

HEPHAISTOSITE, TiPb_2Cl_5 , A NEW THALLIUM MINERAL SPECIES FROM LA FOSSA CRATER, VULCANO, AEOLIAN ISLANDS, ITALY

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ABSTRACT

Hephaistosite, TiPb_2Cl_5 , a newly discovered species of thallium lead chloride, was found in a high-temperature fumarole ($\sim 400^\circ\text{C}$) at the rim of La Fossa crater, Vulcano Island, Aeolian archipelago, Sicily, Italy. The mineral occurs as aggregates of pale yellow-green crystals tabular on {010} up to 0.1 mm in length on fragments of altered pyroclastic breccia, in association with bismuthinite (Bi_2S_3), cotunnite (PbCl_2), chalcocolloite (KPb_2Cl_5) and pseudocotunnite (K_2PbCl_4). The mineral is monoclinic, space group $P2_1/c$. Cell parameters refined from powder-diffraction data are: a 8.9477(6), b 7.9218(7), c 12.4955(5) Å, β 90.092(4)°, V 885.70(7) Å³, with $Z = 4$. The strongest six reflections in the X-ray powder-diffraction data [d (in Å)/(hkl)] are: 3.696(100)(013), 3.971(83)(020), 2.109(45)(402,215), 2.569(42)(204), 1.848(41)(142,026), and 2.851(38)(213). Crystals of hephaistosite show the forms {010}, {101}, {110}, {100}, {001}, and {011}. Chemical analyses obtained by EDS microprobe gave, on average, in wt.%, Ti 23.78, K 0.01, Pb 51.78, Cl 21.40, Br 1.34, F 0.17, for a total of 98.48, corresponding to an empirical formula (based on 8 apfu) of $\text{Ti}_{0.94}\text{Pb}_{2.01}(\text{Cl}_{4.85}\text{Br}_{0.14}\text{F}_{0.07})_{\Sigma 5.06}$. Hephaistosite is isostructural with chalcocolloite; intermediate members of the series between the two species occur in the same fumarole. The calculated density for the synthetic compound (TiPb_2Cl_5) is 5.932 g/cm³. The mean index of refraction n , obtained from a natural sample using Brewster angle measurement, is 2.0(1). The structure was refined using two different crystals, with Ti:K atom ratios of 86:14 and 64:36; the final R index is 0.028 and 0.038, respectively. The mineral, approved by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2006–043), is named in honor of the ancient Greek god of fire, Hephaistos (Hephaestus, $\text{H}\phi\alpha\iota\sigma\tau\omicron\varsigma$), whose workshops were alleged to be located at Vulcano.

Keywords: hephaistosite, new mineral species, crystal structure, chalcocolloite, thallium minerals, Vulcano island, Italy.

