

Filatovite, $K[(Al,Zn)_2(As,Si)_2O_8]$, a new mineral species from the Tolbachik volcano, Kamchatka peninsula, Russia

LIDIYA P. VERGASOVA¹, SERGEY V. KRIVOVICHEV^{2,3,*}, SERGEY N. BRITVIN⁴, PETER C. BURNS⁵
and VLADIMIR V. ANANIEV¹

¹Institute of Volcanology, Russian Academy of Sciences, Bulvar Piypa 9, Petropavlovsk-Kamchatskiy 683006, Russia

²Dept. of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg Russia

³Institut für Geowissenschaften – Mineralogie/Kristallographie, Christian-Albrechts-Universität zu Kiel, Olshausenstrasse 40, 24118 Kiel, Germany

⁴Department of Mineral Deposits, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia

⁵Department of Civil Engineering and Geological Sciences, 156 Fitzpatrick, University of Notre Dame, Notre Dame IN 46556-0767 U.S.A.

Abstract: Filatovite, ideally $K[(Al,Zn)_2(As,Si)_2O_8]$, has been found in products of fumarolic activity on the second cinder cone of the North breach of the great fissure Tolbachik eruption (1975-76, Kamchatka peninsula, Russia). The mineral occurs as prismatic crystals up to 0.3 mm and as intergrowths of crystals, in association with alumoklyuchevskite, lammerite, johillerite, sylvite, As-bearing orthoclase, hematite and tenorite. Filatovite is colourless, with vitreous luster and white streak. The mineral is brittle and transparent. It has a good {100} cleavage. Mohs' hardness is 5-6. The calculated density is 2.92 g/cm³. Biaxial, optically negative, $\alpha = 1.532(1)$, $\beta = 1.535(1)$, $\gamma = 1.537(1)$, $2V_{meas.} = 60(10)^\circ$, $2V_{calc.} = 78^\circ$. Optical orientation: X ~ [100], Y and Z are normal to the {001} and {010} faces, respectively. No pleochroism has been observed. The mineral is monoclinic, space group $I2/c$, $a = 8.772(1)$, $b = 13.370(2)$, $c = 14.690(2)$ Å, $\beta = 115.944(6)^\circ$, $V = 1549.1(4)$ Å³, $Z = 8$ (from single-crystal structure study). The diagnostic lines of the X-ray powder diffraction pattern are ($I-d-hkl$): 70-4.329-202; 70-3.897-130; 100-3.364-220, 204, 040; 50-3.300-004, 40-3.066-132, 60-2.981-042, 40-2.646-242. Chemical composition (wt. %): P₂O₅ 1.63, As₂O₅ 40.60, SiO₂ 12.35, Al₂O₃ 27.33, CuO 0.83, ZnO 3.85, FeO 0.28, Na₂O 0.63, K₂O 12.85, total 100.35. The empirical formula of filatovite, calculated on the basis of O = 8, is $(K_{0.92}Na_{0.07})_{\Sigma=0.99}[(Al_{1.81}Zn_{0.16}Cu_{0.04}Fe_{0.01})_{\Sigma=2.02}(As_{1.20}Si_{0.70}P_{0.08})_{\Sigma=1.98}O_8]$. The simplified formula is $K[(Al,Zn)_2(As,Si)_2O_8]$. The detailed chemical formula can be written as $K[(Al_{2-x}Zn_x)(As_{1+x}Si_{1-x})O_8]$, with $x \sim 0.20$. Filatovite is a new mineral of the feldspar group and is structurally related to celsian. The name honors Prof. Stanislav K. Filatov (b. 1940), Department of Crystallography, St. Petersburg State University, St. Petersburg, Russia, for his important contributions to high temperature crystal chemistry and crystal chemistry of exhalation minerals.

Key-words: filatovite, arsenic, feldspar group, Tolbachik volcano, Russia.

