coordination of the Sb pairs with S atoms.
where □ = a vacancy) but all the positions were found to be fully occupied. Neutral scattering curves for Tl, As and S were taken from the International Tables for X-ray Crystallography (Wilson, 1992). At the last stage, with anisotropic atomic displacement parameters for all the atoms and no constraints, the residual value settled at $R_1 = 0.0243$ for 2655 observed reflections [2σ(I) level] and 182 parameters and at $R_1 = 0.0315$ for all 4520 independent reflections.

Note that the acentric structural model we obtained does not show high values in the correlation matrix between pairs of atoms which are equivalent in the centrosymmetric space group $P2_1/c$. To test whether the acentric model is to be preferred to the centric one we also tested the presence of twinning by inversion in the non-centrosymmetric structure refinement. Indeed, as is well known, a centrosymmetric structure that is refined as non-centrosymmetric will show a twin scale factor, equivalent to the Flack parameter in the case of inversion twinning (Flack et al., 2006; Müller et al., 2006), that refines to 50% within analytical uncertainty. We found the racemic twin-component scale factor refined to 0.09(2), consistent with a highly asymmetrical distribution of the enantiomorph components and indicating the acentric model as the right choice.

Experimental details and $R$ indices are given in Table 2. Fractional atomic coordinates and atomic displacement parameters are reported in Table 3. Bond distances are given in Table 4. The crystallographic information files have been deposited with the Principal Editor of Mineralogical Magazine and are available as Supplementary material (see below).

Powder X-ray diffraction data (Table 5) were collected with an Oxford Diffraction Excalibur PX Ultra diffractometer fitted with a 165 mm diagonal Onyx CCD detector and using copper radiation (CuKα, $\lambda = 1.54138$ Å). The least squares refinement gave the following values: $a = 11.0999(9)$, $b = 14.273(1)$, $c = 7.9323(7)$ Å, $\beta = 96.29(1)^\circ$ and $V = 1249.1(1)$ Å$^3$.

**Description of the structure and discussion**

The structure of biagioniite projected down [001] is reported in Fig. 2. It is isostructural with dervillite, Ag$_2$AsS$_2$ (Bindi et al., 2013). An enlarged projection of the structure (Fig. 3) allows one to distinguish Tl$_4$(Sb$_2$)$_2$S$_6$ ribbons parallel to [001], stacked along [010], to form undulated layers along [100]. These layers are separated by a one-atom-thick Tl$_4$S$_2$ layer. It is noteworthy, there are two Sb–Sb pairs, Sb$_1$–Sb$_3$ (2.843 Å) and Sb$_2$–Sb$_4$ (2.830 Å).

The coordination of these pairs is represented in Fig. 4. Coordination of each pair with four S atoms corresponds to a hemi-octahedron cut along a symmetry plane (through two opposite edges of the cube). Two neighbouring hemi-octahedra brought closer allow the rebuilding of the octahedron (above).

In the Tl$_4$(Sb$_2$)$_2$S$_6$ ribbon layer, Tl$_1$ and Tl$_3$ exhibit a tetrahedral coordination with S, whereas the coordination is triangular for Tl$_4$ and Tl$_5$. Nevertheless, the coordination environment for Tl$_4$ and Tl$_5$ is completed by additional short Tl–Sb bonds (Tl$_5$–Sb$_1 = 3.067$ Å and Tl$_4$–Sb$_4 = 3.175$ Å).

The coordination of Tl atoms of the Tl$_4$S$_2$ layer is shown in Fig. 6. There is a central zig-zag row of tetrahedral Tl atoms, flanked by two stripes of triangular Tl, and then two stripes of linear Tl. Contrary to the Tl$_4$(Sb$_2$)$_2$S$_6$ ribbon-layer (see below), here there is linear Tl on one mirror position, and tetrahedral Tl along the second mirror position. It is worth noting the linear coordination of Tl$_7$. To the best of our knowledge, biagioniite seems to be
Fig. 7. Sb$_2$ pairs have been replaced by a single atom (G, green) at their gravity centre, and an anionic vacancy (□, red) has been added. One Tl$_4$(Sb$_2$)$_2$S$_6$ ribbon (now Tl$_4$G$_2$S$_6$□$_2$) has been selected.