SOMMAIRE

Nous avons récemment découvert la hephaistosite, TiPb_2Cl_5 , nouvelle espèce de chlorure de thallium et de plomb, dans une fumerolle de haute température ($\sim 400^\circ\text{C}$) en bordure du cratère La Fossa, sur l'île de Vulcano, dans l'archipel Aéolien, partie de la Sicile, en Italie. Le minéral se présente en agrégats de cristaux jaune-vert pâle, tabulaires sur {010}, jusqu'à 0.1 mm de long, sur des fragments de brèche pyroclastique altérée; lui sont associés bismuthinite (Bi_2S_3), cotunnite (PbCl_2), chalcocolloite (KPb_2Cl_5) et pseudocotunnite (K_2PbCl_4). Le minéral est monoclinique, groupe spatial $P2_1/c$. Les paramètres réticulaires, affinés à partir du spectre de diffraction sur poudre, sont: a 8.9477(6), b 7.9218(7), c 12.4955(5) Å, β 90.092(4)°, V 885.70(7) Å³, avec $Z = 4$. Les six raies les plus intenses de ce spectre [d (en Å)/(hkl)] sont: 3.696(100)(013), 3.971(83)(020), 2.109(45)(402,215), 2.569(42)(204), 1.848(41)(142,026), et 2.851(38)(213). Les cristaux de hephaistosite montrent les formes {010}, {101}, {110}, {100}, {001}, et {011}. Les analyses chimiques effectuées avec une microsonde électronique en dispersion d'énergie ont donné, en moyenne, en pourcentages pondéraux, Ti 23.78, K 0.01, Pb 51.78, Cl 21.40, Br 1.34, F 0.17, pour un total de 98.48, ce qui correspond à une formule empirique fondée sur huit atomes par formule unitaire de $\text{Ti}_{0.94}\text{Pb}_{2.01}(\text{Cl}_{4.85}\text{Br}_{0.14}\text{F}_{0.07})_{\Sigma 5.06}$. La hephaistosite est isostructurale avec la chalcocolloite; des membres intermédiaires de la série entre les deux pôles coexistent dans la même fumerolle. La densité calculée de l'analogue synthétique (TiPb_2Cl_5) est 5.932 g/cm³. L'indice de réfraction n moyen d'un échantillon naturel, obtenu en mesurant l'angle de Brewster, est 2.0(1). Nous avons affiné la structure de deux cristaux, de composition en terme de rapports atomiques Ti:K de 86:14 et 64:36, jusqu'à un résidu R de 0.028 et 0.038, respectivement. Le minéral a été approuvé par la Commission sur les Nouveaux Minéraux, Nomenclature et Classification de l'IMA (no. 2006–043); son nom est inspiré du dieu du feu, en mythologie grecque, Hephaistos (Hephaestus, $\text{H}\phi\alpha\iota\sigma\tau\omicron\varsigma$), dont les ateliers, semble-t-il, étaient situés à Vulcano.

(Traduit par la Rédaction)

Mots-clés: hephaistosite, nouvelle espèce minérale, structure cristalline, chalcocolloite, minéraux de thallium, île de Vulcano, Italie.

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INTRODUCTION

The island of Vulcano, part of the Aeolian Archipelago, is situated in proximity of the northern coast of Sicily. Its notably interesting geological features have long been known. Mercalli & Silvestri (1890) described the last series of explosive eruptions, which took place from 1888 to 1890. More recent documents on the geology of Vulcano were published by Sicardi (1973), Barberi *et al.* (1974), Keller (1980), and Frazzetta *et al.* (1983).

In recent years, a substantial set of important works concerning this island have been published in the fields of volcanology and geochemistry. A detailed survey of the fumarole field was performed by Harris & Maciejewski (2000). A semiquantitative estimate of fluxes of trace elements in these fumaroles was provided by Cheynet *et al.* (2000), and a chemical mapping of the fumarolic field has been published by Aiuppa *et al.* (2005, and references therein). Such a renewed interest was stimulated by a notable increase in fumarolic flow-rates and temperatures, which started in 1987 and reached a maximum in 1993.

Turning our attention to the most relevant mineralogical works, important contributions are due to Alfonso Cossa, who described the occurrence of the new species hieratite, K_2SiF_6 (Cossa 1881–1882, 1882, 1884). Years later, additional new fluorides were also observed, such as barberiite, NH_4BF_4 (Garavelli & Vurro 1994), demartinite, a hexagonal (6mm) 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.* 2008).

The same fumaroles are the type locality for the lead–bismuth sulfosalt cannizzarite, $Pb_{45}Bi_{54}S_{127}$ (Zambonini *et al.* 1924), which occurs together with bismuthinite (Bi_2S_3) and galenobismutite ($PbBi_2S_4$), pointing out the importance of bismuth minerals in this environment. In more recent times, and in connection with the increased activity of the fumaroles, there has been a renewed interest in the rare minerals occurring at La Fossa crater, leading to the discovery of native gold and tellurium (Fulignati & Sbrana 1998). In addition, a number of Bi-bearing sulfosalts (*e.g.*, lillianite, $Pb_3Bi_2S_6$, and kirkiite, $Pb_{10}Bi_3As_3S_{19}$; see, for instance, Pinto 2005) have also been discovered, even including new species such as mozgovaite, $PbBi_4(S,Se)_7$, and vurroite, $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$ (Vurro *et al.* 1999, Garavelli *et al.* 2005, and references therein), pointing to an analogy with high-sulfidation epithermal ore deposits. Furthermore, interesting chlorides, such as lafossaite, $TiCl$ (Roberts *et al.* 2006), were also discovered. In line with all such recent discoveries, the occurrence in the same environment of hephaistosite, $TiPb_2Cl_5$, another Ti-rich chloride, is here reported. The mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (No. 2006–043); the name derives from that of

