

Demicheleite, BiSBr, a new mineral from La Fossa crater, Vulcano, Aeolian Islands, Italy

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ABSTRACT

Demicheleite, ideally BiSBr, is the first natural bismuth sulfobromide so far discovered. It is identical with the corresponding and analogous synthetic compound and is one of the very few minerals where bromine is an essential component. It was found in an active high-temperature fumarole at the rim of La Fossa crater, Vulcano Island, Aeolian archipelago, Sicily, Italy. The mineral occurs as prismatic translucent crystals up to 0.5 mm in size in an altered pyroclastic breccia, together with pseudocotunnite, bismoclite, bismuthinite, cotunnite, and chalcocite.

The mineral is orthorhombic, space group *Pnam*, with $a = 8.0424(9)$, $b = 9.8511(11)$, and $c = 4.0328(5)$ Å, $V = 319.50(6)$ Å³, $Z = 4$ (from single crystal); the habit is prismatic with {110} and {210} as prevailing forms, terminated by minor faces of another prism {011}, a pinacoid {010}, and a bipyramid {111}. The color is dark red to black; the streak is red; the luster submetallic. Non-fluorescent. Tenacity: brittle. Cleavage and fracture: not observed. The calculated density is 6.312 g/cm³.

The chemical analysis obtained by EDS microprobe gave (wt%) Bi 67.6(4), Br 17.4(7), Cl 4.1(4), I 0.6(1), S 10.1(1), total 99.8, corresponding to the empirical formula (based on 3 apfu): Bi_{0.99}S_{0.97}(Br_{0.67}Cl_{0.35}I_{0.02})_{Σ=1.04}

The crystal structure has been refined to a final *R* index of 0.037 and contains Bi in sevenfold coordination at the center of a monocapped trigonal prism. By sharing the triangular bases, such polyhedra form rows extending along [001]. These rows are connected to symmetry-related rows by sharing S-S edges of the pyramidal caps; these double rows are connected to each other by sharing Br/Cl atoms. The bond lengths are close to those of the synthetic counterparts BiSBr and BiSCl, with Bi-S bonds 2.593(3) and 2.720(2) Å long and Bi-Br/Cl bonds 3.009(1) and 3.488(2) Å long.

The strongest 6 lines in the X-ray powder diffraction pattern [d_{obs} (Å) (*hkl*)] are: 4.220 (68) (120), 3.740 (62) (210), 2.909 (100) (121), 2.036 (47) (321), 1.865 (63) (022), and 1.774 (88) (411).

The mineral is named after Vincenzo de Michele (b. 1936), former curator of the Section of Mineralogy of the Museo di Storia Naturale, Milano, Italy. Both the mineral and the mineral name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2007-022). The type specimen is deposited (no. 2007-1) in the Reference Collection of Dipartimento di Chimica Strutturale e Stereochimica Inorganica of Università degli Studi di Milano.

Keywords: Demicheleite, new mineral species, bismuth, sulfobromides, crystal structure, Vulcano Island, Aeolian Islands, Italy

INTRODUCTION

The fumaroles at La Fossa crater, Vulcano, Aeolian Islands, have long been the object of mineralogical investigation. By the end of the nineteenth century, two new species, hieratite (Cossa 1881–1882, 1882, 1884) and cannizzarite (Zambonini et al. 1924) had been discovered. After a long period of reduced activity, in 1988–1990 these fumaroles have notably increased their temperature. Therefore, in recent years a renewed interest in the rare minerals occurring in this environment has arisen, leading to the discovery of additional lead-bismuth sulfosalts, including new species such as mozgovaite PbBi₄(S,Se)₇ (Vurro et al. 1999) and vurroite Pb₂₀Sn₂(Bi,As)₂₂S₃₄Cl₆ (Garavelli et al. 2005, and refer-

