The Canadian Mineralogist
Vol. 47, pp. 367-372 (2009)
DOI: 10.3749/canmin.47.2.367

PANICHIITE, NATURAL AMMONIUM HEXACHLOROSTANNATE(IV), $(NH_4)_2SnCl_6$, FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

Francesco DEMARTIN[§], Italo CAMPOSTRINI and Carlo Maria GRAMACCIOLI

Dipartimento di Chimica Strutturale e Stereochimica Inorganica,
Università degli Studi di Milano, via Venezian 21, I–20133 Milano, Italy

Abstract

Panichiite, ammonium hexachlorostannate(IV), $(NH_4)_2SnCl_6$, is a new mineral species found in a medium-temperature intracrater fumarole (~250°C) at La Fossa crater, Vulcano Island, Aeolian Islands, Sicily, Italy. The mineral occurs as aggregates of minute colorless octahedra up to 0.2 mm in diameter on fragments of altered pyroclastic breccia, in association with alunite, anhydrite, bismuthinite, godovikovite, demicheleite-(Br) (BiSBr), BiSCl (IMA 2008–020) and two other new species, a sodium ammonium aluminum sulfate chloride (IMA 2008–057) and an ammonium bismuth chloride that is presently under study. Panichiite is cubic, space group $Fm\bar{3}m$ (no. 225), with $Z = 4$; the unit-cell parameter a is 10.064(1) Å, and V is equal to 1019.4(2) Å^3. The X-ray powder-diffraction pattern is in excellent agreement with that of the synthetic compound; the strongest six reflections [d_{obs} in Å(I)(hkl)] are: 5.811(100)(111), 5.032(73)(200), 2.516(69)(400), 3.035(48)(311), 1.779(42)(440), and 2.250(39)(420). Chemical analyses obtained with an electron microprobe in energy-dispersion mode gave, on average, Cl 56.57, Sn 31.62, Br 1.53, K 1.05, total 90.77, with NH_4^+ (by difference) 9.23, for a total of 100.00 wt.%, corresponding to the empirical formula $[(NH_4)_{1.90}K_{0.10}]_{\Sigma 2.00}Sn_{0.99}(Cl_{5.94}Br_{0.07})_{\Sigma 6.01}$. The calculated density for the compound with the above empirical formula is 2.423 g/cm^3. The index of refraction n obtained using immersion methods is 1.68(1) (λ = 589 nm). The structure, including the positions of the hydrogen atoms of the ammonium ion, was refined from single-crystal diffraction data to a final R of 0.030 for 153 independent observed reflections [$I > 2\sigma(I)$]. The six equivalent Sn–Cl distances in the octahedral $SnCl_6^{2-}$ ion are 2.429(1) Å, and the Cl...N distances are 3.559(1) Å. The mineral (IMA 2008–005) is named in honor of Prof. Ugo Panichi, a pioneer in the study of minerals from Vulcano.

Keywords: panichiite, new mineral species, ammonium hexachlorostannate(IV), tin minerals, Vulcano island, Italy.