the ancient Greek god of fire, Hephaistos (Hephaestus, Ἡφαίστος), whose workshops were alleged to be located at Vulcano. The holotype is deposited (No. 2006–2) 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 new thallium–lead chloride was noticed by one of us (I.C.) on fragments of altered pyroclastic breccia collected in a high-temperature fumarole ($\sim 400^\circ\text{C}$) at the rim of the crater, using an EDS-equipped electron microprobe. The mineral forms aggregates of pale yellow-green crystals tabular on $\{010\}$, up to 0.1 mm in length. It is associated with bismuthinite (Bi_2S_3), cotunnite ($PbCl_2$), chalcocolloite (KPb_2Cl_5) and pseudocotunnite (K_2PbCl_4).

Quantitative analyses performed using a JEOL JSM 5500 LV scanning electron microscope equipped with an IXRF EDS 2000 microprobe (20 kV, 10^{-11} A, 2 μm beam diameter) showed Ti, Pb, and Cl to be the main constituents, with minor amounts of Br, K and F; the mean analytical results for a specimen close to the Ti-end member are reported in Table 1. An electron-microprobe analysis in wavelength-dispersion mode was also attempted, but the results were poor owing to volatilization of the sample under the electron beam. The empirical formula (based on eight atoms per formula unit) is $Ti_{0.94}Pb_{2.00}(Cl_{4.85}Br_{0.14}F_{0.07})_{\Sigma 5.06}$, leading to a simplified formula: $TiPb_2Cl_5$, which ideally requires: Ti 25.67, Pb 52.06, Cl 22.27 wt.%. In both EDS and WDS scans, traces of K were detected also, but no Rb or Cs. The nature of the analyzed sample was confirmed by the practical identity of the X-ray powder-diffraction pattern with that of the synthetic pure compound $TiPb_2Cl_5$ of monoclinic $P2_1/c$ symmetry, which is near that of the isostructural potassium salt KPb_2Cl_5 or chalcocolloite (Table 2, and see below). However, the existence of a series of more potassium-rich samples in the same environment is suggested by the results of a series of preliminary EDS-microprobe analyses and

TABLE 1. CHEMICAL COMPOSITION OF HEPHAISTOSITE

Constituent	Ideal formula	wt.%	Range	Standard deviation	Microprobe standard
Ti		23.78	23.03–24.20	0.1	Synthetic TiBr
K		0.01	0.00–0.02	0.1	Synthetic KF
Pb		51.78	51.40–52.11	0.1	Phosgenite
Cl		21.40	20.96–22.01	0.1	Phosgenite
Br		1.34	1.31–1.38	0.1	Synthetic TiBr
F		0.17	0.05–0.35	0.2	Fluorite
Total	100.00	98.48	97.84–99.09		

The chemical analyses (8) were carried out by means of an electron microprobe (EDS mode, 20 kV, 10^{-11} A, 2 μm beam diameter).

by a structure refinement carried out on two different crystals (see below). This result is not surprising in view of the relationship to chalcocollite; the corresponding compound KPb_2Cl_5 was also observed in this locality as a result of deposition from fumarole gases in silica glass tubes (Garavelli *et al.* 1997).

An important problem concerning hephaistosite arises because the samples corresponding to the Tl end-member are suitable for adequate polishing to perform quantitative chemical analysis, but they are not so for single-crystal studies; conversely, those richer in K provide good single crystals, but are instead unsuitable for polishing. For this reason, the composition of the (Tl, K) site in the single crystals was best obtained from refinement of the site occupancy. Here this procedure is particularly reliable, in view of the very different scattering power of the two atoms (the standard deviation obtained for the occupancy of Tl and K is less than 0.01).