ences therein). Moreover, four new complex fluorides, barberiite, NH₄BF₄ (Garavelli and Vurro 1994), demartinite K₂SiF₆ (Gramaccioli and Campostrini 2007), IMA 2006-42 K₃Na₄(SiF₆)₃BF₄, and IMA 2007-030 K₂AlF₃SO₄, were discovered, as well as two new thallium chlorides, lafossaite Tl(Cl,Br) (Roberts et al. 2006) and hephaestosite TIPb₂Cl₅ (Campostrini et al. 2008). Here we report the discovery of another new mineral, demicheleite, ideally BiSBr, which also occurs in a high-temperature fumarole (~450 °C) at the rim of the crater. A picture of the fumarole field with indications is reported in Borodaev et al. (2000).

OCCURRENCE AND PHYSICAL PROPERTIES

Demicheleite forms well-shaped red to black translucent crystals up to 0.5 mm long on altered pyroclastic breccia, together with pseudocotunnite, bismoclite, bismuthinite, cotunnite and

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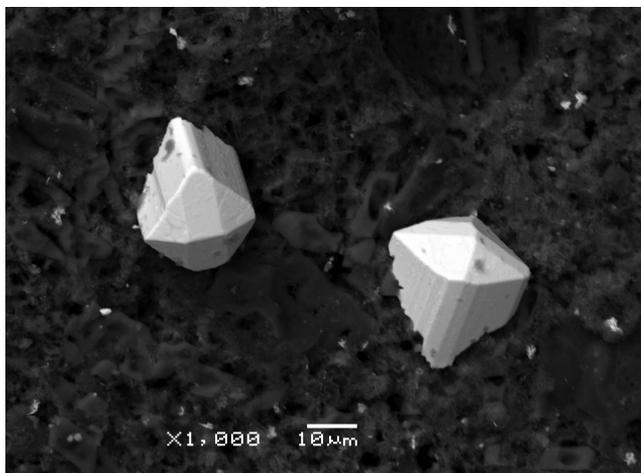


FIGURE 1. Scanning electron microscope (SEM) image (BSE) of demicheleite.

challacolloite. The crystal habit is prismatic $\{110\}$ and $\{210\}$, terminated by minor faces of another prism $\{011\}$, a pinacoid $\{010\}$, and a bipyramid $\{111\}$ (see Figs. 1 and 2). The streak is red; the luster submetallic. Non-fluorescent. Tenacity: brittle. Cleavage and fracture: not observed. The calculated density is 6.312 g/cm^3 . The indices of refraction were not determined because they are too high to be measured using the immersion method, and even more so because the crystals are attacked by all the available liquids.

Demicheleite is the natural equivalent of bismuth sulfide bromide, a substance belonging to a well-known group of synthetic thiohalogenides that have drawn much attention in recent years because of their optical, photoconducting, and ferroelectric properties (Voutsas and Rentzeperis 1980, 1984, and references therein). The same substance was also observed as a component of volcanic sublimates collected in quartz tubes in the fumaroles at Mutnovski, Kamchatka (Zelenski and Bortnikova 2005), and at least one bismuth chlorosulfide was also observed in the same conditions at Vulcano (Garavelli et al. 1997, 2005).

The mineral is named after Vincenzo de Michele (b. 1936), former curator of the Section of Mineralogy of the Museo di Storia Naturale, Milan, Italy. de Michele is one of the founders of the amateur mineral group in Milan (Gruppo Mineralogico Lombardo) and his activities were essential in providing new minerals for study, in describing Italian occurrences as well as in applying mineralogy to teaching gemology. Both the mineral and the mineral name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2007-022). The type specimen is deposited (no. 2007-1) in the Reference Collection of Dipartimento di Chimica Strutturale e Stereochimica Inorganica of Università degli Studi di Milano.

