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**Pliniusite, Ca₅(VO₄)₃F, a new apatite-group mineral and the novel natural ternary solid-
solution system pliniusite–svabite–fluorapatite**

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28 **ABSTRACT**

29 The new apatite-group mineral pliniusite, ideally $\text{Ca}_5(\text{VO}_4)_3\text{F}$, was found in fumarole deposits at the
30 Tolbachik volcano (Kamchatka, Russia) and in a pyrometamorphic rock of the Hatrurim Complex
31 (Israel). Pliniusite, together with fluorapatite and svabite, forms a novel and almost continuous
32 ternary solid-solution system characterized by wide variations of $T^{5+} = \text{P, As and V}$. In paleo-
33 fumarolic deposits at Mountain 1004 (Tolbachik), members of this system, including the holotype
34 pliniusite, are associated with hematite, tenorite, diopside, andradite, kainotrope, baryte and
35 supergene volborthite, brochantite, gypsum and opal. In sublimates of the active Arsenatnaya
36 fumarole (Tolbachik), pliniusite–svabite–fluorapatite minerals occur with anhydrite, diopside,
37 hematite, berzeliite, schäferite, calciojohillerite, forsterite, enstatite, magnesioferrite, ludwigite,
38 rhabdorbite-group fluoroborates, powellite, baryte, udinaite, arsenudinaite, paraberzeliite, and
39 spinel. At Nahal Morag, Negev Desert, Israel, the pliniusite cotype and V-bearing fluorapatite occur
40 in schorlomite-gehlenite paralava with rankinite, walstromite, zadovite-aradite series minerals,
41 magnesioferrite, hematite, khesinite, barioferrite, perovskite, gurimite, baryte, tenorite, delafossite,
42 wollastonite and cuspidine. Pliniusite forms hexagonal prismatic crystals up to $0.3 \text{ mm} \times 0.1 \text{ mm}$
43 and open-work aggregates up to 2 mm across (Mountain 1004) or grains up to 0.02 mm (Nahal
44 Morag and Arsenatnaya fumarole). Pliniusite is transparent to semitransparent, colorless or whitish,
45 with vitreous lustre. The calculated density is 3.402 g cm^{-3} . Pliniusite is optically uniaxial (–), $\omega =$
46 $1.763(5)$, $\epsilon = 1.738(5)$. The empirical formulae of pliniusite type specimens calculated based on 13
47 anions (O+F+Cl) per formula unit are
48 $(\text{Ca}_{4.87}\text{Na}_{0.06}\text{Sr}_{0.03}\text{Fe}_{0.02})_{\Sigma 4.98}(\text{V}_{1.69}\text{As}_{0.66}\text{P}_{0.45}\text{S}_{0.12}\text{Si}_{0.09})_{\Sigma 3.01}\text{O}_{11.97}\text{F}_{1.03}$ (Mountain 1004) and
49 $(\text{Ca}_{4.81}\text{Sr}_{0.12}\text{Ba}_{0.08}\text{Na}_{0.05})_{\Sigma 5.06}(\text{V}_{2.64}\text{P}_{0.27}\text{S}_{0.07}\text{Si}_{0.03})_{\Sigma 3.01}\text{O}_{12.15}\text{F}_{0.51}\text{Cl}_{0.34}$ (Nahal Morag). Pliniusite has a
50 hexagonal structure with space group $P6_3/m$, $a = b = 9.5777(7)$, $c = 6.9659(5) \text{ \AA}$, $V = 553.39(7) \text{ \AA}^3$
51 and $Z = 2$. The structure was solved using single-crystal (holotype) X-ray diffraction, $R = 0.0254$.
52 The mineral was named in honor of the famous Roman naturalist Pliny the Elder, born Gaius Plinius

53 Secundus (AD 23–79). It is suggested that the combination of high temperature, low pressure and
54 high oxygen fugacity favors the incorporation of V^{5+} into calcium apatite-type compounds, leading
55 to the formation of fluorovanadates.