Introduction

Arsenic is one of the relatively low abundance elements in the lithosphere. Its total concentration in Earth's crust is estimated as 1.0-1.8 mg·kg⁻¹ (Taylor & McLennan, 1995; Wedepohl, 1995; Lide, 1996; Matschullat, 2000). Most arsenate minerals are of secondary origin due to the tendency of As to concentrate in fluids and vapors, and its low solubility in naturally occurring melts. Generally, As and P may only be incorporated into major rock-forming minerals in small quantities. For example, feldspars, the most abundant rock-forming minerals in the crust, only contain up to 1.2 wt. % P₂O₅ (Kontak *et al.*, 1996; Deer

et al., 2001). The substitution scheme is 2Si ↔ Al + P and the occurrence of P-bearing alkali feldspars is associated with peraluminous granites, pegmatites and rhyolites (London, 1992). Arsenic is even more volatile than phosphorus. For instance, Mambo *et al.* (1991) reported that the partition coefficient $(As/P)_{gas}/(As/P)_{rock}$ in volcanic environments is in the range from 10⁴ to 10⁵.

In this paper, we report the discovery of a feldspar-group mineral that has As as a major chemical constituent, with As₂O₅ reaching 41.9 wt. %. The mineral is named filatovite, in honour of Prof. Stanislav K. Filatov (b. 1940), Department of Crystallography, St. Petersburg State University, St. Petersburg, Russia, for his important contri-

* correspondence author. E-mail: skrivovi@mail.ru.

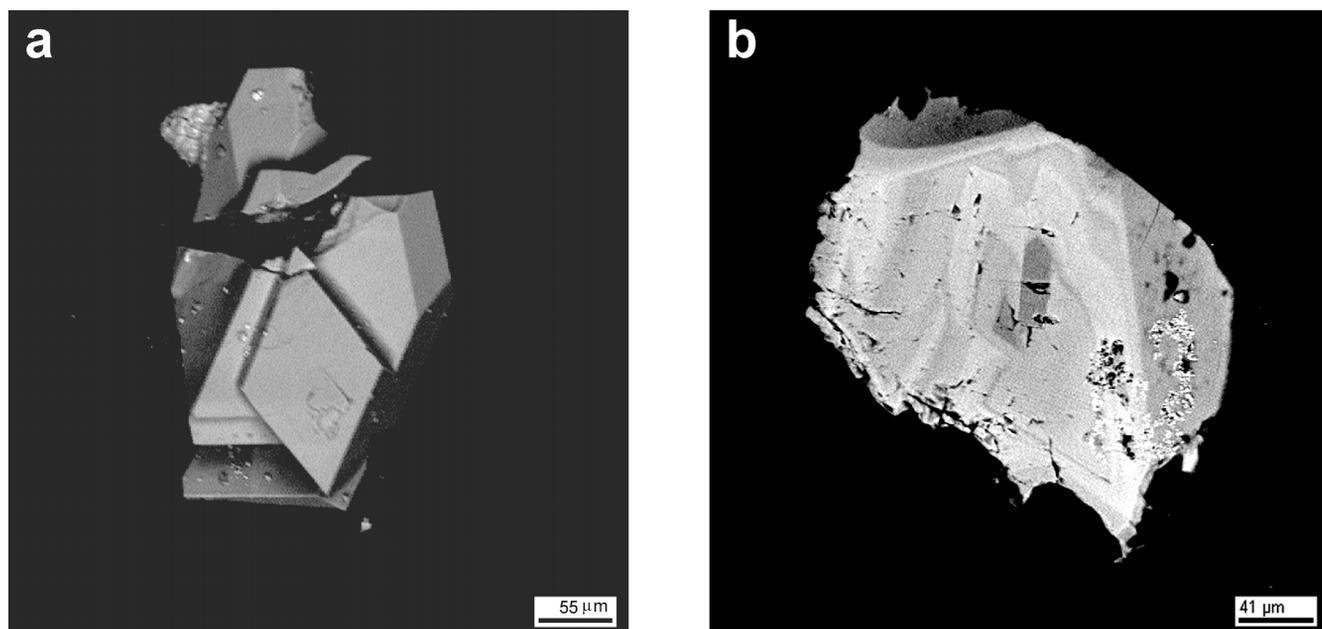


Fig. 1. SEM image of the intergrown crystals of filatovite (a) and backscattered electron image of one of the filatovite grains used for chemical analyses (b). The difference in color in (b) is caused by a variable As content.

