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**PAUFLERITE, β -VO(SO₄), A NEW MINERAL SPECIES
 FROM THE TOLBACHIK VOLCANO, KAMCHATKA PENINSULA, RUSSIA**

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ABSTRACT

Pauflerite, β -VO(SO₄), is a new mineral species from the fumaroles of the Great Fissure Tolbachik eruption (GFTE), Kamchatka Peninsula, Russia. It was found in 1977 in the first cinder cone of the North breach of the GFTE. The mineral occurs as light green prismatic crystals up to 0.1 mm in length, associated with shcherbinaite (V₂O₅), an unknown Tl–Bi sulfate and finely crystalline Mg, Al, Fe and Na sulfates. Pauflerite is light green with a white streak and vitreous luster; the mineral is transparent and non-fluorescent. The Mohs hardness is 3–4. Pauflerite is brittle, and without visible cleavage. The density is 3.36(4) (measured) and 3.294 g/cm³ (calculated). The mineral is biaxial, optically positive, α 1.731(4), β 1.778(2), γ 1.845(4), with $2V_{\text{meas}} \approx 90^\circ$, and $2V_{\text{calc}}$ equal to 83° . The orientation was determined as $X = a$; further details are unclear. Pleochroism is clear in green tones: X light green, Y bluish green, Z light green-blue. A chemical analysis with an electron microprobe gave VO₂ 50.40, SO₃ 49.30, total 99.70 wt.%. The empirical formula, calculated on the basis of 5O, is V_{0.99}S_{1.01}O₅. The simplified formula is VO(SO₄). Pauflerite is orthorhombic, *Pnma*, a 7.3890(13), b 6.2740(11), c 7.0788(11) Å, V 328.16(10) Å³, $Z = 4$. The structure has been solved by direct methods and refined to R_1 of 0.034, calculated for the 457 unique observed reflections ($|F_o| > 4\sigma|F_o|$). The structure contains one symmetrically independent V⁴⁺ cation in distorted octahedral coordination to the O atoms (one vanadyl V⁴⁺–O bond of 1.607 Å, four bonds of 1.992–1.996 Å, and one bond of 2.267 Å). One symmetrically independent S⁶⁺ cation is tetrahedrally coordinated by four O²⁻ anions with the mean <S⁶⁺–O> bond length of 1.470 Å. The structure of pauflerite consists of a three-dimensional framework of distorted V⁴⁺O₆ octahedra and SO₄ tetrahedra with a titanite-type topology. Pauflerite is a natural analog of β -VO(SO₄). The powder-diffraction pattern was not obtained because of the paucity of natural material. The calculated powder-diffraction pattern is in excellent agreement with that reported for the synthetic analogue (PDF 19–1400). The name chosen honors Peter Paufler, professor at the Technical University of Dresden in recognition of his important contributions to physical and structural crystallography and mineralogy.

Keywords: pauflerite, crystal structure, vanadium sulfate, Tolbachik volcano, Russia.