56

57 **Keywords:** pliniusite, apatite group, new mineral, calcium fluoride vanadate, fluorapatite,
58 svabite, crystal structure, fumarole sublimate, pyrometamorphic rock, Tolbachik volcano, Hatrurim

59 Complex

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INTRODUCTION

63

64 The family of apatite-type compounds (apatites, in the common chemical terminology) is
65 huge. It includes more than forty natural members, valid mineral species belonging to the apatite
66 supergroup, and several hundred synthetic phases. This family is well-known and does not need a
67 special presentation, as well as the importance of apatites in natural sciences, modern technologies
68 and human life in general (Kohn et al. 2002).

69 The general simplified formula of apatites is $M_5(TO_4)_3X$ and the crystal chemical formula is
70 ${}^{IX}M1_2{}^{VII}M2_3({}^{IV}TO_4)_3X$ ($Z = 2$), where the Roman numerals indicate the ideal coordination numbers.

71 Apatite-type compounds are hexagonal or pseudo-hexagonal. The space group of the archetype
72 structure of apatite is $P6_3/m$. In minerals of the apatite supergroup, the following components are
73 now known as the species-defining ones: $M = Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+}, Na^+, Y^{3+}, La^{3+},$
74 $Ce^{3+}, Nd^{3+}, Bi^{3+}; T = P^{5+}, As^{5+}, V^{5+}, Si^{4+}, S^{6+}, B^{3+}; X = F^-, (OH)^-, Cl^-, O^{2-}$ (Pasero et al. 2010; The
75 [New IMA List... 2021](#)). Based on both chemical and crystal chemical (first of all, ordering of metal
76 cations between different M sites) criteria, five groups have been distinguished within the apatite
77 supergroup: apatite group, hedyphane group, belovite group, britholite group, and ellestadite group.
78 The most widespread in nature and the most numerous apatite-supergroup members belong to the
79 apatite group which includes minerals with pentavalent T constituents ($T^{5+} = P, As$ or V) containing
80 the same prevailing (species-defining) bivalent cation at both the $M1$ and $M2$ sites (Pasero et al.
81 [2010](#)).

82 Phosphates and arsenates are the most diverse among apatite-supergroup minerals. In
83 contrast, natural apatite-type vanadates before recently were represented by the only species
84 vanadinite $Pb_5(VO_4)_3Cl$, a member of the apatite group ([The New IMA List... 2021](#)). In this paper
85 we describe the second natural apatite-supergroup vanadate, **pliniusite**, ideally $Ca_5(VO_4)_3F$. This

86 new mineral belonging, like vanadinite, to the apatite group, originates from fumaroles of the
87 Tolbachik volcano (Kamchatka, Russia) and from pyrometamorphic rocks of the Hatrurim Complex
88 (Israel).

89 Pliniusite (Cyrillic: **ПЛИНИУСИТ**) was named in honor of the famous Roman naturalist, natural
90 philosopher, author and statesman Pliny the Elder, born Gaius Plinius Secundus (AD 23–79), who
91 wrote the encyclopedic *Naturalis Historia*, which became, in fact, a model for encyclopedias in
92 general. He observed the famous eruption of the Vesuvius volcano in 79 AD and died as a victim of
93 this catastrophic eruption; this kind of volcanic eruptions was named in his memory a Plinian
94 eruption. It is worthy to note that the holotype pliniusite was formed at the Tolbachik volcano during
95 or immediately after the ancient eruption happened about two thousand years ago, approximately in
96 the same time when Pliny the Elder lived.

97 Both the new mineral and its name have been approved by the Commission on New
98 Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA No.
99 2018–031). The type specimens are deposited in the systematic collection of the Fersman
100 Mineralogical Museum of the Russian Academy of Sciences, Moscow under the catalogue numbers
101 96261 (Tolbachik) and 96262 (Hatrurim).

102 Vanadium is an exotic constituent in the majority of apatite-supergroup minerals, whereas many
103 synthetic apatites with various V^{5+} contents at the *T* site are known ([White et al. 2005](#)). In this light, we
104 considered of interest to characterize the novel ternary solid-solution system between fluorapatite
105 $Ca_5(PO_4)_3F$, svabite $Ca_5(AsO_4)_3F$ and pliniusite with wide variations of the tetrahedrally coordinated
106 constituents $T^{5+} = P, As$ and V .