butions to high temperature crystal chemistry and crystal chemistry of exhalation minerals (see, *e.g.* Filatov, 1990). Type material is deposited in the Museum of Department of Mineralogy, St. Petersburg State University, St. Petersburg, Russia (catalogue # 1/19086). The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names, IMA (2002-052).

Locality and occurrence

Filatovite was found in fumaroles of the Great fissure Tolbachik eruption (GFTE), Kamchatka peninsula, Russia. 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.

Beginning in the late 1970s, fumarolic activity of the GFTE resulted in the crystallization of a unique mineral assemblage, with twenty-four new mineral species discovered to date. Crystals of filatovite were found in 1980 and 1983 in products of fumarolic activity on the second cinder cone of the North breach of GFTE. The temperature of gases in the fumarole where it was found were ~ 410-420°C.

Filatovite is associated with alumoklyuchevskite, lammerite, johillerite, sylvite, As-bearing orthoclase, hematite and tenorite. The mineral occurs as prismatic crystals up to 0.3 mm and intergrowths of crystals (Fig. 1a), in close association with elongated crystals of As-bearing orthoclase. Separation of filatovite from orthoclase is always a problem and only minor amount of pure filatovite was available for study.

Chemical composition

Several grains of filatovite (< 0.3 mm in size) were mounted in epoxy and chemically analyzed at 15 kV and 10 nA with a Cameca SX-50 electron microprobe. The following standards were used: sanidine (Na, K, Si), synthetic apatite (P), spinel (Al), arsenopyrite (As), zincite (Zn), chalcopyrite (Cu) and hematite (Fe). No elements other than those mentioned above were detected. The results of the analyses are summarized in Table 1. The empirical formula of filatovite, calculated on the basis of O = 8, is $(K_{0.92}Na_{0.07})_{\Sigma=0.99}[(Al_{1.81}Zn_{0.16}Cu_{0.04}Fe_{0.01})_{\Sigma=2.02}(As_{1.20}Si_{0.70}P_{0.08})_{\Sigma=1.98}O_8]$. The simplified formula is $K[(Al_{1-x}Zn_x)(As_{1+x}Si_{1-x})O_8]$, with $x \sim 0.20$ in the crystals studied. Considering $K[AlSi_3O_8]$ as an ideal formula of orthoclase, the chemical transition from orthoclase to fila-

Table 1. Chemical composition of filatovite

| Constituent | wt. % | Range |
|--------------------------------|--------|-----------|
| P ₂ O ₅ | 1.63 | 1.1-3.7 |
| As ₂ O ₅ | 40.60 | 39.9-41.9 |
| SiO ₂ | 12.35 | 11.3-13.7 |
| Al ₂ O ₃ | 27.33 | 26.3-28.5 |
| ZnO | 3.85 | 3.5-4.3 |
| CuO | 0.83 | 0.7-0.9 |
| FeO | 0.28 | 0.2-0.3 |
| Na ₂ O | 0.63 | 0.0-1.2 |
| K ₂ O | 12.85 | 12.3-13.2 |
| Total | 100.35 | |

Empirical formula (based upon O = 8):

$(K_{0.92}Na_{0.07})_{\Sigma=0.99}[(Al_{1.81}Zn_{0.16}Cu_{0.04}Fe_{0.01})_{\Sigma=2.02}(As_{1.20}Si_{0.70}P_{0.08})_{\Sigma=1.98}O_8]$.