Sommaire

La panichiite, hexachlorostannate(IV) d'ammonium, $(NH_4)_2SnCl_6$, est une nouvelle espèce minérale découverte dans une fumerolle de température intermédiaire (~250°C) dans le cratère de La Fossa, à Vulcano, îles Éoliennes, en Sicile, Italie. Elle se présente en agrégations d'octaèdres incolores atteignant 0.2 mm de diamètre, déposés sur des fragments de brèche pyroclastique altérés, en association avec alunite, anhydrite, bismuthinite, godovikovite, demicheleïte-(Br) (BiSBr), BiSCl (IMA 2008–020) et deux autres espèces nouvelles, un sulfate–chlorure de sodium, ammonium et aluminium (IMA 2008–057) et un chlorure d'ammonium et de bismuth présentement en cours d'étude. La panichiite est cubique, groupe spatial $Fm\bar{3}m$ (no. 225), avec $Z =$ 4; le paramètre réticulaire a est 10.064(1) Å, et V est égal à 1019.4(2) Å^3. Le spectre de diffraction X obtenu sur poudre concorde très bien avec celui de l'analogue synthétique; les six raies les plus intenses [d_{obs} en Å(I)(hkl)] sont: 5.811(100)(111), 5.032(73)(200), 2.516(69)(400), 3.035(48)(311), 1.779(42)(440), et 2.250(39)(420). Les analyses chimiques faites en dispersion d'énergie avec une microsonde électronique ont donné, en moyenne, Cl 56.57, Sn 31.62, Br 1.53, K 1.05, total 90.77, avec NH_4^+ (par différence) 9.23, pour un total de 100.00% (poids), ce qui correspond à la formule empirique $[(NH_4)_{1.90}K_{0.10}]_{\Sigma 2.00}Sn_{0.99}(Cl_{5.94}Br_{0.07})_{\Sigma 6.01}$. La densité calculée pour le composé ayant cette formule empirique est 2.423 g/cm^3. L'indice de réfraction n obtenu par méthodes d'immersion est 1.68(1) (λ = 589 nm). La structure, y inclus la position des atomes d'hydrogène de l'ion NH_4^+, a été affinée à partir de données diffractométriques prélevées sur monocristal, jusqu'à un résidu R final de 0.030 pour 153 réflexions indépendantes observées [$I > 2\sigma(I)$]. Les six distances Sn–Cl équivalentes dans l'ion octaédrique $SnCl_6^{2-}$ sont 2.429(1) Å, et la distance Cl...N est 3.559(1) Å. Nous avons nommé le minéral (IMA 2008–005) en l'honneur du professeur Ugo Panichi, pionnier dans l'étude des minéraux de Vulcano.

(Traduit par la Rédaction)

Mots-clés: panichiite, nouvelle espèce minérale, hexachlorostannate(IV) d'ammonium, minéral d'étain, île de Vulcano, Italie.

[§] *E-mail address*: francesco.demartin@unimi.it

INTRODUCTION

The island of Vulcano, a part of the Aeolian Islands, is situated in proximity of the northern coast of Sicily. Its interesting geological features have long been known; Mercalli & Silvestri (1890) described the last series of explosive eruptions, which took place from 1888 to 1890. Sicardi (1973), Barberi *et al.* (1974), Keller (1980), and Frazzetta *et al.* (1983) added further documentation of volcanic activity at Vulcano.

In recent years, in connection with the increased activity of the fumaroles, results of further important investigations have been published in the fields of volcanology and geochemistry (see Campostrini *et al.* 2008, and references therein). At the same time, renewed interest in the rare halide minerals occurring at La Fossa crater has led to the discovery of a substantial set of further new species, such as barberiite, NH_4BF_4 (Garavelli & Vurro 1994), lafossaite, TlCl (Roberts *et al.* 2006), demartinite (a hexagonal polymorph of K_2SiF_6) (Gramaccioli & Campostrini 2007), and a most interesting hexafluorosilicate–tetrafluoroborate, knasibfite $K_3Na_4[SiF_6]_3[BF_4]$ (Demartin *et al.* 2008a). Still more recently, hephaistosite, a new thallium and lead chloride with the formula $TlPb_2Cl_5$, isostructural with challacolloite KPb_2Cl_5 (Campostrini *et al.* 2008, Mitolo *et al.* 2009), as well as a new complex fluoride–sulfate, thermessaite, $K_2[AlF_3 | SO_4]$, have also been discovered (Demartin *et al.* 2008b).

Here, we describe the new species panichiite $(NH_4)_2SnCl_6$, which was found on a pyroclastic breccia collected at the rim of an active medium-temperature intracrater fumarole (~250°C) at La Fossa crater. The mineral was approved as a new species by the IMA Commission on New Minerals, Nomenclature and Classification (no. 2008–005) and is named in honor of Prof. Ugo Panichi (1872–1966), Past President (1941–1948) of the Italian Mineralogical Society (now SIMP), and author of several publications about the minerals from Vulcano Island, *e.g.*, the new species millosevichite (Panichi 1913, 1914). The holotype specimen of panichiite is deposited (no. 2008–01) in the Reference Collection of Dipartimento di Chimica Strutturale e Stereochimica Inorganica of Università degli Studi di Milano.