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108

ANALYTICAL METHODS

109

110 The chemical composition of the minerals was determined by electron microprobe in two
111 laboratories. The chemical data for samples from Tolbachik were obtained in the Laboratory of
112 Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University
113 (MSU) using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500
114 wavelength-dispersive spectrometer, with an acceleration voltage of 20 kV, a beam current of 20
115 nA, and a 3 μm beam diameter. Pliniusite from Hatrurim was examined at the Institute of
116 Geochemistry, Mineralogy and Petrology, University of Warsaw (UW) using a Cameca SX100
117 instrument (WDS mode, 15 kV, 10 nA, 1 μm beam diameter). The reference materials used are as
118 follows (MSU / UW): Na (jadeite / albite), K (KTiOPO₄ / orthoclase), Ca (CaSiO₃ / diopside), Fe
119 (FeS₂ / Fe₂O₃), Sr (SrSO₄ / SrSO₄), Ba (BaSO₄ / BaSO₄), Si (jadeite / diopside), P (KTiOPO₄ /
120 Ca₅P₃O₁₂F), V (V / V₂O₅), As (GaAs / GaAs), S (ZnS / BaSO₄), F (MgF₂ / Ca₅P₃O₁₂F), and Cl
121 (NaCl / tugtupite). Contents of other elements with atomic numbers higher than that of carbon are
122 below detection limits.

123 The electron microscopic studies of Tolbachik samples were carried out using the same
124 scanning electron microscope at MSU. The samples from Hatrurim were studied using a Phenom
125 XL scanning electron microscope, Faculty of Earth Sciences, University of Silesia, Sosnowiec,
126 Poland.

127 Raman spectra of pliniusite from both localities were collected using a WITec alpha 300R
128 Confocal Raman Microscope (Department of Earth Science, University of Silesia) equipped with an
129 air-cooled solid-state laser (532 nm) and a CCD camera operating at -61°C . An air Zeiss LD EC
130 Epiplan-Neofluar DIC-100/0.75NA objective was used. Raman scattered light was focused on a
131 broadband single-mode fibre with an effective pinhole size of about 30 μm . A monochromator with
132 a 600 gr mm^{-1} grating was used, and the resolution was 3 cm^{-1} . The power of the laser at the sample
133 position was *ca.* 30 mW. Integration times of 3 s with an accumulation of 30 scans were chosen. The
134 monochromator was calibrated using the Raman scattering line of a silicon plate (520.7 cm^{-1}).

135 Spectra processing such as baseline correction and smoothing was performed using the SpectraCalc
136 software package GRAMS (Galactic Industries Corporation, NH, USA). The fitting of Raman
137 spectra was performed using a Gauss and Lorentz cross-product function, with a minimum number
138 of component bands used for the fitting process.

139 Powder X-ray diffraction (XRD) of the holotype pliniusite was carried out using a Rigaku R-
140 AXIS Rapid II single-crystal diffractometer equipped with a curved image plate detector (Debye-
141 Scherrer geometry, $r = 127.4$ mm) and $\text{CoK}\alpha$ radiation source (rotating anode, 40 kV, 15 mA), with
142 Rigaku VariMax microfocus mirror optics. Imaging plate-to-profile data conversion was performed
143 using osc2xrd software (Britvin et al. 2017).

144 Single-crystal XRD of the holotype pliniusite was carried out using an Xcalibur S CCD
145 diffractometer ($\text{MoK}\alpha$ radiation). A full sphere of three-dimensional data was collected. Data
146 reduction was performed using CrysAlisPro Version 1.171.37.35 (Agilent et al. 2014). The data
147 were corrected for Lorentz and polarization effects. The structure was solved by direct methods and
148 refined with the use of SHELX software package (Sheldrick 2008) on the basis of 416 independent
149 reflections with $I > 2\sigma(I)$ to $R = 0.0254$ in the frame of space group $P6_3/m$. Trials to lower the
150 symmetry to $P6_3$, $P2_1/m$ or $P-1$ (two latter space groups were reported for synthetic vanadate
151 apatites: see below) did not result in any improvement of the structural model and the R value
152 increased in all these cases. A complete set of crystallographic data can be retrieved from the CIF
153 file attached as the Supplementary Material.