As for other chlorides of the fumaroles at La Fossa crater, there is a remarkable content of bromine, the Br:Cl weight ratio being for our mineral 6.3×10^{-2} , a value much higher than the marine value of $3.4 \times$

10^{-3} . This value is even higher than 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 lafossaitite by Roberts *et al.* (2006). A similar enrichment was also noted by Fulignati & Sbrana (1998). Owing to the very small size of the single crystals, no goniometric measurements could be performed, although the electron-microscope images satisfactorily match a drawing including the pinacoids $\{010\}$, $\{101\}$, $\{100\}$, $\{001\}$, and the prisms $\{011\}$, $\{110\}$ (Figs. 1, 2). No fluorescence is observed under either long- or short-wave ultraviolet light. The mineral is not hygroscopic; the density could not be measured because of the small grain-size of reasonably pure material; for the synthetic compound, the calculated density is 5.932 g/cm^3 . Owing to the reactive nature of liquids with a very high index of refraction, the mean index $n = 2.0(1)$ was obtained from Brewster angle measurement on grains in polished mounts.

CRYSTALLOGRAPHY

The crystal structure of the synthetic compound TlPb_2Cl_5 was solved by Keller (1976); it is isostructural with the corresponding ammonium compound $\text{NH}_4\text{Pb}_2\text{Cl}_5$ (Ras *et al.* 1977) and with the artificial low-temperature phase of the potassium analogue KPb_2Cl_5 (Virovets *et al.* 2001, Velásquez *et al.* 2006), which is important for practical applications as a host crystal for optical amplifiers in lasers (Merkulov *et al.* 2005, Velásquez *et al.* 2006). The synthetic KPb_2Cl_5 phase is identical with the mineral chalcocollite (Schlüter *et al.* 2005).

X-ray powder-diffraction data for the Tl end-member (Table 2) were obtained using a Rigaku D/MAX diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$) and a graphite monochromator on the reflected

TABLE 2. X-RAY POWDER-DIFFRACTION DATA: COMPARISON OF HEPHAISTOSITE WITH ITS SYNTHETIC COUNTERPART

l/l_0	$d_{\text{obs.}} (\text{\AA})$	$d_{\text{calc.}} (\text{\AA})$	l/l_0	$d (\text{\AA})$ (calc.)	$h \ k \ l^{\dagger}$
Our data			Keller (1976) [†]		
2	5.949	5.931	7	5.932	1 1 0
4	4.311	4.304	8	4.301	1 1 2
83	3.971	3.961	46	3.96	0 2 0
13	3.733	3.720	83	3.720	2 1 1
100	3.696	3.687	100	3.684	0 1 3
9	3.646	3.640	51	3.638	2 0 2
			12	3.478	1 2 1
			7	2.966	2 2 0
9	2.912	2.906	8	2.904	0 1 4
12	2.892	2.886	20	2.886	2 2 1
38	2.851	2.847	26	2.845	2 1 3
14	2.686	2.680	54	2.679	2 2 2, 3 0 2
6	2.591	2.584	5	2.583	0 3 1
42	2.569	2.563	30	2.561	2 0 4
12	2.353	2.347	14	2.347	1 3 2
			13	2.341	3 2 1
22	2.273	2.274		2.30	2 3 0
25	2.236	2.237	31	2.239	2 3 1, 4 0 0
15	2.220	2.225	21	2.229	3 2 2, 0 3 3
5	2.156	2.155	11	2.150	2 2 4, 3 0 4
45	2.109	2.107	28	2.103	4 0 2, 2 1 5
11	2.088	2.083	13	2.081	3 1 4, 0 0 6
6	1.985	1.980	6	1.996	0 4 0, 2 3 3
4	1.972	1.977	3	1.977	3 3 0, 0 4 0
10	1.961	1.964	6	1.967	1 1 6, 1 3 4
6	1.952	1.952	4	1.956	3 3 1, 0 4 1
			12	1.949	4 2 0
17	1.915	1.914	29	1.913	4 1 3
16	1.889	1.888	6	1.885	0 4 2, 2 0 6
41	1.848	1.847	14	1.842	1 4 2, 0 2 6
			10	1.838	2 3 4
			8	1.580	4 3 3
4	1.539	1.539	3	1.535	052, 343, 108
4	1.528	1.529	9	1.524	2 2 7, 4 0 6

^{††} Calculated from the following unit-cell parameters: a 8.9477(6), b 7.9218(7), c 12.4955(5) Å, β 90.092(4)°.