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SOMMAIRE

Nous décrivons la pauflerite, β -VO(SO₄), nouvelle espèce minérale découverte dans les fumerolles associées à la grande éruption fissurale du volcan Tolbachik, péninsule de Kamchatka, en Russie. Elle a été découverte en 1977 dans le premier cône de scories de la zone fissurale du Nord. Le minéral, en cristaux prismatiques vert pâle atteignant une longueur de 0.1 mm, est associé à la shcherbinaïte (V₂O₅), un sulfate de Tl–Bi méconnu, et des sulfates à grains fins de Mg, Al, Fe et Na. La pauflerite est vert pâle, avec une rayure blanche et un éclat vitreux; les cristaux sont transparents et non fluorescents. La dureté de Mohs est 3–4. La pauflerite est cassante, et apparemment sans clivage. Sa densité est 3.36(4) (mesurée) et 3.294 g/cm³ (calculée). Il s'agit d'un minéral biaxe, optiquement positif, α 1.731(4), β 1.778(2), γ 1.845(4), avec $2V_{\text{mes}} \approx 90^\circ$, et $2V_{\text{calc}}$ égal à 83° . L'orientation $X = a$ a été déterminée, sans autres précisions. Le pléochroïsme, en teintes de vert, est évident: X vert pâle, Y vert bleuâtre, Z vert bleuâtre pâle. Une analyse chimique avec une microsonde électronique a donné: VO₂ 50.40, SO₃ 49.30, pour un total de 99.70% (poids). La formule empirique, calculée sur une base de 5O, est V_{0.99}S_{1.01}O₅. La formule simplifiée est VO(SO₄). La pauflerite est orthorhombique, *Pnma*, *a* 7.3890(13), *b* 6.2740(11), *c* 7.0788(11) Å, *V* 328.16(10) Å³, *Z* = 4. Nous en avons résolu la structure, et nous l'avons affiné par méthodes directes jusqu'à un résidu *R*₁ de 0.034, calculé en utilisant 457 réflexions uniques observées ($|F_o| > 4\sigma(F_o)$). La structure chimique avec un cation V⁴⁺ symétriquement indépendant en coordinence octaédrique difforme avec les atomes d'oxygène (une liaison vanadyle, V⁴⁺–O, de 1.607 Å, quatre liaisons de 1.992–1.996 Å, et une de 2.267 Å). Le cation S⁶⁺ symétriquement indépendant possède une coordinence tétraédrique avec des anions O²⁻, la longueur moyenne, <S⁶⁺–O>, étant égale à 1.470 Å. La structure de la pauflerite contient une trame tri-dimensionnelle d'octaèdres difformes de V⁴⁺O₆ et de tétraèdres SO₄ ayant une topologie de type titanite. La pauflerite est l'analogue naturel de β -VO(SO₄). Nous n'avons pas pu obtenir le spectre de diffraction X faute de matériau. Le spectre calculé concorde étroitement avec le spectre observé de l'analogue synthétique (PDF 19–1400). Le nom honore Peter Paufler, professeur à l'Université Technique de Dresde, pour souligner ses contributions importantes en cristallographie physique et structurale et en minéralogie.

(Traduit par la Rédaction)

Mots-clés: pauflerite, structure cristalline, sulfate de vanadium, volcan Tolbachik, Russie.

INTRODUCTION

In the literature, five oxosulfate hydrates of tetravalent vanadium are reported as minerals with the general formula VO(SO₄)(H₂O)_n (*n* = 3, 5, 6): stanleyite (*n* = 6) (Livingstone 1982), minasragrite (*n* = 5) (Schaller 1917, Smith & Marinenko 1973), orthominasragrite (*n* = 5) (Hawthorne *et al.* 2001), anorthominasragrite (*n* = 5) (Cooper *et al.* 2003) and bobjonesite (*n* = 3) (Schindler *et al.* 2003). These minerals are of secondary origin and form as a result of the alteration of primary vanadium minerals. Thus, stanleyite and minasragrite form on the surface of patrónite, V(S₂)₂, whereas the recently discovered association of orthominasragrite, anorthominasragrite and bobjonesite crystallizes from the highly acidic solutions that resulted from oxidation of primary pyrite replacing a fossil tree in the Temple Mountain mining district, Emery County, Utah. In this paper, we describe pauflerite, β -VO(SO₄), a new mineral species found in fumaroles of the Great fissure Tolbachik eruption (GFTE), Kamchatka Peninsula, Russia. In contrast to the hydrous sulfates of V⁴⁺ mentioned above, pauflerite has formed in a "dry" high-temperature fumarole environment, which accounts for its anhydrous character.

The mineral is named in honor of Prof. Dr. Peter Paufler (b. 1940), of the Technical University of Dresden, Germany, for his important contributions to physical and structural crystallography and mineralogy. The new mineral and mineral name were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association

(proposal 2005–004). The type material is deposited in the Mineralogical Museum, Department of Mineralogy, St. Petersburg University, St. Petersburg, Russia.

OCCURRENCE

The GFTE is the largest basaltic eruption in modern history (Fedotov 1984). It was active in 1975–76 and consisted of two breaches (North and South) and seven cones; see Vergasova *et al.* (1999) for further details. Beginning in the late 1970s, fumarolic activity at the GFTE resulted in the crystallization of a unique assemblage of minerals, with twenty-seven new species discovered to date. Most of these minerals are anhydrous, which is a result of their crystallization from dry high-temperature gases.