154

155

RESULTS AND DISCUSSION

156 Occurrence and mineral associations

157 The holotype of pliniusite originates from the Tolbachik volcano. This material was collected
158 in July 2017 from paleo-fumarolic deposits of the Southern fumarole field at Mountain 1004, a
159 scoria cone located 20 km SSW of the active volcano Ploskiy Tolbachik. Mountain 1004 is a

160 monogenetic volcano formed as a result of an ancient eruption of Tolbachik, approximately two
161 thousand years ago ([Fedotov and Markhinin 1983](#)). All fumaroles at Mountain 1004 are extinct;
162 however, some water-insoluble sublimate minerals are well-preserved to date. The members of the
163 pliniusite–svabite–fluorapatite solid-solution system are associated here with hematite, tenorite,
164 diopside, andradite, kainotrope, and baryte. The secondary mineralization, formed as a result of the
165 supergene alteration of unstable sublimate minerals, is represented by volborthite, brochantite,
166 gypsum and opal.

167 In 2018, pliniusite and V-rich varieties of svabite and fluorapatite were found in the active
168 Arsenatnaya fumarole located at the Second scoria cone of the Northern Breakthrough of the Great
169 Tolbachik Fissure Eruption of 1975–1976. This scoria cone is a monogenetic volcano formed in
170 1975. It is situated 2 km north of Mountain 1004 and demonstrates strong fumarole activity at
171 present day. The Arsenatnaya fumarole is one of the most mineralogically interesting fumaroles at the
172 Tolbachik volcano and, in general, one of the brightest representatives of strongly mineralized
173 oxidizing-type fumaroles in the world. From the mineralogical point of view, this fumarole was
174 characterized, including the data on zonation in distribution of mineral associations, by [Pekov et al.](#)
175 [\(2018\)](#) and [Shchipalkina et al. \(2020\)](#). Minerals of the pliniusite–svabite–fluorapatite solid-solution
176 system were found in the deepest and hottest zone of the Arsenatnaya fumarole. It is located at the
177 depth of 3–4 m under day surface; temperatures in the pockets with these minerals measured by us
178 using a chromel–alumel thermocouple were 450–490°C. The associated minerals include anhydrite,
179 diopside, hematite, berzeliite, schäferite, calciojohillerite and subordinate forsterite, enstatite,
180 magnesioferrite, ludwigite, rhabdoborite-group fluoroborates, powellite, baryte, wagnerite (As-
181 bearing variety), udinaite, arsenudinaite, paraberzeliite, and spinel.

182 The cotype material of pliniusite originates from the Nahal Morag canyon area, about 10 km
183 southeast of Arad city, Negev Desert, Israel. The new mineral occurs in pyrometamorphic rocks
184 belonging to the Hatrurim Basin, which is one of the largest unit of the Hatrurim Complex. It is

185 generally recognised that terrigenous-carbonate protolith of the Hatrurim Complex was driven by
186 combustion processes. The geology and origin of the Hatrurim Complex have been discussed
187 previously in detail (Gross 1977; Burg et al. 1999; Novikov et al. 2013; Galuskina et al. 2014). The
188 Nahal Morag canyon crosscuts the central part of the Hatrurim Basin from west to east. In its eastern
189 part there are several cliff-like outcrops (up to 10 m across and up to 1 m in height) of gehlenite-
190 bearing rocks rising along the borders of Nahal Morag. At least in part of them coarse-grained veins
191 (typically 1–3 cm thick) of paralavas occur. Pliniusite was found in vein-like bodies of schorlomite-
192 gehlenite paralava hosted by melilite hornfels. The assemblage of major minerals of the paralavas
193 includes melilite of the gehlenite-alumoåkermanite series, garnet of the andradite-schorlomite series,
194 rankinite, fluorapatite, walstromite, minerals of the zadovite-aradite series, magnesioferrite,
195 hematite, khesinite, barioferrite, and Fe³⁺-enriched perovskite. Pliniusite is typically confined to
196 small oval polymineralic inclusions in rankinite and closely associated with gurimite, baryte,
197 walstromite, tenorite, delafossite, wollastonite, cuspidine and secondary Ca hydrosilicates.