OCCURRENCE, CHEMICAL DATA AND PHYSICAL PROPERTIES

In 2006, the presence of a very rare mineral containing essential tin and chlorine was noticed by one of us (I.C.) on the basis of preliminary tests carried out using our EDS-equipped scanning electron microscope. The identity with the synthetic $(NH_4)_2SnCl_6$ compound [ammonium hexachlorostannate(IV)] was confirmed by the X-ray powder-diffraction pattern (Table 1).

This mineral forms aggregates of colorless octahedral crystals up to 0.2 mm in length and is associated with alunite, anhydrite, bismuthinite, godovikovite, demicheleite-(Br) (BiSBr), BiSCl (IMA 2008–020), and two additional new species, *i.e.*, a sodium ammonium aluminum sulfate chloride (IMA 2008–057) isostructural with $(NH_4,K)_4(Fe,Al)_2(OH)_2(SO_4)_4$•NaCl, a product from a burning coal dump (Kolitsch & Brandstätter 2007), and an ammomium bismuth chloride presently under study.

Owing to the small size of the single crystals, no goniometric measurements could be performed, although the electron microscope photographs clearly show a prevailing octahedral habit (Fig. 1), in some cases with minor faces of the cube. The mineral is not hygroscopic; it is colorless to white or very pale yellow, with a white streak and vitreous luster. Cleavage and fracture were not observed. No fluorescence was observed under both short-wave and long-wave ultraviolet radiation.

The density [= 2.43(1) g/cm^3] was measured by flotation in a tribromomethane–trichloromethane mixture; the observed value is close to the one [2.423 g/cm^3] calculated using the unit-cell data for the compound with the empirical formula reported below. The index of refraction $n = 1.68(1)$ ($\lambda = 589$ nm) was measured by immersion in monobromonaphtalene-CH_2I_2; the corresponding Gladstone–Dale value calculated using Mandarino's constants (1981) is 1.682, leading to a compatibility index $[1 - (K_P/K_C)]$ of –0.0004 (superior).

In order to avoid sample decomposition under the intense beam of electrons in the WDS mode of the electron microprobe, quantitative chemical analyses

TABLE 1. X-RAY POWDER-DIFFRACTION PATTERN OF PANICHIITE AND ITS SYNTHETIC EQUIVALENT

	Panichiite*		Synthetic $(NH_4)_2SnCl_6$ PDF2 entry 00-007-0198		
I/*I*o	*d*(obs.) (Å)	*d*(calc.) (Å)	*d*(obs.) (Å)	*d*(calc.) (Å)	*h k l*
100	5.811	5.810	100	5.813	1 1 1
73	5.032	5.032	85	5.032	2 0 0
18	3.558	3.558	20	3.557	2 2 0
48	3.035	3.034	45	3.033	3 1 1
18	2.905	2.905	25	2.9033	2 2 2
69	2.516	2.516	55	2.5153	4 0 0
16	2.309	2.309	18	2.3081	3 3 1
39	2.250	2.250	35	2.2499	4 2 0
7	2.054	2.054	8	2.0535	4 2 2
23	1.937	1.937	20	1.9367	5 1 1
42	1.779	1.779	30	1.7787	4 4 0
22	1.701	1.701	20	1.7004	5 3 1
20	1.677	1.677	16	1.6765	6 0 0
3	1.591	1.591	4	1.5908	6 2 0
			6	1.5340	5 3 3
5	1.517	1.517	4	1.5165	6 2 2
3	1.453	1.453	8	1.4519	4 4 4
14	1.409	1.409	10	1.4087	7 1 1
11	1.396	1.396	6	1.3950	6 4 0
9	1.345	1.345	4	1.3442	6 4 2

* From these data, the unit-cell parameter *a* was calculated to be 10.064(5) Å using the program UNITCELL (Holland & Redfern 1997). It can be compared with the value [10.038(2) Å] acquired in a single-crystal investigation of the synthetic compound by Lerbscher & Trotter (1976).