Pauflerite was found in 1977 within fumaroles of the first cinder cone of the North breach of the GFTE. The temperature of the gases at the sampling site was about 500–600°C. Several light green prismatic crystals of the mineral attain up to 0.1 mm in maximum dimension, and are associated with shcherbinaite (V₂O₅), an unknown Tl–Bi sulfate, and finely crystalline Mg, Al, Fe and Na sulfates.

PHYSICAL AND OPTICAL PROPERTIES

Pauflerite is light green with a white streak and a vitreous luster. The mineral is transparent and non-fluorescent. The Mohs hardness is 3–4. Pauflerite is brittle. No cleavage was observed. Its density was measured on a single grain in a mixture of CH₂I₂ (*D* = 3.32 g/cm³)

and solution of GeI₄ in CH₂I₂ (*D* = 3.40 g/cm³), and was determined to be 3.36(4) g/cm³. The calculated density is 3.294 g/cm³.

Pauflerite is biaxial, optically positive, α 1.731(4), β 1.778(2), γ 1.845(4) (589 nm wavelength). The angle 2*V*_{meas} is equal to ~90°, and 2*V*_{calc} is 83°. Its orientation was determined as *X* = *a*, but further details are unclear. Pleochroism is evident in green tones: *X* light green, *Y* bluish green, *Z* light green-blue.

CHEMICAL COMPOSITION

The composition of pauflerite was determined by wavelength-dispersion spectroscopy using a Cameca MS-46 electron microprobe operating at 20 kV and 1 nA, with a beam diameter of ~2 μm. Four analyses were done; Table 1 provides the mean chemical composition. The empirical formula, calculated on the basis of five atoms of oxygen, is V_{0.99}S_{1.01}O₅. The simplified formula is VO(SO₄).

X-RAY CRYSTALLOGRAPHY

Experimental

The crystal of pauflerite selected for data collection was mounted on a glass fiber. Data were collected by means of a STOE IPDS II diffractometer using monochromated MoKα radiation and framewidths of 2° in ω. The unit-cell parameters (Table 2) were refined

by least-squares techniques. The data were corrected for Lorentz, polarization, absorption, and background effects. The intensity statistics indicated the centrosymmetric space-group *Pnma*. We solved and refined the structure by means of the program SHELX-97. Refinement of all atom-position parameters, allowing for the anisotropic displacement of all atoms and the inclusion of a refinable weighting scheme of the structure factors, resulted in a final agreement index (*R*₁) of 0.034, calculated for the 457 unique observed reflections (*I*F_{ol} > 4σ*I*F_{ol}). The final atom parameters are listed in Table 3, and selected interatomic distances are listed in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data on the MAC web site [document Pauflerite CM45_921].

Cation coordination

The structure of pauflerite contains one symmetrically independent V⁴⁺ cation in distorted octahedral coordination to oxygen atoms (one *vanadyl* V⁴⁺-O bond of 1.607 Å, four equatorial bonds of 1.992–1.996 Å, and one bond of 2.267 Å). Both the short vanadyl and long V⁴⁺-O bonds are to the O(2) site and are *trans* to each other (Fig. 1). This type of strongly distorted octahedral coordination of the V⁴⁺ cations is well known and was identified by Schindler *et al.* (2000) as a [1 + 4 + 1] coordination. The symmetrically independent S⁶⁺ cation

TABLE 1. CHEMICAL COMPOSITION OF PAUFLERITE

Constituent	Wt.%	Range	Standard deviation	Probe standard
VO ₂	50.40	49.80 - 50.90	0.54	V
SO ₃	49.30	48.60 - 49.80	0.53	celestine
Total	99.70			

Empirical formula (based on five atoms of oxygen *apfu*): V_{0.99}S_{1.01}O₅.
Simplified formula: VO(SO₄)
Ideal composition: VO, 50.88, SO₃, 49.12, Total 100.00 wt.%.