198

199 **General appearance, physical properties and optical data of pliniusite**

200 At Mountain 1004 (Tolbachik), pliniusite and vanadium-bearing varieties of svabite and
201 fluorapatite, which are visually indistinguishable, occur as hexagonal prismatic (from long- to short-
202 prismatic, equant), usually distorted and/or skeletal, cavernous crystals up to 0.3 mm long and up to
203 0.05 mm (rarely up to 0.1 mm) thick. Crystals are isolated or, more commonly, form near-parallel or
204 chaotic clusters (Fig. 1) that are typically combined into open-work aggregates (Fig. 2) up to 2 mm
205 across. These crystals overgrow hematite crusts which cover the surface of the basalt scoria altered
206 by fumarolic gases. In some samples, members of the pliniusite–svabite–fluorapatite solid-solution
207 system occur on diopside aggregates or directly on basaltic scoria. The major forms of pliniusite
208 crystals from Mountain 1004 are the hexagonal prism {10-10} and the hexagonal bipyramid {10-
209 11}; the pinacoid {0001} is common but subordinate and the hexagonal bipyramid {11-21} is minor

210 and rare. Some crystals are zoned, with a pliniusite core and svabite peripheral parts, or with a
211 fluorapatite core and a pliniusite rim.

212 At the Arsenatnaya fumarole (Tolbachik), pliniusite and V-rich varieties of svabite and
213 fluorapatite occur inside sublimate incrustations mainly consisting of anhydrite, diopside, hematite,
214 garnets of the berzeliite–schäferite series, calciojohillerite, and V-poor svabite. Pliniusite forms
215 grains up to 0.02 mm.

216 In coarse-grained paralava at Nahal Morag (Hatrumim), pliniusite typically occurs in
217 polymineralic inclusions in rankinite (Figs. 3A and 3B). The new mineral forms grains commonly
218 not exceeding 15 μm in size; rarely, its elongated prismatic crystals up to 40 μm in length are
219 observed (Fig. 3C).

220 Pliniusite is transparent to semitransparent, colorless or whitish, with white streak and
221 vitreous lustre. It does not fluoresce in ultraviolet light. Pliniusite is brittle, has (100) imperfect
222 cleavage (as observed under microscope), and its fracture is uneven. The Vickers microhardness
223 HVIT is 511 kg mm^{-2} [mean of 3 measurements, min = 490, max = 530 kg mm^{-2} ; max load: 20.00
224 mN; the Nanoindentation Tester (NHT³) Anton-Paar was used], which corresponds to *ca.* 5 in the
225 Mohs hardness scale. Density could not be measured because crystals are small and typically
226 cavernous and aggregates are open-work. Density calculated for the holotype, using the empirical
227 formula and unit-cell volume determined from the single-crystal XRD data, is 3.402 g cm^{-3} .

228 Under a plane polarized light microscope, pliniusite (the holotype) is colourless and non-
229 pleochroic. It is optically uniaxial (–), $\omega = 1.763(5)$ and $\epsilon = 1.738(5)$ (589 nm). Elongation is
230 negative.

231

232 **Chemical composition**

233 Representative electron-microprobe analyses of minerals of the pliniusite–svabite–
234 fluorapatite solid-solution system from Tolbachik fumaroles and pyrometamorphic rocks of Nahal

235 Morag are given in Table 1. The empirical formulae are calculated on the basis of 13 anions
236 (O+F+Cl) per formula unit.

237 Calcium strongly prevails among *M* cations in these minerals with > 4.7 Ca atoms per
238 formula unit (*apfu*). The major admixed *M* cations are Sr and Ba in samples from Nahal Morag (*ca.*
239 0.1 *apfu*: an. 2 and 3 in Table 1) and Na in samples from the Arsenatnaya fumarole (0.10–0.16 *apfu*:
240 an. 13, 15, 17 and 19 in Table 1).