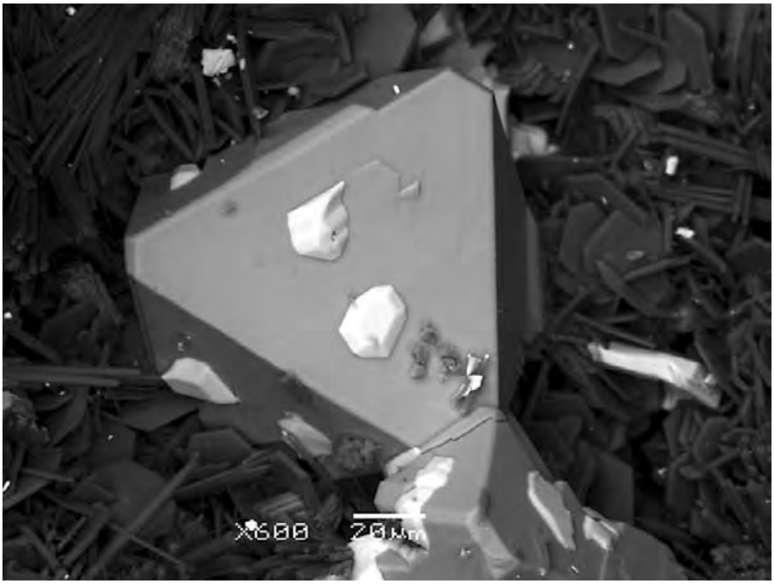

FIG. 1. Scanning electron photomicrograph of panichiite crystals on alunite (BSE image), accompanied by IMA 2008–057 and another phase currently under study (see text).

TABLE 2. CHEMICAL COMPOSITION OF PANICHIITE

Constituent	wt.%	Range	Stand. dev.	Probe Standard
NH_4	9.23	–	–	–
K	1.05	0.00 – 2.20	0.2	KCl
Cl	56.57	54.17 – 58.02	0.2	KCl
Br	1.53	0.77 – 2.23	0.1	TlBr
Sn	31.62	29.95 – 33.54	0.1	SnO_2
Total	100.00			

The chemical analyses (12) were carried out by means of an electron microprobe (EDS mode, 20 kV, 10 pA, beam diameter 2 µm). The ammonium content was obtained by difference.

(12) were carried out using a JEOL JSM 5500 LV scanning electron microscope equipped with an IXRF EDS 2000 microprobe (20 kV, 10 pA, 2 µm beam diameter). Element concentrations were measured using the $K\alpha$ lines for Cl and K and the $L\alpha$ lines for Sn and Br; the mean analytical results are reported in Table 2. The empirical formula obtained (NH_3 by difference) is: $[(NH_4)_{1.90}K_{0.10}]_{\Sigma 2.00}Sn_{0.99}(Cl_{5.94}Br_{0.07})_{\Sigma 6.01}$; the idealized formula is $(NH_4)_2SnCl_6$, which requires: NH_4 9.82, Sn 32.30, Cl 57.88, total 100.00 wt.%; it is in excellent agreement with the results of the crystal-structure refinement. The presence of small amounts of potassium and bromine in most of the analyzed samples is not surprising in view of the similarities in their ionic radii to those of NH_4^+ and Cl^-, respectively (see also below).

X-RAY DATA

X-ray powder-diffraction data have been obtained using a Rigaku DMAX–II diffractometer, with Cu$K\alpha$ radiation (λ = 1.54059 Å) (Table 1). A least-squares fit of these data provided the unit-cell parameters a 10.064(5) Å, V 1019.3(14) Å^3. Single-crystal diffraction data for structure determination were collected from a crystal fragment (0.05 × 0.05 × 0.04 mm) with Mo$K\alpha$ radiation (λ = 0.71073 Å), using a Bruker Apex II diffractometer equipped with a 2K CCD detector. A one-minute frame-time and 0.3° frame width (omega scan) were used. A total of 3045 reflections, corresponding to a complete scan of the reciprocal lattice up to $2\theta_{max}$ = 71.98°, were measured; of these, 162 were found to be unique (R_{int} = 0.027). A least-squares estimate of the unit-cell parameter a obtained from 1024 single-crystal reflections with $I > 5\sigma(I)$ is reported in Table 3, together with other details concerning collection and refinement of the data. It is identical to the value obtained from the powder-diffraction data. The intensity data were reduced using the Bruker program SAINT, and corrected for Lorentz, polarization, and background. An absorption correction was also applied (minimum and maximum transmission-factors 0.397 and 1.000, respectively) using the SADABS program (Sheldrick 2000). The structure was refined with the SHELXL97 program (Sheldrick 2007) implemented in the WINGX suite (Farrugia 1999), down to a final R = 0.030 for 153 observed reflections [$I > 2\sigma(I)$]. As a starting point, the atom positions for Sn, Cl, and N reported by Lerbscher & Trotter (1976) for the synthetic compound were used; then the independent hydrogen atom (which is not disordered), located from a difference-Fourier map, was added and isotropically refined. In view of the possible presence of potassium substituting for ammonium in some crystals, the occupancy of the N site also was refined, but we observed no significant deviation from the ideal composition. The final coordinates and displacement parameters of the atoms are reported in Table 4. A table of observed and calculated structure-factors may be obtained from the Depository of Unpublished Data on the MAC website [document Panichiite CM47_367].