Simplified formula: $K[(Al,Zn)_2(As,Si)_2O_8]$

toivite is described using the substitution schemes $2\text{Si}^{4+} \leftrightarrow \text{Al}^{3+} + \text{As}^{5+}$ and $\text{Al}^{3+} + \text{Si}^{4+} \leftrightarrow \text{Zn}^{2+} + \text{As}^{5+}$. Note that complete substitution according to the first scheme results in the composition $\text{K}[\text{Al}_2\text{AsSiO}_8]$, whereas the second scheme is responsible for the incorporation of Zn into the Al site and As into the Si site. According to the results of crystal-structure refinement reported by Filatov *et al.* (2004), filatovite has a celsian-type structure with two types of tetrahedral sites: one is solely occupied by Al and Zn, whereas the other contains As and Si. From the crystal-chemical viewpoint, it is reasonable to define filatovite as a mineral with the celsian structure type and with $\text{As} \geq \text{Si}$.

Physical and optical properties

Filatovite is colourless, with vitreous luster and white streak. The mineral is brittle and transparent. It has a good $\{100\}$ cleavage. Mohs' hardness is 5-6. The calculated density is 2.92 g/cm³. The experimental density could not be accurately measured due to many gaseous inclusions within the mineral grains. The mineral does not fluoresce in either short- or long-wave ultraviolet radiation.

Filatovite is optically negative, $\alpha = 1.532(1)$, $\beta = 1.535(1)$, $\gamma = 1.537(1)$, $2V_{\text{meas.}} = 60(10)^\circ$, $2V_{\text{calc.}} = 78^\circ$. The orientation: X \sim [100], Y and Z are normal to the $\{001\}$ and $\{010\}$ faces, respectively.

X-ray crystallography

Unit-cell parameters of filatovite were determined using a three-circle Bruker PLATFORM diffractometer equipped with a 4K SMART APEX CCD (charge-coupled device) detector and were further refined by crystal-structure analysis. The mineral is monoclinic, space group $I2/c$, $a = 8.772(1)$, $b = 13.370(2)$, $c = 14.690(2)$ Å, $\beta = 115.944(6)^\circ$, $V = 1549.1(4)$ Å³, $Z = 8$. Only a small amount of material was available for study, so X-ray powder-diffraction data (Table 2) were obtained using a Debye-Scherrer powder camera with a diameter of 114.6 mm (CuK α -radiation, $2\theta_{\text{max}} = 60^\circ$). The diagnostic lines of the X-ray powder diffraction pattern are (I - d - hkl): 70-4.329-202; 70-3.897-130; 100-3.364-220, 204, 040; 50-3.300-004, 40-3.066-132, 60-2.981-042, 40-2.646-242. The refined unit-cell parameters from the X-ray powder-diffraction pattern, $a = 8.80(1)$, $b = 13.39(1)$, $c = 14.69(1)$ Å, $\beta = 116.09(12)^\circ$, $V = 1555(2)$ Å³, are of poor quality but are in good agreement with the unit-cell parameters determined from single-crystal study. The details of crystal-structure refinement are reported by Filatov *et al.* (2004).

Discussion

Filatovite is the fifth new arsenate mineral discovered in the GFTE fumaroles. The three other minerals are alarsite, AlAsO_4 (Semenova *et al.*, 1994), coparsite, $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$

Table 2. Powder X-ray diffraction data of filatovite.