241 The F:Cl ratio significantly varies in minerals from the Arsenatnaya fumarole and Nahal
242 Morag whereas the samples from Mountain 1004 are the F-richest and practically Cl-free.

243 The most interesting chemical feature of the studied minerals is their wide variations in ratios
244 of the major tetrahedrally coordinated constituents $T^{5+} = V, P$ and As, based on 270 electron-
245 microprobe analyses (Fig. 4). The V-richest samples originate from Nahal Morag (an. 2 in Table 1).
246 At this locality, only As-free pliniusite and fluorapatite were found. In contrast, all studied samples
247 from Tolbachik fumaroles contain As. The V:As:P ratios in Tolbachik samples vary widely, and in
248 some samples the contents of the three *T* constituents are comparable (an. 5 and 6 in Table 1; Fig.
249 4). In general, the natural ternary solid-solution system among fumarolic fluorapatite, svabite and
250 pliniusite is close to being continuous (Fig. 4).

251 Some samples from all three localities contain distinct amounts of admixed Si and S which
252 sometimes demonstrate coupled substitutions according to the so-called ellestadite scheme: $Si^{4+} +$
253 $S^{6+} \rightarrow 2T^{5+}$ (up to 0.8 Si+S *apfu*: no. 16 in Table 1).

254 The empirical formulae of two type specimens of pliniusite are as follows:

255 holotype (Mountain 1004, Tolbachik: no. 1 in Table 1):

256 $(Ca_{4.87}Na_{0.06}Sr_{0.03}Fe_{0.02})_{\Sigma 4.98}(V_{1.69}As_{0.66}P_{0.45}S_{0.12}Si_{0.09})_{\Sigma 3.01}O_{11.97}F_{1.03}$;

257 cotype (Nahal Morag, Hatrurim Basin: #2 in Table 1):

258 $(Ca_{4.81}Sr_{0.12}Ba_{0.08}Na_{0.05})_{\Sigma 5.06}(V_{2.64}P_{0.27}S_{0.07}Si_{0.03})_{\Sigma 3.01}O_{12.15}F_{0.51}Cl_{0.34}$.

259 The idealized, end-member formula of pliniusite is $\text{Ca}_5(\text{VO}_4)_3\text{F}$, which has CaO 49.70, V_2O_5
260 48.35, F 3.37, O=F -1.42, total 100 wt%.

261

262 Raman spectroscopy

263 In the Raman spectra of pliniusite (Fig. 5) the main bands are related to vibrations of the
264 VO_4^{3-} , PO_4^{3-} , SO_4^{2-} , AsO_4^{3-} groups. The bands assigned to symmetric (ν_1) and asymmetric (ν_3)
265 stretching vibrations of tetrahedral groups are above 750 cm^{-1} . Bands related to bending vibrations
266 (ν_2 and ν_4) occur in the range $300\text{--}700\text{ cm}^{-1}$. Bands below 300 cm^{-1} can be assigned to lattice
267 vibrations. The main bands in the Raman spectrum of pliniusite from Nahal Morag and their
268 assignments are [cm^{-1}]: 204, 227 (lattice modes), 350 ($\nu_2\text{ VO}_4^{3-}$), 390 ($\nu_4\text{ VO}_4^{3-}$), 804, 831 ($\nu_3\text{ VO}_4^{3-}$)
269 850, 868, 881 ($\nu_1\text{ VO}_4^{3-}$), 955 ($\nu_1\text{ PO}_4^{3-}$), 1000 ($\nu_1\text{ SO}_4^{2-}$) (Frost et al. 2010; Comodi et al. 1999;
270 Galuskin et al. 2015). The Raman spectrum of pliniusite from Mountain 1004 (Tolbachik) shows
271 additional bands that can be assigned to arsenate and phosphate groups at 455 cm^{-1} ($\nu_2\text{ AsO}_4^{3-}$), 575
272 cm^{-1} ($\nu_4\text{ PO}_4^{3-}$), 859 cm^{-1} ($\nu_1\text{ AsO}_4^{3-}$) and 1030 cm^{-1} ($\nu_3\text{ PO}_4^{3-}$). Accurate bands assignment in the
273 Raman spectra of pliniusite from Tolbachik is hampered by overlapping bands corresponding to
274 vibrations of VO_4^{3-} , AsO_4^{3-} , PO_4^{3-} and SiO_4^{4-} . The bands at 424 cm^{-1} can be attributed to symmetric
275 bending vibrations (ν_2) of AsO_4^{3-} or $\nu_2\text{ PO}_4^{3-}$ (Comodi et al. 1999; Frost et al. 2015). The absence or
276 very low content of OH groups in pliniusite from both localities are confirmed by Raman
277 spectroscopic data: bands in the region of $3600\text{--}3700\text{ cm}^{-1}$ are absent.