CHEMICAL DATA

Initial EDS scanning electron microscope examination showed Bi, S, Br, and Cl with traces of I to be the only constituents. A WDS analysis was attempted, but the results were poor, owing to volatilization of the sample under the electron beam. Therefore, chemical analyses were carried out by means of a JEOL JSM 5500 LV scanning electron microscope equipped with an IXRF EDS 2000 microprobe; (20 kV, 10^{-11} A , $2 \mu\text{m}$ beam diameter). The mean analytical results are reported in Table 1. The empirical formula (based on 3 apfu) is $\text{Bi}_{0.99}\text{S}_{0.97}(\text{Br}_{0.67}\text{Cl}_{0.35}\text{I}_{0.02})_{\Sigma=1.04}$,

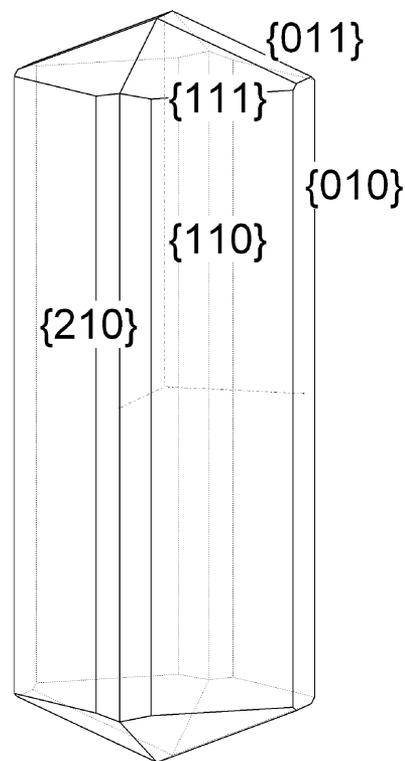


FIGURE 2. Idealized drawing of a demicheleite crystal.

the simplified formula is BiSBr , which requires Bi 65.11, S 9.99, Br 24.90, total 100.00 wt%. The natural sample here studied contains about 1/3 chlorine (in atoms) replacing Br, and is an intermediate between BiSBr and the isostructural (and most likely isomorphous) sulfide chloride, BiSCl (Voutsas and Rentzeperis 1980, 1984). This content is consistent with the result of the crystal structure refinement (see below).

DETERMINATION AND REFINEMENT OF THE STRUCTURE

X-ray powder diffraction data have been obtained using a Gandolfi camera 114.6 mm in diameter, with $\text{CuK}\alpha$ radiation (Table 2). A least-squares fit of these data provided the following orthorhombic unit-cell parameters: $a = 8.0675(4)$, $b = 9.8803(8)$, $c = 4.0264(2) \text{ \AA}$, and $V = 320.94(3) \text{ \AA}^3$. A comparison between these data and those of the corresponding synthetic compounds BiSBr and BiSCl (Voutsas and Rentzeperis 1980, 1984) is reported in Table 3. Single-crystal diffraction data were collected from a crystal fragment ($0.18 \times 0.04 \times 0.04 \text{ mm}$) with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), using a BRUKER Apex II diffractometer equipped with a 2K CCD detector. A 1 min frame-time

TABLE 1. Chemical composition of demicheleite

| Constituent | wt% | apfu | Range | Standard deviation | Probe standard |
|-------------|-------|------|-------------|--------------------|--------------------------|
| Bi | 67.65 | 0.99 | 66.50–69.10 | 0.4 | Bi_2Se_3 |
| S | 10.10 | 0.97 | 9.83–10.28 | 0.1 | FeS_2 |
| Br | 17.35 | 0.67 | 14.24–18.96 | 0.7 | TlBr |
| Cl | 4.09 | 0.35 | 3.19–5.81 | 0.4 | Phosgenite |
| I | 0.61 | 0.02 | 0.31–0.99 | 0.1 | AgI |
| Total | 99.80 | 3 | | | |

Notes: The empirical formula (based on 3 apfu) is $\text{Bi}_{0.99}\text{S}_{0.97}(\text{Br}_{0.67}\text{Cl}_{0.35}\text{I}_{0.02})_{\Sigma=1.04}$. The simplified formula is $\text{BiS}(\text{Br},\text{Cl})$. The end-member formula is BiSBr , which requires Bi 65.11, S 9.99, Br 24.90, Total 100.00 wt%.