| $I/I_{o(\text{obs})}$ | $d_{\text{obs.}}$ | $I/I_{o(\text{calc})}^*$ | $d_{\text{calc.}}$ | hkl |
|-----------------------|-------------------|--------------------------|--------------------|------------------|
| 70 | 4.329 | 59 | 4.332 | $\overline{2}02$ |
| 70 | 3.897 | 75 | 3.886 | $\overline{1}30$ |
| 20 | 3.545 | 43 | 3.542 | $\overline{1}14$ |
| 100 | 3.364 | 100 | 3.403 | $\overline{2}20$ |
| | | 66 | 3.362 | 204 |
| | | 36 | 3.348 | 040 |
| 50 | 3.300 | 89 | 3.300 | 004 |
| 40 | 3.066 | 67 | 3.071 | 132 |
| 60 | 2.981 | 38 | 2.985 | 042 |
| 40 | 2.646 | 55 | 2.649 | $\overline{2}42$ |
| 10 | 2.228 | 33 | 2.232 | $\overline{0}60$ |
| 10 | 2.061 | 24 | 2.061 | $\overline{4}24$ |
| 5 | 1.894 | 11 | 1.894 | $\overline{1}16$ |
| 30 | 1.836 | 47 | 1.836 | $\overline{2}08$ |
| 20 | 1.543 | 54 | 1.541 | 280 |

* calculated on the basis of crystal-structure data using program PowderCell for Windows 1.0 (Kraus & Nolze, 1997).

(Vergasova *et al.*, 1999), urusovite, CuAlAsO_5 (Vergasova *et al.*, 2000), and bradaczekite, $\text{NaCu}_4(\text{AsO}_4)_3$ (Filatov *et al.*, 2001).

Filatovite is the first arsenate with a structure based upon a mixed-cation tetrahedral framework with the feldspar topology. Its discovery indicates that As has a strong affinity for the feldspar structure and, under appropriate conditions, may be incorporated into it. This also suggests that As may form complexes on the surface of the feldspar-group minerals. Indeed, Prasad (1994) and Singh *et al.* (1996) suggested the use of feldspar as an adsorbent for removal of arsenic from As^{5+} -rich solutions in treatment plants. Prasad (1994) identified surface complexation as a major process that controls removal of arsenic by feldspar. It is likely that complexation involves formation of an adsorbate layer in which AsO_4^{3-} tetrahedra polymerize with AlO_4^{5-} and SiO_4^{4-} tetrahedra, just as it is observed in the structure of filatovite.

The formation of filatovite in fumaroles may be the result of either of two processes: (a) direct deposition from As-rich volcanic gases and (b) metasomatic replacement of feldspar minerals (mainly orthoclase) already existing in volcanic tuffs. The latter scenario is more likely and may involve a dissolution-reprecipitation process known to be dominant in replacement reactions in alkali feldspars (Walker *et al.*, 1995) and other mineral systems (Korzhinskii, 1970; Glikin, 1995; Putnis, 2002). In this case, crystallographic information may be transferred from "parent" orthoclase to "daughter" filatovite that inherited the structural topology of the parent phase. Some evidence for this mechanism exists in the microporosity of filatovite crystals (Fig. 1b) and its close association with As-bearing orthoclase that may contain up to 18 wt. % of As_2O_5 . Detailed analysis of the chemical composition and structural characteristics of As-bearing orthoclase will be a subject of a separate paper.

Acknowledgements: We thank Frédéric Hatert and Mario Tribaudino for useful comments on the manuscript. This work was supported by the Russian Foundation for Basic research (RFBR, grant 03-05-64853). Collaboration between S.V.K. and P.C.B. was supported by the NATO Science Collaborative Linkage grant (EST.CLG.977834).