278

279 X-ray diffraction data and crystal structure of pliniusite

280 Powder XRD data of the holotype pliniusite are given in Table 2. Unit-cell parameters of
281 pliniusite obtained from powder data are: $a = 9.618(1)$, $c = 6.978(1)\text{ \AA}$ and $V = 559.0(2)\text{ \AA}^3$. In
282 comparison, those from single-crystal XRD data are: $a = 9.5777(7)$, $c = 6.9659(5)\text{ \AA}$ and $V =$
283 $553.39(7)\text{ \AA}^3$.

284 Although the apatite structure archetype is hexagonal, $P6_3/m$ (Pasero et al. 2010), cation
285 ordering and/or topological distortions can reduce the symmetry. The synthetic compound with the
286 idealized formula $\text{Ca}_5(\text{VO}_4)_3\text{F}$ demonstrates symmetry variations. The hexagonal ($P6_3/m$) form (Aia
287 and Lublin 1966; White et al. 2005) is isostructural with other "ordinary" apatites. Dong and White
288 (2004) reported monoclinic distortion and space group $P2_1/m$ for $\text{Ca}_{10}(\text{VO}_4)_6(\text{F}_{0.90}\text{O}_{0.05}\square_{0.05})_2$. Baikie
289 et al. (2007) determined space group $P-1$ for $\text{Ca}_5(\text{VO}_4)_3\text{F}$ in which the symmetry lowering is caused
290 by the tilting of VO_4 tetrahedra.

291 To check the symmetry of pliniusite (holotype), we tried to solve and refine its structure in
292 space group $P-1$ and obtained the following unit-cell parameters: $a = 9.5750(8)$, $b = 9.5767(12)$, $c =$
293 $6.9645(5)$ Å, $\alpha = 90.039(8)$, $\beta = 89.981(6)$ and $\gamma = 119.956(10)^\circ$. Baikie et al. (2007) reported for
294 synthetic triclinic $\text{Ca}_5(\text{VO}_4)_3\text{F}$ the following unit-cell data: $a = 9.6987(3)$, $b = 9.6933(3)$, $c =$
295 $7.0170(2)$ Å, $\alpha = 90.637(3)$, $\beta = 89.172(3)$ and $\gamma = 120.136(2)^\circ$. Thus, the deviations of parameters
296 of the synthetic compound from the hexagonal cell are significantly greater than those for pliniusite.
297 The T position in the hexagonal structure of pliniusite transforms to three crystallographically non-
298 equivalent sites in the triclinic model. However, they have site occupancy factors (s.o.f.) [0.959(3),
299 0.954(3) and 0.963(3); vanadium scattering curve is used] and average T -O distances [1.631, 1.634
300 and 1.630 Å, respectively], compared with a T s.o.f. of 0.956(3) ($e_{\text{ref}} = 21.99$) and an average T -O
301 distance of 1.631 Å in the hexagonal model (Table 3). Thus, the three TO_4 tetrahedra in the triclinic
302 model are equivalent in both occupancy and dimensions. In addition, tetrahedral tilting was not
303 found in this model.