[†] Calculated from single-crystal data for synthetic TlPb_2Cl_5 (Keller 1976).

[‡] Because of pseudo-orthorhombic symmetry ($\beta = 90^\circ$), there is coincidence of hkl with $-hkl$.

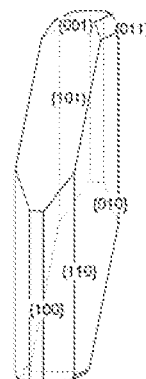


FIG. 1. A drawing of a typical crystal of hephaistosite. The indices of the observed forms are reported.

beam. The unit-cell parameters, calculated from these data with the software UNIT CELL (Holland & Redfern 1997), are: a 8.9477(6), b 7.9218(7), c 12.4955(5) Å, β 90.092(4)°, V 885.70(7) Å³. These are in excellent agreement with those reported by Keller (1976) for the pure synthetic compound: a 8.954, b 7.920, c 12.487 Å, β 90°, V 885.5 Å³.

Two different fragments of natural crystals, in which Tl is partly replaced by K (atomic Tl:K = 86:14 and

Tl:K = 64:36, respectively) were examined using a Bruker Apex II diffractometer equipped with a 2K CCD detector (MoK α radiation, λ = 0.71073 Å). For these single crystals, the unit-cell parameters are reported in Table 3. Because of the smaller ionic radius of K⁺ with respect to Tl⁺, the volume of the crystal richer in K is significantly smaller than that of the pure thallium compound (885.5 Å³). Details concerning the data collection and refinement for both crystals are reported in Table 3.

An absorption correction was applied using the SADABS program (Sheldrick 2000). The structure was refined starting from the known positions of atoms with the SHELXL97 program (Sheldrick 1997) implemented in the WINGX suite (Farrugia 1999). An extinction parameter x was also refined, where F_c is multiplied by $k [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$, k being the overall scale-factor. During the refinement, the R index remained above 0.12 for both crystals, and the anisotropic displacement parameters of atoms were found to be unrealistic. However, in agreement with the results by Merkulov *et al.* (2005) for synthetic K₂Pb₂Cl₅ and Aizu's (1970) theory, the possible presence of twinning on {100} was considered. A $[\bar{1} 0 0 / 0 1 0 / 0 0 1]$ twin matrix was introduced, and the relative percentages of the twins were refined to 0.52:0.48 and 0.57:0.43 for the two crystals, respectively, leading to a substantial lowering of the R index and providing reasonable and nearly isotropic displacement parameters for all atoms. The final coordinates and displacement parameters of the

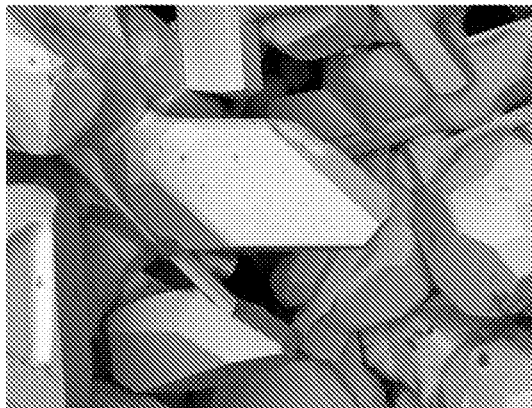


FIG. 2. Back-scattered electron image of hephaistosite crystals; the maximum length of the crystals is 0.1 mm.