Fig. 8. One Tl$_4$G$_2$S$_6$□$_2$ ribbon in the crystal structure of biagioniite can be described as a distorted derivative of PbS structure.
the first example of a natural chalcogenide showing Tl in linear coordination. For a review of Tl chalcogenides see Makovicky (2018).

In Fig. 7, the Sb2 pairs have been replaced by a single atom (G) at their gravity centre, and an anionic vacancy (□) has been added. One Tl4(Sb2)2S6 ribbon (now Tl4G2S6□2) has been selected. Projection of this ribbon (Fig. 8) shows that it is a distorted derivative of the PbS structure. The Pb6S8 ideal ribbon (Fig. 9) is parallel to [310], two-atoms-thick, and three-octahedra large. The junction between two ribbons along [010] (mirror in the structure, with a shift along c, to preclude S–S short bond in the interface) corresponds to (131) of PbS. The two sides of such a junction (the two different mirror positions) have the same topology.

Bond-valence calculations (Table 6) have been computed on the basis of the following bond parameters: $R_{Sb,S} = 2.45$ (Brese and O’Keeffe, 1991), $R_{Tl,S} = 2.55$ (Biagioni et al., 2014) and $R_{Sb,Sb} = 2.82$ (O’Keeffe and Brese, 1992). Tl atoms are overbonded (bond valence from 1.11 up to 1.36 valence units, vu), but we have not considered in the computation the presence of minor Ag disordered at the Tl positions, although it would be very minor. Sb–Sb bond lengths (2.830 and 2.843 Å) agree well with $R_{Sb,Sb}$ corresponding to one vu; nevertheless, Sb atoms are underbonded varying from 2.31 to 2.57 vu. This feature has also been observed in sartorite (Berlepsch et al., 2003) and in minerals such as dasdonite (Makovicky et al., 2006), and was discussed in detail by Mills et al. (2009). The overall bond-valence sum of the eight S sites is 15.95, very close to the theoretical value (16 vu). These results may be due to uncertainty in the positions of some S atoms: a small shift closer to Sb atoms would reduce Sb underbonding together with Tl overbonding, without significant change of the S bond-valence sum.

The presence of dimeric [Sb2S4]$^{4-}$ ions with a central Sb–Sb bond in biagioniite means the formula could be written as [Tl$^{+1}$]$_4$[Sb$_2$]$^{18+}$[S$^2-$.]$_4$. However, it is difficult to analyse such poly-cationic compounds in strict bond-valence terms, as the electronegativity of such elements lies between that of common cations and common anions. The weak Tl–Sb bonds in biagioniite are good examples of the ‘anionic’ behaviour, which could be explained through dative donation of the Sb lone pair to the closed-shell d$^{10}$ Tl cations. On the contrary, in dervillite, short Ag–As bonds are lacking (Bindi et al., 2013).

Tl$_2$Sb$_2$S$_4$ has never been described either in Nature or as synthetic compound. Actually, the experimental TlSb$_2$–Tl section includes three ternary compounds, namely Tl$_2$Sb$_2$, Tl$_4$Sb$_2$ and Tl$_5$Sb$_2$. The former two compounds melt congruently at 613 and 683 K, whereas the latter one decomposes by peritectic reaction at 663 K (Jafarov et al., 2016). But, in fact, the Tl$_2$Sb$_2$ compound has been found to be Tl$_2$SbS$_3$ + Sb – a two-phase mixture instead of a single, independent chemical compound. Such a S-deficient formula for biagioniite indicates its formation at Hemlo at low f$_S$, in accordance to its association with stibarsen, SbAs, aurostibite, AuSb$_2$, and criddleite, TlAg$_2$Au$_3$Sb$_{10}$S$_{10}$ (also S-deficient).

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