TABLE 2. X-ray powder-diffraction data for demicheleite and related synthetic compounds

| Demicheleite | | | BiSBr* | | BiSCI* | | <i>hkl</i> |
|---------------------------|-----------------------------|-------------------------------|-------------------------|------------------------------|-------------------------|------------------------------|------------|
| <i>l/l</i> _o † | <i>d</i> _{obs} (Å) | <i>d</i> _{calc} (Å)‡ | <i>l/l</i> _o | <i>d</i> _{calc} (Å) | <i>l/l</i> _o | <i>d</i> _{calc} (Å) | |
| 24 | 6.254 | 6.249 | 50 | 6.288 | 100 | 6.124 | 110 |
| | | | 3 | 4.926 | 1 | 4.996 | 020 |
| 68 | 4.220 | 4.213 | 60 | 4.218 | 90 | 4.199 | 120 |
| 62 | 3.740 | 3.735 | 40 | 3.772 | 52 | 3.613 | 210 |
| 44 | 3.721 | 3.729 | 21 | 3.745 | 51 | 3.710 | 011 |
| 100 | 2.909 | 2.911 | 100 | 2.921 | 87 | 2.895 | 121 |
| 40 | 2.848 | 2.850 | 40 | 2.875 | 47 | 2.782 | 201 |
| 33 | 2.732 | 2.738 | 21 | 2.760 | 12 | 2.680 | 211 |
| 40 | 2.547 | 2.549 | 22 | 2.551 | 32 | 2.558 | 031 |
| 25 | 2.466 | 2.470 | 12 | 2.463 | 36 | 2.498 | 040 |
| 43 | 2.429 | 2.431 | 20 | 2.435 | 41 | 2.429 | 131 |
| 26 | 2.356 | 2.362 | 9 | 2.383 | 10 | 2.295 | 320 |
| 25 | 2.188 | 2.181 | 4 | 2.202 | 6 | 2.120 | 311 |
| 17 | 2.149 | 2.155 | 1 | 2.163 | 1 | 2.163 | 231 |
| 33 | 2.086 | 2.083 | 12 | 2.096 | 13 | 2.041 | 330 |
| 47 | 2.036 | 2.037 | 13 | 2.054 | 32 | 1.990 | 321 |
| 5 | 2.015 | 2.013 | 21 | 2.025 | 19 | 1.998 | 002 |
| 63 | 1.865 | 1.864 | 17 | 1.871 | 17 | 1.855 | 022 |
| 88 | 1.774 | 1.774 | 23 | 1.793 | 16 | 1.718 | 411 |
| 29 | 1.591 | 1.591 | 12 | 1.603 | 15 | 1.561 | 312 |
| 25 | 1.533 | 1.534 | 5 | 1.550 | 4 | 1.481 | 520 |
| 26 | 1.333 | 1.332 | 5 | 1.338 | 5 | 1.314 | 451 |

* For these synthetic compounds, the reported data have been calculated from the structural data obtained by Voutsas and Rentzeperis (1980, 1984).

† Determined densitometrically from a Gandolfi camera film.

‡ Calculated from the unit cell: *a* = 8.0675(4), *b* = 9.8803(8), *c* = 4.0264(2) Å obtained from least-squares refinement from the data above using the program UNITCELL (Holland and Redfern 1997).

TABLE 3. Unit-cell parameters for demicheleite and synthetic BiSBr and BiSCI

| | Demicheleite | BiSBr* | BiSCI* |
|----------------------------|--------------|-----------|------------|
| <i>a</i> (Å) | 8.0424(9) | 8.1666(9) | 7.7508(16) |
| <i>b</i> (Å) | 9.8511(11) | 9.8532(9) | 9.9920(5) |
| <i>c</i> (Å) | 4.0328(5) | 4.0492(6) | 3.9955(5) |
| <i>V</i> (Å ³) | 319.50(6) | 325.83(7) | 309.44(8) |

* From Voutsas and Rentzeperis (1980, 1984).