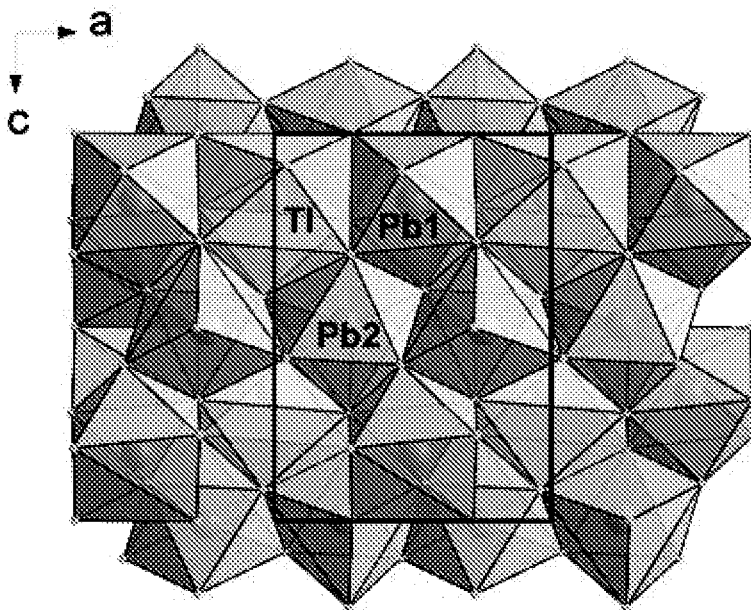


FIG. 3. A view of the crystal structure along $[0 1 0]$.

atoms for the crystal having an atom ratio Ti:K equal to 86:14 (*i.e.*, closer to the hephaistosite end-member) are reported in Table 4. Selected interatomic distances are reported in Table 5. For the other crystal with Ti:K = 64:36, the corresponding data may be obtained from the Depository of Unpublished Data on the MAC web site [document Hephaistosite CM46_701], together with tables of observed and calculated structure-factors for both crystals.

TABLE 3. SINGLE-CRYSTAL DATA FOR HEPHAISTOSITE

	Ti:K = 86:14	Ti:K = 64:36
Crystal system	monoclinic	
Space group	$P2_1/c$ (no. 14)	
a (Å)	8.9357(5)	8.9163(5)
b (Å)	7.9283(5)	7.9279(5)
c (Å)	12.5017(7)	12.5039(8)
β (°)	90.01(1)	90.01(1)
V (Å ³)	885.7(1)	883.9(1)
Z	4	
Scan mode	ω	
D _{calc} (g/cm ³)	5.796	5.535
μ (mm ⁻¹)	55.02	51.24
q max (°)	29.32	34.53
Measured reflections	10995	13296
Independent reflections	2321	3637
Observed reflections [$I > 2\sigma(I)$]	2238	3219
Minimum transmission factor	0.342	0.392
Parameters refined	77	77
Extinction parameter ($\times 10^{-3}$)	1.5(1)	1.7(1)
Final R and wR2	0.0275, 0.0664	0.0379, 0.0917
Goodness of fit S	1.054	0.915
Largest diffraction peak and hole (e Å ⁻³)	2.90, -3.65	2.78, -2.43

$R = \sum |F_o| - |F_c| / \sum |F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)]^{1/2}$
 $w = 1/[\sigma^2(F_o^2) + (0.0298p)^2 + 3.819p]$, where $p = (F_o^2 + 2F_c^2)/3$;
 $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

TABLE 4. FRACTIONAL COORDINATES AND DISPLACEMENT PARAMETERS FOR THE TI-RICH CRYSTAL (Ti:K = 86:14)

Atom	X/a	Y/b	Z/c	U _{eq} /U
Pb1	0.49483(5)	-0.00984(5)	0.17439(3)	0.0235(1)
Pb2	0.75346(4)	0.43582(4)	0.00622(2)	0.0206(1)
Ti, K	0.98934(5)	-0.05117(6)	0.16638(4)	0.0341(2)
C1	1.0409(3)	0.3220(3)	0.0800(2)	0.0269(5)
C2	0.4574(2)	0.3343(3)	0.0965(2)	0.0210(4)
C3	0.2748(2)	0.1575(3)	0.3118(2)	0.0209(4)
C4	0.7189(2)	0.0408(2)	0.0016(2)	0.0203(4)
C15	0.7308(3)	0.1875(3)	0.2782(2)	0.0221(4)