TABLE 2. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR PAUFLERITE

<i>a</i> (Å)	7.3890(13)	Crystal size (mm)	0.08 × 0.04 × 0.008
<i>b</i> (Å)	6.2740(11)	Radiation	MoKα
<i>c</i> (Å)	7.0788(11)	Total reflections	2957
<i>V</i> (Å ³)	328.16(10)	Unique reflections	489
Space group	<i>Pnma</i>	Unique [<i>F</i> _o] > 4σ <i>F</i> _o]	457
<i>F</i> ₀₀₀	316	<i>R</i> ₁	0.034
μ (cm ⁻¹)	3.528	<i>wR</i> ₂	0.086
<i>Z</i>	4	<i>S</i>	1.119
<i>D</i> _{calc} (g/cm ³)	3.299		

Note: *R*₁ = Σ||*F*_o|| - ||*F*_c|| / Σ||*F*_o||; *wR*₂ = {Σ[w(*F*_o² - *F*_c²)²] / Σ[w(*F*_o²)²]}^{1/2};
w = 1/[σ²(*F*_o²) + (*aP*)² + *bP*], where *P* = (*F*_o² + 2*F*_c²)/3;
σ = {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.

TABLE 3. COORDINATES AND DISPLACEMENT PARAMETERS OF ATOMS IN PAUFLERITE

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
V	0.33473(10)	¼	0.26710(11)	0.0082(2)	0.0096(4)	0.0060(3)	0.0091(4)	0	-0.0020(2)	0
S	0.37696(12)	¾	0.36810(14)	0.0064(2)	0.0063(4)	0.0055(4)	0.0074(5)	0	-0.0006(3)	0
O(1)	0.3752(3)	0.5627(4)	0.2434(3)	0.0120(5)	0.0191(11)	0.0055(10)	0.0115(10)	-0.0019(8)	0.0005(8)	-0.0005(8)
O(2)	0.1264(4)	¼	0.3324(5)	0.0127(6)	0.0094(13)	0.0139(15)	0.0146(16)	0	-0.0009(12)	0
O(3)	0.5448(4)	¾	0.4807(4)	0.0124(6)	0.0084(13)	0.0198(15)	0.0088(14)	0	-0.0029(11)	0
O(4)	0.2157(4)	¾	0.4901(5)	0.0125(6)	0.0101(14)	0.0196(15)	0.0078(14)	0	0.0018(11)	0

is tetrahedrally coordinated by four O^{2-} anions, with a mean $\langle S^{6+}-O \rangle$ bond length of 1.470 Å, very close to the mean $\langle S^{6+}-O \rangle$ bond length of 1.473 Å calculated for sulfate minerals by Hawthorne *et al.* (2000).

The bond-valence analysis was performed using the $V^{4+}-O$ and $S^{6+}-O$ bond-valence curves taken from Brown & Altermatt (1985). The bond-valence sums are 4.15, 6.05, 2.09, 1.88, 2.07 and 2.07 valence units (vu) for the V, S, O(1), O(2), O(3) and O(4) sites, respectively, and are in a good agreement with the expected values.

Description of the structure

The structure of paufferite consists of a three-dimensional (3D) framework of distorted $V^{4+}O_6$ octahedra and SO_4 tetrahedra. The $V^{4+}O_6$ octahedra share the O(2) corners to produce $[V^{4+}O_5]$ chains extending along the x axis so that short vanadyl ($V=O$) and long ($V\cdots O$) bonds alternate along the chain extension: $\dots V=O\cdots V=O\cdots V=O\dots$ (Fig. 1). The chains of octahedra are linked into the 3D framework by sharing corners with SO_4 tetrahedra (Fig. 2). Note that each SO_4 tetrahedron shares two of its corners with two octahedra of the same