TABLE 4. Single-crystal data and refinement parameters for demicheleite

| | |
|---|----------------------|
| Crystal system | orthorhombic |
| Space group | <i>Pnam</i> (no. 62) |
| <i>a</i> (Å) | 8.0424(9) |
| <i>b</i> (Å) | 9.8511(11) |
| <i>c</i> (Å) | 4.0328(5) |
| <i>V</i> (Å ³) | 319.50(6) |
| <i>Z</i> | 4 |
| <i>F</i> ₀₀₀ | 508 |
| Radiation | MoKα |
| <i>μ</i> (mm ⁻¹) | 63.47 |
| <i>D</i> _{calc} (g/cm ³) | 6.312 |
| Measured reflections | 3129 |
| Independent reflections | 478 |
| Observed reflections [<i>I</i> > 2σ(<i>I</i>)] | 431 |
| Parameters refined | 21 |
| Final <i>R</i> and <i>wR2</i> | 0.0369, 0.0940 |
| <i>S</i> | 1.082 |

Notes: *R* = Σ||*F*_o - |*F*_c||/Σ|*F*_o|; *wR2* = {Σ[w(*F*_o² - *F*_c²)]/Σ[w(*F*_o²)]^{1/2}; *w* = 1/[σ²(*F*_o²) + (0.0688*p*)²] where *p* = (*F*_o² + 2*F*_c²)/3; *S* = {Σ[w(*F*_o² - *F*_c²)]/(*n* - *p*)^{1/2} where *n* is the number of reflections and *p* is the number of refined parameters

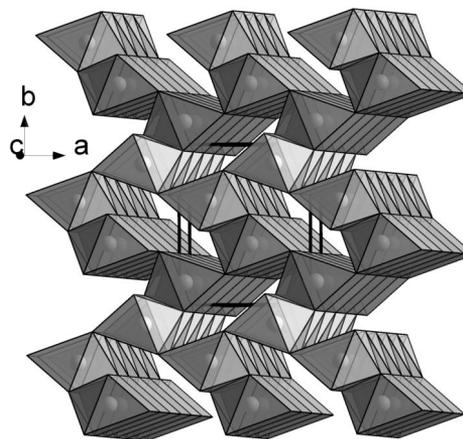
and 0.3° frame width were used. A total of 3129 reflections, corresponding to a complete scanning of the reciprocal lattice up to 2θ_{max} = 58.32°, were measured; of these 478 were unique. The unit-cell dimensions were refined by least-squares from 1825 reflections with *I* > 5σ(*I*); the refined values are given in Table 4, together with other details concerning the data collection and refinement. The data were integrated using the Bruker program

TABLE 5. Atomic coordinates and displacement parameters for demicheleite [*U*_{eq}/*U*_j × 10⁴]

| Atom | <i>X/a</i> | <i>Y/b</i> | <i>Z/c</i> | <i>U</i> _{eq} | | |
|-------|------------|------------|------------|------------------------|--|--|
| Bi | 0.13741(5) | 0.13177(5) | 1/4 | 189(3) | | |
| Br/Cl | 0.5133(2) | 0.8222(2) | 1/4 | 224(6) | | |
| S | 0.8303(4) | 0.0516(3) | 1/4 | 157(6) | | |

| Atom | <i>U</i> ₁₁ | <i>U</i> ₂₂ | <i>U</i> ₃₃ | <i>U</i> ₂₃ | <i>U</i> ₁₃ | <i>U</i> ₁₂ |
|-------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Bi | 191(4) | 188(4) | 189(4) | 0 | 0 | -30(2) |
| Br/Cl | 219(9) | 241(10) | 211(9) | 0 | 0 | -26(7) |
| S | 139(12) | 170(14) | 163(14) | | | 15(11) |

Notes: The anisotropic displacement factor exponent takes the form: -2π²[*U*₁₁*h*²(*a*^{*})² + ... + 2*U*₁₂*hka*^{*}*b*^{*} + ...]; *U*_{eq} = 1/3(*U*₁₁ + *U*₂₂ + *U*₃₃).