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Pb1	0.0250(2)	0.0239(2)	0.0215(2)	-0.0017(1)	0.0003(2)	-0.0028(1)
Pb2	0.0185(2)	0.0223(2)	0.0209(2)	-0.0015(1)	0.0011(2)	0.0007(1)
Ti, K	0.0314(3)	0.0340(3)	0.0368(3)	0.0059(2)	0.0030(2)	0.0058(2)
C1	0.0170(9)	0.0262(11)	0.0375(13)	0.0156(10)	0.0005(9)	-0.0005(8)
C2	0.0179(9)	0.0185(9)	0.0266(10)	0.0044(8)	-0.0003(8)	0.0017(8)
C3	0.0269(11)	0.0206(9)	0.0152(8)	0.0047(7)	0.0073(9)	0.0073(8)
C4	0.0220(9)	0.0207(8)	0.0183(8)	-0.0015(9)	0.0006(8)	0.0003(7)
C15	0.0245(11)	0.0223(9)	0.0196(9)	-0.0019(7)	-0.0001(8)	-0.0021(9)

The anisotropic displacement factor exponent takes the form:
 $-2\pi^2(h^2U_{11} + a^2U_{22} + \dots + 2U_{12}hka^*b^* + \dots)$; $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$.

DISCUSSION

The structure of hephaistosite is practically identical with that of a series of well-known synthetic compounds (Keller 1976, Ras *et al.* 1977, Schlüter *et al.* 2005, Merkulov *et al.* 2005, Velásquez *et al.* 2006). Using the present twinned model, no extra peaks showing positional disorder could be detected in the final difference-Fourier map. A view of the crystal structure is provided in Figure 3. It contains two eight-coordinate bicapped trigonal prisms, one centered by lead (Pb1) and the other by thallium (in part replaced by potassium). These polyhedra alternate and share their bases to form chains along [1 0 0]. Another seven-coordinate monocapped octahedron is centered by a lead atom (Pb2). In view of the existence of isostructural intermediates, the mineral can be considered to be isomorphous with chalcocolite KPb_2Cl_5 , with potassium replaced by variable amounts of thallium. The situation is plausible because the radius of the eight-coordinate Ti^{+} ion (1.73 Å, according to Shannon & Prewitt 1970), is near that of K^{+} (1.65 Å), in line with many examples in the mineral world; the average Ti-Cl distance for the Ti-rich crystal [3.325(1) Å] is slightly but significantly longer than that [3.318(1) Å] of the other sample. In view of the low accuracy of the results obtained by Keller (1976), no comparison of our data with the reported distances in the synthetic compound has been considered. In agreement with Velásquez *et al.* (2006), who found no disordered replacement for the eight-coordinate Pb by K in the low-temperature phase of KPb_2Cl_5 , here the observed values of U for the two independent lead atoms are comparable, thereby suggesting no appreciable substitution.

TABLE 5. INTERATOMIC DISTANCES (Å) FOR THE TI-RICH CRYSTAL

Pb1Cl ₆ polyhedron			
Pb1-Cl2	2.916(2)	Pb1-Cl4 ^a	2.924(2)
Pb1-Cl2 ^a	3.148(2)	Pb1-Cl4	2.972(2)
Pb1-Cl3	2.929(2)	Pb1-Cl5	2.929(2)
Pb1-Cl3 ^a	3.350(2)	Pb1-Cl5 ^a	3.190(2)
Pb1-Cl (average)	3.045		
Pb2Cl ₆ polyhedron			
Pb2-Cl1 ^c	2.868(2)	Pb2-Cl3 ^a	2.886(2)
Pb2-Cl1	2.874(2)	Pb2-Cl4	3.147(2)
Pb2-Cl2 ^a	2.920(2)	Pb2-Cl5 ^a	3.020(2)
Pb2-Cl2	2.987(2)		
Pb2-Cl (average)	2.957		
TiCl ₆ polyhedron			
Ti, K-Cl1 ^f	3.337(3)	Ti, K-Cl4 ^a	3.349(2)
Ti, K-Cl1	3.183(2)	Ti, K-Cl4	3.258(2)
Ti, K-Cl3 ^a	3.314(2)	Ti, K-Cl5	3.297(2)
Ti, K-Cl3 ^a	3.542(2)	Ti, K-Cl5 ^f	3.202(2)
Ti, K-Cl (average)	3.325		