References

- Deer, W.A., Howie, R.A., Zussman, J. (2001): "Rock-Forming minerals" Vol. 4a. *Framework Silicates: Feldspars*. The Geological Society, London.
- Fedotov, S.A., ed. (1984): "The Great Fissure Tolbachik Eruption" Moscow, Nauka.
- Filatov, S.K. (1990): "High-Temperature Crystal Chemistry" Leningrad, Nedra (in Russian).
- Filatov, S.K., Vergasova, L.P., Gorskaya, M.G., Krivovichev, S.V., Ananiev V.V. (2001): Bradaczekite, $\text{NaCu}_4(\text{AsO}_4)_3$, a new mineral species from the Tolbachik Volcano, Kamchatka Peninsula, Russia. *Can. Mineral.*, **39**, 1115-1119.
- Filatov, S.K., Krivovichev, S.V., Burns, P.C., Vergasova L.P. (2004): Crystal structure of filatovite, $\text{K}[(\text{Al,Zn})_2(\text{As,Si})_2\text{O}_8]$, the first arsenate of the feldspar group. *Eur. J. Mineral.*, **16**, 537-543.
- Glikin, A.E. (1995): Theory of isomorphic-mixed crystal formation. *Zap. Vseross. Mineral. Obshch.*, **124**, 124-133 (in Russian).
- Kontak, D.J., Martin, R.F., Richard, L. (1996): Patterns in phosphorus enrichment in alkali feldspar, South Mountain batholith, Nova Scotia, Canada. *Eur. J. Mineral.*, **8**, 805-824.
- Korzhinskii, D.S. (1970): "Theory of Metasomatic Zoning" Clarendon Press, Oxford, U.K.
- Kraus, W. & Nolze, G. (1997): "PowderCell for Windows" Version 1.0. Federal Institute for Material Research and Testing, Berlin
- Lide, D.R., ed. (1996): "CRC Handbook of Chemistry and Physics" CRC Press, Boca Raton, U.S.A.
- London, D. (1992): Phosphorus in S-type magmas: the P_2O_5 content of feldspars from peraluminous granites, pegmatites and rhyolites. *Am. Mineral.*, **77**, 126-145.
- Mambo, V.S., Yoshida, M., Matsuo, S. (1991): Partition of arsenic and phosphorus between volcanic gases and rock. Part I: Analytical data and magmatic conditions of Mt. Usu, Japan. *J. Volcanol. Geotherm. Res.*, **46**, 37-47.
- Matschullat, J. (2000): Arsenic in the geosphere – a review. *Sci. Total Environ.*, **249**, 297-312.
- Prasad, G. (1994): Removal of arsenic(V) from aqueous systems by adsorption onto some geological materials. *Adv. Environ. Sci. Technol.*, **26**, 133-154.
- Putnis, A. (2002): Mineral replacement reactions: from macroscopic observations to microscopic mechanisms. *Min. Mag.*, **66**, 689-708.
- Semenova, T.F., Vergasova, L.P., Filatov, S.K., Anan'ev, V.V. (1994): Alarsite AlAsO_4 , a new mineral from volcanic sublimates. *Dokl. Akad. Nauk*, **338**, 501-505.
- Singh, D.B., Prasad, G., Rupainwar, D.C. (1996): Adsorption technique for the treatment of As(V)-rich effluents. *Coll. Surf. A: Physicochem. Eng. Asp.*, **111**, 49-56.
- Taylor, S.R., & McLennan, S.M. (1995): The geochemical evolution of the continental crust. *Rev. Geophys.*, **33**, 241-265.
- Vergasova, L.P., Starova, G.L., Krivovichev, S.V., Filatov, S.K., Ananiev, V.V. (1999): Coparsite, $\text{Cu}_4\text{O}_2[(\text{As,V})\text{O}_4]\text{Cl}$, a new mineral species from the Tolbachik Volcano, Kamchatka Peninsula, Russia. *Can. Mineral.*, **37**, 911-914.
- Vergasova, L.P., Filatov, S.K., Gorskaya, M.G., Molchanov, A.A., Krivovichev, S.V., Ananiev, V.V. (2000): Urusovite, $\text{Cu}[\text{AlAsO}_5]$, a new mineral from the Tolbachik volcano, Kamchatka, Russia. *Eur. J. Mineral.*, **12**, 1041-1044.
- Walker, F.D.L., Lee, M.R., Parsons, I. (1995): Micropores and micropore texture in alkali feldspars: geochemical and geophysical implications. *Min. Mag.*, **59**, 505-534.
- Wedepohl, K.H. (1995): The composition of the continental crust. *Geochim. Cosmochim. Acta*, **59**, 1217-1232.

Received 4 August 2003

Modified version received 24 October 2003

Accepted 2 February 2004