**FIGURE 3.** A view of the crystal structure of demicheleite seen almost along [001] to show the join of the polymeric rows.

SAINT, and corrected for Lorentz, polarization, and background. An absorption correction was applied (minimum transmission factor 0.366) using the SADABS program (Sheldrick 2000). The non-standard setting for the space group no. 62 as *Pnam* was adopted to afford easy comparison with the data reported by Voutsas and Rentzeperis (1980, 1984). The structure was refined starting from the atomic positions reported by these authors using the SHELXL97 program (Sheldrick 1997) implemented in the WinGX suite (Farrugia 1999); the occupation parameter for the halide site was also refined and the result [Br = 0.61(2), Cl = 0.39(2)] is consistent with the chemical analysis (see Table 1). The final coordinates and displacement parameters of the atoms are reported in Table 5; selected interatomic distances are reported in Table 6.

RESULTS AND DISCUSSION

A projection of the crystal structure along [001] is shown in Figure 3. If the criterion reported by Voutsas and Rentzeperis (1980, 1984) for selecting the bond distances is followed, the bismuth atom is seven coordinated by three S atoms at distances 2.593(3)–2.720(2) Å and four Br/Cl atoms at distances 3.009(1)–3.488(2) Å; the corresponding polyhedron can be described as a distorted trigonal monocapped prism (see Fig. 4) of height equal to the unit-cell parameter *c*. The vertices of the triangular bases are occupied by two bromine atoms and one sulfur atom; those of one lateral face are occupied by four bromine atoms, whereas at the vertices of the other two there are instead two sulfur and two bromine atoms. One of the latter faces is almost square and

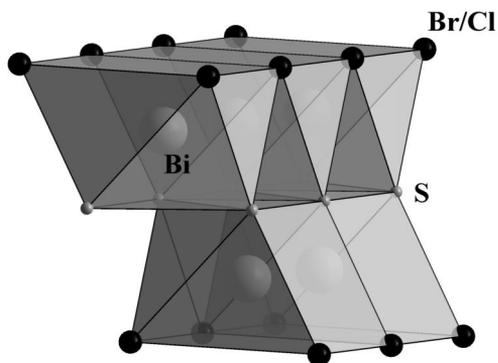


FIGURE 4. A detail of one double row of the coordination polyhedra around Bi.

is capped by a sulfur atom. By sharing the triangular bases of the prisms, the polyhedra form polymeric rows extended along [001]; these rows are joined to symmetry-related rows by sharing S-S edges of the pyramidal caps of the constituent polyhedra, thereby forming infinite double chains of composition $[\text{Bi}_2\text{S}_4(\text{Br}/\text{Cl})_8]_n$. On their turn, these coupled rows are linked to the others by sharing Br/Cl atoms. Such aggregations result in forming planes parallel to (130) or its symmetry equivalents which are made exclusively either by S or Br/Cl atoms.