RESULTS AND DISCUSSION

The structure contains Sn-centered undistorted $SnCl_6^{2-}$ octahedra with Sn–Cl distances of 2.429(1) Å, and tetrahedral NH_4^+ cations with N–H distances of 0.99(4) Å (Fig. 2). The NH_4^+ cations have twelve Cl neighbors, three from each of four $SnCl_6^{2-}$ ions, at 3.559(1) Å with H...Cl interactions of 2.83(4) Å, consistent with the presence of weak hydrogen bonds, which render the position of the NH_4^+ ions ordered. As was already pointed out by Lerbscher & Trotter (1976, and references therein), the structure of ammonium hexachlorostannate(IV), like that of its potassium equivalent, is the same as that of K_2PtCl_6 (which can be considered to be an antifluorite type, and shows interesting similarities to those of perovskite, cryolite, and ReO_3). The same kind of structure occurs for several complex halides [see, for instance, Wells (1962)], among which the Rb, Cs and Tl analogues of our mineral and the cubic modification of K_2SiF_6 (hieratite), which was also first discovered in nature at La Fossa crater, Vulcano (Cossa 1881–1882, 1882, 1884, Gramaccioli & Campostrini 2007). In panichiite, the NH_4^+ and Cl^- ions together are in cubic closest packing, whereas the smaller Sn^{4+} ions are located at the center of the chloride octahedra. According to Brown (1964) and Lerbscher & Trotter (1976), the structure type of A_2BX_6 compounds mainly depends on the ratio of the size of the *A* cation and that of the hole in the BX_6 lattice available for it: thus a small *A* cation results in distortion from cubic to tetragonal or lower symmetry. Instead, for a value of this ratio greater than 0.98 (for panichiite it is 0.99), a cubic structure is observed at any temperature, whereas a ratio in the range 0.89 to 0.98 yields a structure that is cubic at room temperature but transforms to lower symmetry at lower temperatures [for K_2SnCl_6, the ratio is 0.92: see also Boysen & Hewat (1978)].

Panichiite is the second natural chloride containing tin as an essential constituent, and this element is in the 4+ oxidation state; this case turns out to be indeed unique as the other "natural" tin chloride, abhurite, $Sn^{2+}_{21}O_6Cl_{16}(OH)_{14}$, contains Sn^{2+} instead of Sn^{4+}, and its origin is the result of ship wreckage in all the known occurrences (Matzko *et al.* 1985). The presence of minor amounts of tin is already known in the complex sulfides from the fumaroles at La Fossa crater, as for instance in the chlorine-bearing vurroite $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$ (Garavelli *et al.* 2005). In any case, in the gases at Vulcano, tin is very likely to be present as a very volatile substance such as tin tetrachloride, $SnCl_4$; this chloride is probably an important vector of tin not only at La Fossa crater at Vulcano, but also in general, in the formation of hydrothermal mineral deposits, where transport from the vapor is probably essential in many cases [see for instance Williams-Jones *et al.* (2002) and references therein]. The formation of stannic tetrachloride instead of other chlorides containing Sn^{2+}, which

TABLE 3. SINGLE-CRYSTAL DATA AND REFINEMENT PARAMETERS FOR PANICHIITE

Crystal system	cubic	Space group	*Fm*$\bar{3}$*m* (no. 225)
a (Å)	10.064(1)	Z	4
V (Å^3)	1019.4(2)	F_{000}	696
Radiation	Mo*K*α	μ (mm^{-1})	4.011
(λ = 0.71073 Å)		D_{calc} (g/cm^3)	2.423
Measured reflections		3045	
Independent reflections		162	
Observed reflections [$I > 2\sigma(I)$]		153	
Parameters refined		8	
Final *R* and w*R*2		0.030, 0.066	
S		1.14	

Notes: $R = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$; $wR2 = \{\Sigma[w(Fo^2 - Fc^2)^2] / \Sigma[w(Fo^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(Fo^2) + (0.040q)^2]$, where $q = (Fo^2 + 2Fc^2)/3$; $S = \{\Sigma[w(Fo^2 - Fc^2)]/(n - p)\}^{1/2}$ where n is the number of reflections, and p is the number of refined parameters.