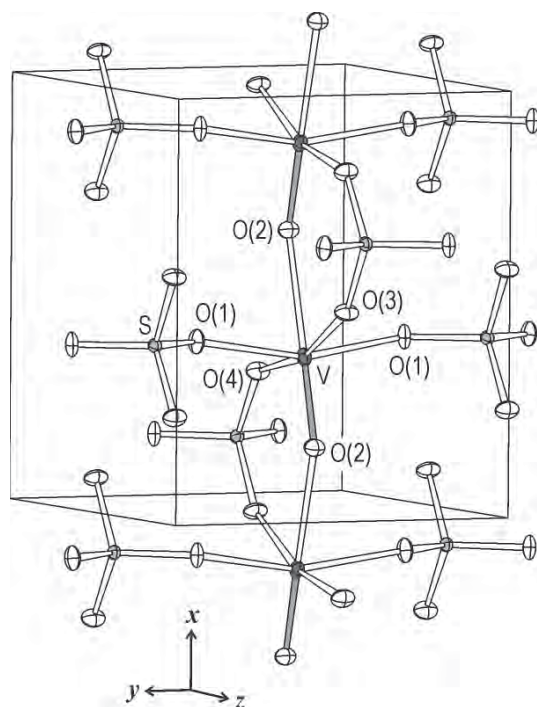


FIG. 1. Fragment of the crystal structure of paufferite showing one chain of $V^{4+}O_6$ octahedra and adjacent SO_4 tetrahedra. The short vanadyl $V^{4+}-O(2)$ bonds are shown as grey. Legend: O: white, V: dark grey, S: light grey. Ellipsoids are drawn at 50% probability level.

chain, which causes bending of the chain within the (010) plane (Fig. 1). The other two corners of the SO_4 tetrahedron are shared with octahedra from two adjacent chains. Thus, each tetrahedron shares its four corners with octahedra from three different $[V^{4+}O_5]$ chains.

Note on the powder-diffraction pattern

Because of the paucity of the material available, we were unable to obtain any reliable powder-diffraction pattern of paufferite. However, paufferite has a synthetic analogue with a well-defined powder pattern (PDF #19-1400). The X-ray powder-diffraction pattern calculated from the single-crystal data determined for natural material is in excellent agreement with that reported for the synthetic analogue (Table 5).

DISCUSSION

Paufferite is a natural analog of the β -modification of the anhydrous V^{4+} oxosulfate, $VO(SO_4)$. The structure of the synthetic β - $VO(SO_4)$ was first reported by Kierkegaard *et al.* (1965) and refined by Boghosian *et al.* (1995). Its details are essentially the same as those we have obtained for the natural material. The structure of another polymorph, α - $VO(SO_4)$, was determined by Longo & Arnott (1970). Its backbone is again a chain of corner-sharing $V^{4+}O_6$ octahedra linked into a 3D framework through SO_4 tetrahedra. However, in the framework of the α polymorph, each SO_4 tetrahedron shares corners with octahedra from four different $[V^{4+}O_5]$ chains. Thus, the α - and β - $VO(SO_4)$ frameworks can be considered as combinatorial polymorphs in the sense of Moore (1970, 1975). The difference between the two frameworks can be described using a nodal representation of their local topology (Krivovichev 2004, 2005). With this approach, the octahedron-tetrahedron framework is symbolized by a black-and-white graph with black and white nodes corresponding to the octahedra and tetrahedra, respectively. The nodes are linked where a linkage is present between their respective polyhedra. The frameworks of the α and β polymorphs of $VO(SO_4)$ can be considered as being based upon chains of corner-sharing octahedra surrounded by tetrahedra. These chains are shown in Figures 3e and 3g for the β and α modifications, respectively. The corresponding graphs

TABLE 4. SELECTED BOND-LENGTHS (Å) IN THE STRUCTURE OF PAUFFERITE

V-O(2)	1.607(3)	S-O(1)	1.469(2)
V-O(1)	1.992(2)	S-O(1)	1.469(2)
V-O(1)	1.992(2)	S-O(4)	1.472(3)
V-O(3)	1.995(3)	S-O(3)	1.474(3)
V-O(4)	1.996(3)	$\langle S-O \rangle$	1.470
V-O(2)	2.267(3)		
$\langle V-O \rangle$	1.975		