Demicheleite is another example of natural sulfosalide. Contrary to these substances that are mercury minerals [corderoite (Foord et al. 1974), lavrientievite $\text{Hg}_5\text{S}_2\text{Cl}_2$ and arzakite $\text{Hg}_5\text{S}_2(\text{Br},\text{Cl})_2$ (Vasil'ev et al. 1984), sometimes also containing silver [perrouditite $\text{Hg}_5\text{Ag}_3\text{S}_5(\text{Cl},\text{I},\text{Br})_4$ (Sarp et al. 1987), capgaronnite $\text{HgAgS}(\text{Cl},\text{Br},\text{I})$ (Mason et al. 1992)], the new species here described is instead a bismuth mineral and the prevailing halogen is bromine, a most unusual case. There are, however, similarities with respect to Pb-As sulfosalts also occurring in volcanic fumaroles and where halogens act as essential constituents, such as especially mutnovskiite $\text{Pb}_2\text{AsS}_3(\text{I},\text{Cl},\text{Br})$ (Zelenski et al. 2006 and references therein) where important amounts of iodine and bromine are also present together with chlorine. For La Fossa crater at Vulcano, a significant enrichment in bromine was already observed by Coradossi et al. (1996) in samples of ammonium chloride. Furthermore, a relatively high bromine content was noted by Garavelli et al. (2005) for chlorine-rich sulfosalts such as vuroite $\text{Pb}_{20}\text{Sn}_2(\text{Bi},\text{As})_{22}\text{S}_{54}\text{Cl}_6$; a similar enrichment was also observed at Vulcano by Roberts et al. (2006) for lafossaite $\text{Tl}(\text{Cl},\text{Br})$ and at Mutnovski volcano, Kamchatka by Zelenski and Bortnikova (2005) for volcanic sublimates. Sulfochlorides of Bi and Pb (such as $\text{Bi}_{19}\text{Cl}_3\text{S}_{27}$ and Pb_4SCl_6) formed at temperatures from 300 to 500 °C in quartz tubes inserted into the outlet of fumaroles at La Fossa crater, Vulcano were already observed by Garavelli et al. (1997, 2005). According to these authors (see also the list of references reported in their works) the deposition of lead sulfosalts is due to reaction of PbCl_2 (cotunnite) with H_2S or galena. Similar reactions occur in the formation of bismuth sulfochlorides from BiCl_3 and H_2S , and the sulfosal occurrence in these conditions might well be due to reaction of previously grown chlorosulfides with H_2S . All such observations underline the chemical complexity of such volcanic environments, which are currently the object of active interest.

TABLE 6. Interatomic distances (Å)

| | Demicheleite | BiSBr* | BiSCl* | Weighted averaget |
|----------------------|--------------|--------|----------|-------------------|
| Bi-S | 2.593(3) | 2.607† | 2.605(2) | 2.606 |
| Bi-S (2×) | 2.720(2) | 2.721 | 2.711(1) | 2.717 |
| Bi-S | 3.484(3) | | | |
| Bi-Br/Cl (2×) | 3.009(1) | 3.038 | 2.927(2) | 3.001 |
| Bi-Br/Cl (2×) | 3.488(2) | 3.539 | 3.367(2) | 3.481 |
| S-S (2×) | 3.543(4) | 3.556 | 3.549(3) | 3.553 |
| S-S (2×) = c | 4.0328(5) | 4.049 | 3.996(1) | 4.031 |
| S-Br/Cl (2×) | 3.407(3) | 3.450 | 3.360(3) | 3.420 |
| S-Br/Cl (2×) | 3.571(3) | 3.596 | 3.492(3) | 3.561 |
| S-Br/Cl (2×) | 3.965(3) | 3.990 | 3.873(3) | 3.952 |
| S-Br/Cl (2×) | 3.640(3) | | | |
| Br/Cl-Br/Cl (2×) | 4.265(2) | 4.340 | 4.041(4) | 4.240 |
| Br/Cl-Br/Cl (2×) = c | 4.0328(5) | 4.049 | 3.996(1) | 4.031 |

* From Voutsas and Rentzeperis (1980, 1984).

† Weighted average of columns 3–4 on assuming the site occupation from structure refinement (Br = 0.61 Cl = 0.39).

‡ No e.s.d. values are reported for these data.

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In view of the recent occurrence of the Cl-analogue in the same environment (IMA 2008-020), a suggestion of the Chairman of the IMA CNMN is that of modifying the name of the mineral into “demicheleite-(Br).”