TABLE 4. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN PANICHIITE

Atom	*X/a*	*Y/b*	*Z/c*	*Ueq*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	0	0	0	0.02359(5)	0.02359(5)	0.02359(5)	0.02359(5)	0	0	0
Cl	0	0.24131(5)	0	0.03669(12)	0.0443(2)	0.0215(2)	0.0443(2)	0	0	0
N	¼	¼	¼	0.0400(7)	0.0400(7)	0.0400(7)	0.0400(7)	0	0	0
H	0.307(4)	0.307(4)	0.307(4)	0.25(4)						

The exponent of the anisotropic displacement factor takes the form: $-2\pi^2(U_{11}h^2(a^*)^2 + ... + 2U_{12}hka^*b^* + ...)$; $U_{eq} = ⅓(U_{11} + U_{22} + U_{33})$.

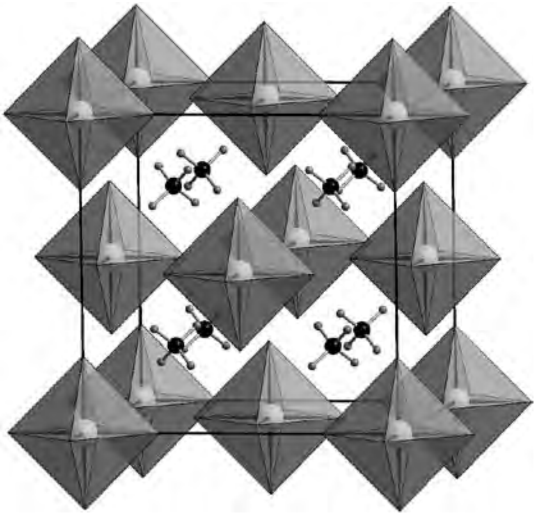

FIG. 2. Crystal structure of panichiite showing the $[SnCl_6]^{2-}$ octahedra and the NH_4^+ ions.

are not so volatile, is favored by the strong decrease in free energy when gaseous compounds are formed at a moderately high temperature. Instead, at the surface of fumaroles, in spite of the temperature drop, the presence of free oxygen prevents possible reduction to Sn^{2+}. In addition, the subsequent condensation into $(NH_4)_2SnCl_6$ is favored by the relatively strong activity of ammonia in the vapor, similarly to what happens for salammoniac and for a number of interesting (and generally new) ammonium-containing minerals that occur in the same fumarole. The above considerations reported indicate that panichiite is exclusively formed by deposition from the vapor phase, and its deposition occurs only within a very limited range of temperature and activity of both $SnCl_4$ and NH_3 in the vapor, thereby accounting for its great rarity.

As with other chlorides of the fumaroles at La Fossa crater, there is a remarkable content of bromine, the Br:Cl ratio (in weight) being for our mineral 2.7×10^{-2}, a value much higher than the marine value of 3.4×10^{-3}. This value is similar to the corresponding average (3.2×10^{-2}) in salammoniac from the same locality (Coradossi *et al.* 1985, 1996, and references therein); however, a still higher one (0.56) was observed for type lafossaite by Roberts *et al.* (2006), in agreement with the earlier observations by Fulignati & Sbrana (1998).

A similar situation occurs for the Pb halides of the same locality, which invariably show a non-negligible content of bromine; for instance, in hephaistosite, $TlPb_2Cl_5$, the Br:Cl ratio is 6.3×10^{-2} (Campostrini *et al.* 2008). The unusually high Br:Cl ratio can be compared with the equally unusual and high Se:S value occurring in most sulfides of the same environment, both at Vulcano and in Kamchatka (see for instance Vurro *et al.* 1999, Garavelli *et al.* 2005, Zelenski & Bortnikova 2005, and references therein).