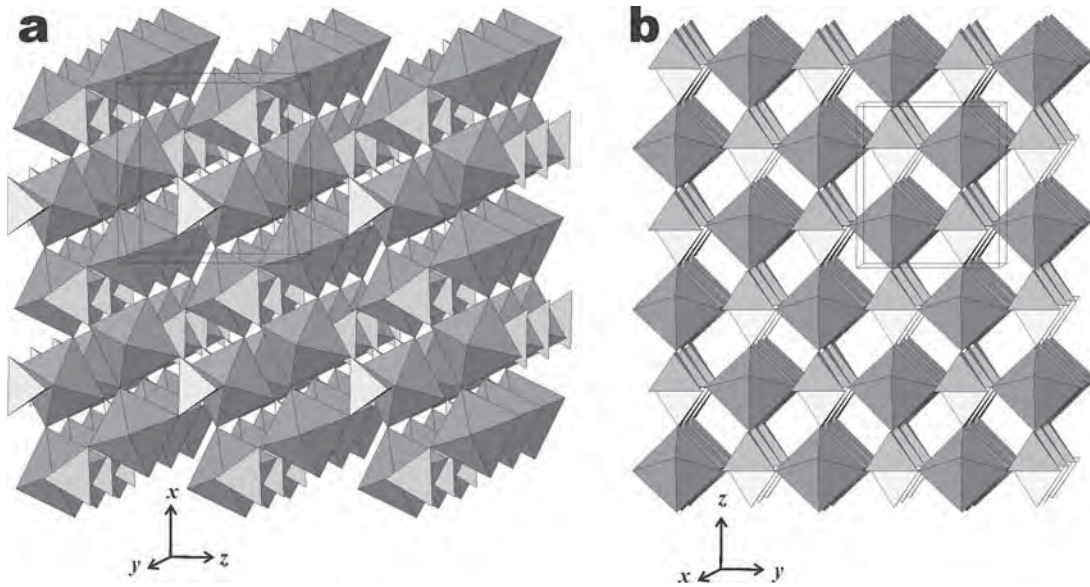


FIG. 2. The structure of paufferite shown along directions approximately perpendicular (a) and parallel (b) to the chains of $V^{4+}O_6$ octahedra. Legend: $V^{4+}O_6$ octahedra: grey; SO_4 tetrahedra: light grey.

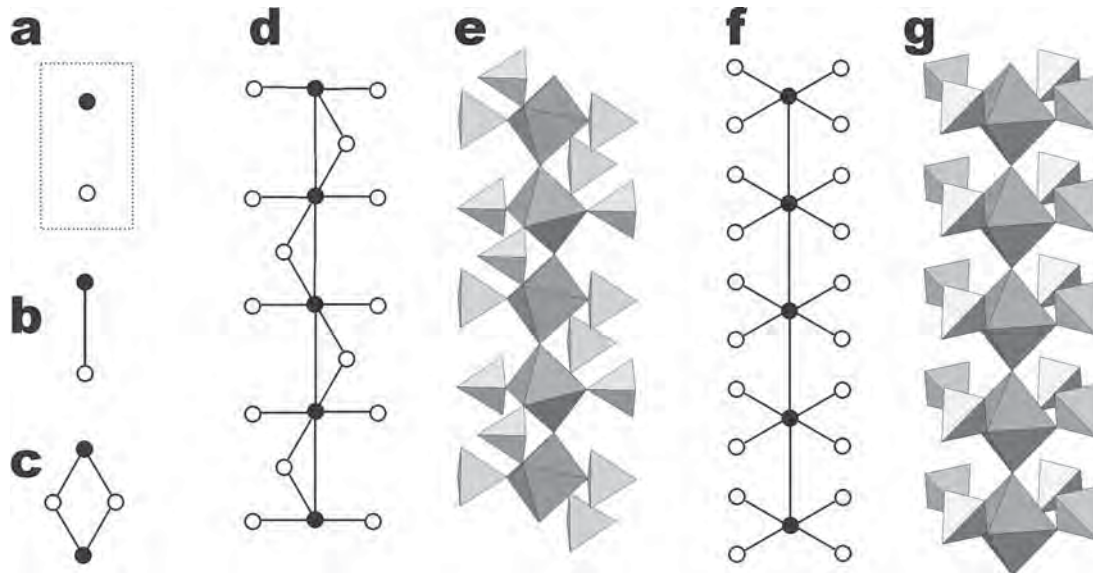


FIG. 3. Black-and-white graphs describing octahedron–tetrahedron units in stanleyite and orthominasragrite (a), minasragrite (b) and anorthominasragrite and bobjonesite (c); black-and-white graphs of the chains of octahedra and tetrahedra in the structures of paufferite (d) and $\alpha\text{-VO}(\text{SO}_4)$ (f), and the chains themselves (e, g, respectively). Legend as in Figure 2.