Symmetry codes: a = 1 - x, y - 1/2, z - 1/2; b = 1 - x, -y, -z; c = 2 - x, 1 - y, -z; d = 1 - x, 1 - y, -z; e = x, 1/2 - y, z - 1/2; f = 2 - x, y - 1/2, 1/2 - z; g = 1 + x, y, z; h = 2 - x, -y, -z.

The existence of well-characterized thallium minerals such as bromian lafossaite, $\text{Tl}(\text{Cl}, \text{Br})$, in volcanic fumaroles was first described by Roberts *et al.* (2006) at La Fossa crater, Vulcano, whence the name of the species, and is consistent with the earlier observations by Fulignati & Sbrana, who already in 1998 had noticed the occurrence of a "thallium bromide chloride" at the same locality. These authors also observed the presence of notable amounts of thallium (up to 282 ppm) in hydrothermally altered rocks in proximity of the fumarolic vents; the presence of thallium minerals in these fumaroles seems to have notably increased in the last years. The possibility of a more widespread existence of thallium minerals in fumarolic environments is also confirmed by our discovery of lafossaite (not bromian) in an old specimen found at Vesuvius in the products of the 1906 eruption, associated with realgar and dimorphite (As_4S_3). A product corresponding to hephaistosite was collected as a sublimate in silica glass tubes from high-temperature fumarolic gases at Mutnovsky volcano, Kamchatka, together with other thallium compounds, such as the iodide TlI , and a still unnamed thallium–lead chloride $\text{PbTl}_3(\text{Cl}, \text{Br}, \text{I})_5$. The latter would already deserve the qualification of new mineral species, since it has also been observed on the ground near the fumaroles (Zelenski & Bortnikova 2005). Sulfides of Tl and Bi, or of Tl and Pb, have been observed in the fumaroles of Satsuma–Iwojima volcano in Japan (Africano *et al.* 2002). Besides the evidence described above and the results of chemical analyses carried out on the gases (Cheynet *et al.* 2000), the possibility of fumarolic enrichment in thallium is further confirmed by the discovery at Vulcano of additional minerals of this element, which are presently under investigation.

The presence of significant amounts of bromine is also interesting. A similar situation occurs for other halides of the same locality, which invariably show a non-negligible content of bromine; the situation is parallel to the relatively high Se:S ratio occurring in most sulfides in the same environment, both at Vulcano and in Kamchatka (see for instance Vurro *et al.* 1999, Garavelli *et al.* 2005, Zelenski & Bortnikova 2005, and the references therein). The variability of the Br/Cl and of the Se/S values in these minerals can be ascribed to the origin of the fumarolic gases, which presumably derive from brines directly exsolved from magma, mixed with variable amounts of seawater; these observations agree with the observed isotopic ratios of elements such as H/D, O, and rare gases (Coradossi & Maleci 1972, Mazor *et al.* 1988, Coradossi *et al.* 1996, Boyce *et al.* 2007, and references therein). However, the enrichment of Br in the sublimes is significantly higher than that in the depositing gases; a possible explanation for this phenomenon is differential sublimation due to the greater volatility of the chlorides with respect to the corresponding bromides. For instance, for

salammoniac, it is well known that the vapor pressure of pure ammonium chloride is 1 mm Hg at 160.4°C, whereas the corresponding temperatures for the bromide and the iodide are 198.3°C and 210.9°C, respectively (Sigma-Aldrich 2006). Thallium chloride is reported to be volatile, its vapor pressure being 10 mm Hg at 517°C, and the boiling point 720°C, whereas the bromide boils at 815°C. On such basis, differential deposition of thallium halides is not unexpected. Unfortunately, for these substances, thermodynamic data are too few, and they are not available for the more complex halides.

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