ACKNOWLEDGEMENTS

The authors are indebted to the Editor Prof. Robert F. Martin for courteous assistance, and to the referees Drs. Uwe Kolitsch and D.E. Hibbs for useful suggestions.

REFERENCES

BARBERI, F., FERRARA, G., KELLER, J., INNOCENTI, F. & VILLARI, L. (1974): Evolution of the Aeolian arc volcanism. *Earth Planet. Sci. Lett.* **21**, 269-276.

BOYSEN, H. & HEWAT, A.W. (1978): A neutron powder investigation of the structural changes in K_2SnCl_6. *Acta Crystallogr.* **B34**, 1412-1418.

BROWN, I.D. (1964): The crystal structure of K_2TeBr_6. *Can. J. Chem.* **42**, 2758-2767.

CAMPOSTRINI, I., DEMARTIN, F., GRAMACCIOLI, C.M. & ORLANDI, P. (2008): Hephaistosite, $TlPb_2Cl_5$, a new thallium mineral species from La Fossa crater, Vulcano, Aeolian Islands, Italy. *Can. Mineral.* **46**, 701-708.

CORADOSSI, N., GARAVELLI, A., SALAMIDA, M. & VURRO, F. (1996): Evolution of Br/Cl ratios in fumarolic salammoniac from Vulcano (Aeolian Islands, Italy). *Bull. Volcanol.* **58**, 310-316.

CORADOSSI, N., PINARELLI, L. & BERTOLINI, G.L. (1985): Fluttuazioni del rapporto Br/Cl nelle esalazioni fumaroliche di Vulcano (Isole Eolie) e in alcuni prodotti delle loro reazioni. *Rend. Soc. Ital. Mineral. Petrol.* **40**, 299-309.

COSSA, A. (1881–1882): Sulla hieratite, nuova specie mineralogica. *Transunti dell'Accademia dei Lincei*, *Ser.* 3, **6**, 141-142.

COSSA, A. (1882): Sur la hiératite, espèce minérale nouvelle. *Bull. Soc. Fr. Minéral.* **5**, 61-62.

COSSA, A. (1884): Hieratit, ein neues Mineral. *Z. Kristallogr.* **8**, 305.

DEMARTIN, F., GRAMACCIOLI, C.M., CAMPOSTRINI, I. & ORLANDI, P. (2008a): Knasibfite, $K_3Na_4[SiF_6]_3[BF_4]$, a new hexafluorosilicate–tetrafluoroborate from La Fossa crater, Vulcano, Aeolian Islands, Italy. *Can. Mineral.* **46**, 447-453.

DEMARTIN, F., GRAMACCIOLI, C.M., CAMPOSTRINI, I. & ORLANDI, P. (2008b): Thermessaite, $K_2[AlF_3|SO_4]$, a new ino-aluminofluoride-sulfate from La Fossa crater, Vulcano, Aeolian Islands, Italy. *Can. Mineral.* **46**, 693-700.

FARRUGIA, L.J. (1999): WINGX suite for small-molecule single-crystal crystallography. *J. Appl. Crystallogr.* **32**, 837-838.

Frazzetta, G., La Volpe, L. & Sheridan, M.F. (1983): Evolution of the Fossa Cone, Vulcano. *J. Volcanol. Geotherm. Res.* **17**, 329-360.

Fulignati, P. & Sbrana, A. (1998): Presence of native gold and tellurium in the active high-sulfidation hydrothermal system of the La Fossa volcano (Vulcano, Italy). *J. Volcanol. Geotherm. Res.* **86**, 187-198.

Garavelli, A., Mozgova, N.N., Orlandi, P., Bonaccorsi, E., Pinto, D., Moëlo, Y. & Borodaev, Yu.S. (2005): Rare sulfosalts from Vulcano, Aeolian Islands, Italy. VI. Vurroite $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$, a new mineral species. *Can. Mineral.* **43**, 703-711.

Garavelli, A. & Vurro, F. (1994): Barberiite, NH_4BF_4, a new mineral from Vulcano, Aeolian Islands, Italy. *Am. Mineral.* **79**, 381-384.