TABLE 5. X-RAY POWDER-DIFFRACTION DATA FOR PAUFLERITE

<i>hkl</i>	Data for synthetic compound (PDF 19-1400)		Data calculated on basis of structure refinement of paufferite	
	<i>d</i> , Å	<i>I</i>	<i>d</i> , Å	<i>I</i>
1 0 1	5.11	80	5.11	27
0 1 1	4.69	80	4.70	18
1 1 1	3.96	60	3.96	13
2 0 0	3.68	20	3.69	6
0 0 2	3.54	80	3.54	31
2 0 1	3.27	100	3.28	100
1 0 2	3.19	80	3.19	22
0 2 0	3.14	90	3.14	73
2 1 1	2.90	40	2.90	13
1 1 2	2.845	60	2.845	18
1 2 1	2.673	40	2.674	10
2 0 2	2.552	10	2.556	3
2 2 0	2.386	20	2.391	3
2 2 1	2.262	40	2.265	8
1 2 2	2.237	60	2.237	17
0 1 3	2.209	40	2.209	17
3 1 1	2.176	10	2.181	2
1 1 3	2.115	10	2.116	3
3 0 2	2.018	10	2.022	2
0 3 1	2.001	90	2.006	13
2 0 3	1.989	60	1.989	10
2 2 2	1.980	10	1.981	3
1 3 1	1.933	10	1.936	2
2 1 3	1.894	20	1.896	2
4 0 0	1.843	20	1.847	9
2 3 0	-	-	1.820	3
4 0 1	-	-	1.787	4
4 1 0	-	-	1.772	3
0 0 4	1.770	40	1.770	4
2 3 1	1.760	20	1.762	3
1 3 2	1.748	40	1.749	4
1 0 4	1.721	10	1.721	1
3 0 3	1.702	20	1.704	3
3 2 2	1.697	20	1.699	3
3 1 3	1.644	20	1.644	3
4 0 2	1.635	40	1.638	10
2 3 2	1.618	40	1.619	6
4 1 2	1.582	10	1.585	5
0 4 0	1.567	90	1.569	10

(Figs. 3d, f) are topologically different, which illustrates the difference between the two frameworks.

It is noteworthy that the topology of the octahedron-tetrahedron framework in paufferite is identical to the topology of sulfates belonging to the kieserite group of minerals $M^{2+}SO_4(H_2O)$ ($M = Mn, Fe, Co, Ni, Zn$) (Wildner & Giester 1991, Hawthorne *et al.* 1987, 2000). In turn, the topology of kieserite is the same as that of the titanosilicate framework in the structure of titanite, $Ca[TiO(SiO_4)]$. Thus, paufferite is a new member of a large family of minerals based upon a framework of octahedra and tetrahedra with the topology of titanite.

Figures 3a, b and c show three graphs that correspond to the topologies of linkage of octahedra and tetrahedra in the structures of natural $VO(SO_4)(H_2O)_n$ sulfates ($n = 3, 5, 6$). There is no linkage between tetrahedra and octahedra in stanleyite and orthominasragrite (Fig. 3a), whereas in minasragrite, each octahedron has a tetrahedron attached (Fig. 3b). In anorthominasragrite

and bobjonessite, octahedra and tetrahedra form four-membered rings $[V_2O_2(SO_4)_2(H_2O)_6]$ (Fig. 3c).

Paufferite is another vanadium mineral that has been discovered in volcanic fumaroles. The V mineralization is common in fumarolic environments and has been observed at a number of localities all over the world; Krivovichev *et al.* (2005) provided relevant references. However, paufferite is the only vanadium sulfate found in fumaroles so far.

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