Gramaccioli, C.M. & Campostrini, I. (2007): Demartinite, a new polymorph of K_2SiF_6 from La Fossa Crater, Vulcano, Aeolian Islands, Italy. *Can. Mineral.* **45**, 1275-1280.

Holland, T.J.B. & Redfern, S.A.T. (1997): Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineral. Mag.* **61**, 65-77.

Keller, J. (1980): The Island of Vulcano. *Rend. Soc. Ital. Mineral. Petrol.* **36**, 369-414.

Kolitsch, U. & Brandstätter, F. (2007): A new salt-inclusion sulphate phase from a burning coal dump: crystal-structural, chemical and Raman-spectroscopic characterization. *16th Croatian-Slovenian Crystallographic Meeting* (*Petrčane*), *Abstr.*, 12.

Lerbscher, J.A. & Trotter, J. (1976): Potassium hexachlorostannate(IV) and ammonium hexachlorostannate (IV). *Acta Crystallogr.* **B32**, 2671-2672.

Mandarino, J.A. (1981): The Gladstone–Dale relationship. IV. The compatibility index and its application. *Can. Mineral.* **19**, 441-450.

Matzko, J.J., Evans, H.T., Jr., Mrose, M.E. & Aruscavage, P. (1985): Abhurite, a new tin hydroxychloride mineral, and a comparative study with a synthetic basic tin chloride. *Can. Mineral.* **23**, 233-240.

Mercalli, G & Silvestri, O. (1890): Le eruzioni dell'Isola di Vulcano dal 3 agosto 1888 al 22 marzo 1890. *Annali dell'Ufficio Centrale di meteorologia e geodinamica* **10**, 71-280.

Mitolo, D., Pinto, D., Garavelli, A., Bindi, L. & Vurro, F. (2009): The role of the minor substitutions in the crystal structure of natural challacolloite, KPb_2Cl_5, and hephaistosite, $TlPb_2Cl_5$, from Vulcano (Aeolian Archipelago, Italy). *Mineral. Petrol.* (In press).

Panichi, U. (1913): Millosevichite, nuovo minerale del Faraglione di Levante, nell'Isola di Vulcano. *Atti R. Acc. Naz. Lincei*, *Ser.* 5. *Rend. Cl. Sc. Fis. Mat. Nat.* **22**, 5, 303.

Panichi, U. (1914): Contributo allo studio dei minerali dell'Isola di Vulcano. *Memorie della Società Italiana delle Scienze* (*detta dei XL*), *Ser.* 3, **19**, 3-55.

Roberts, A.C., Venance, K.E., Seward, T.M., Grice, J.D. & Paar, W.H. (2006): Lafossaite, a new mineral from the La Fossa Crater, Vulcano, Italy. *Mineral. Rec.* **37**, 165-168.

Sheldrick, G.M. (2000): Sadabs *Area-Detector Absorption Correction Program*. Bruker AXS Inc., Madison, Wisconsin.

Sheldrick, G.M. (2007): A short history of Shelx. *Acta Crystallogr.* **A64**, 112-122.

Sicardi, L. (1973): The thermal oscillations of the fumaroles of the Island of Vulcano from 1913 to 1970. *Stromboli* **13**, 65-68.

Vurro, F., Garavelli, A., Garbarino, C., Moëlo, Y. & Borodaev, Yu.S. (1999): Rare sulfosalts from Vulcano, Aeolian Islands, Italy. II. Mozgovaite $PbBi_4(S,Se)_7$, a new mineral species. *Can. Mineral.* **37**, 1499-1506.

Wells, A. F. (1962): *Structural Inorganic Chemistry* (3rd ed.). Clarendon Press, Oxford, U.K.

Williams-Jones, A.E., Migdisov, A.A., Archibald, S.M. & Xiao, Zhifeng (2002): Vapor transport of ore metals. *In* Water–Rock Interactions, Ore Deposits, and Environmental Geochemistry: a Tribute to David A. Crerar (R. Hellmann & S.A. Wood, eds.). *The Geochemical Society, Spec. Publ.* **7**, 279-305.

Zelenski, M. & Bortnikova, S. (2005): Sublimate speciation at Mutnovsky volcano, Kamchatka. *Eur. J. Mineral.* **17**, 107-118.

Received September 28, 2008, revised manuscript accepted March 9, 2009.