304 Kreidler and Hummel (1970) reported the splitting of reflections (111), (211), (202) and
305 (213) (indices are given for the hexagonal setting) in the powder XRD pattern of synthetic
306 $\text{Ca}_5(\text{VO}_4)_3\text{F}$ as an indicator of the symmetry lowering from hexagonal to monoclinic. Our powder
307 XRD pattern of pliniusite (Table 2) does not demonstrate such splitting.

308 Thus, there is no sign of a symmetry lower than hexagonal for pliniusite, and we assume it
309 adopts space group $P6_3/m$, the most typical structure for apatite-group members.

310 The basic features of the crystal structure of pliniusite (Fig. 6) are common to minerals of the
311 apatite group (Pasero et al. 2010). Calcium cations occupy two sites with different coordination
312 numbers: nine-fold polyhedron (6+3) is centered by $Ca1$ (Wyckoff position 4f) and seven-fold
313 polyhedron (6+1) by $Ca2$ (6h). For the $T(V)$ site the refined number of electrons is 21.99. This is in a
314 good agreement with the chemical composition of the holotype specimen (Table 1). $Ca1$ -centred
315 polyhedra share faces to form columns running along the c axis. Adjacent columns are linked by
316 TO_4 tetrahedra, thus forming a quasi-framework with the channels along the c axis (White et al.
317 2005) which host $Ca2$ sites in seven-fold coordination and F^- anions located in the centre of the
318 channels in symmetry plane at $z = 0.25$.

319

320 **Conditions of pliniusite formation**

321 At the Tolbachik volcano, members of the pliniusite–svabite–fluorapatite solid-solution
322 system are fumarolic minerals deposited directly from the gas phase as volcanic sublimates or
323 formed as a result of the interaction between volcanic gas (as an obvious source of V, As, F and Cl)
324 and basalt scoria. The latter way seems more probable taking into account low volatility of Ca in
325 volcanic gases (Symonds and Reed 1993). These minerals crystallized in fumaroles belonging to the
326 oxidizing type in which hot volcanic gas is mixed with atmospheric air that causes high oxygen
327 fugacity (Africano et al. 2005). For active Tolbachik fumaroles it is concluded in the result of both
328 direct determination of gas composition and detailed studies of sublimate minerals (Meniaylov et al.
329 1980; Zelenski et al. 2011; Pekov et al. 2020 and references therein). In the Arsenatnaya fumarole,
330 minerals of the pliniusite–svabite–fluorapatite solid-solution system crystallized at temperatures not
331 lower than 500°C and, based on data published by Meniaylov et al. (1980), not higher than 800°C.

332 The mineral assemblage observed in paleo-fumarolic deposits at the Southern fumarole field of
333 Mountain 1004 allows us to suggest the same or similar conditions of formation.

334 At Nahal Morag, the formation of pliniusite in schorlomite-gehlenite paralava (Fig. 3A),
335 which forms veinlets in gehlenite hornfels, is related to the formation of small portions of Ba-, Ti-,
336 P-, V-, Cu-, U- and F-enriched residual melts. This melt, remained after the relatively rapid
337 crystallization of rock-forming minerals of the paralava, gave the specific polymineralic enclaves in
338 rankinite (Fig. 3B) or in interstices between gehlenite and schorlomite crystals (Krzężala et al. 2020).
339 Pliniusite is associated here with Ba- and/or V-bearing minerals, e.g., walstromite $\text{BaCa}_2(\text{Si}_3\text{O}_9)$ and
340 gurimite, $\text{Ba}_3(\text{VO}_4)_2$ (Fig. 3C), and it is Ba-richer, compared to fumarolic pliniusite from Tolbachik,
341 and is As-free as well (Table 1). The presence of pseudowollastonite in the schorlomite-gehlenite
342 paralava (Seryotkin et al. 2012) indicates that it was formed at temperatures not lower than 1100°C.
343 Pliniusite crystallized from a melt locally enriched in vanadium which could be extracted from
344 underlying phosphorites or, hypothetically, from bitumen contained in a protolith of
345 pyrometamorphic rocks of the Hatrurim Complex.

346 Noteworthy, pliniusite is the second mineral containing both species-defining anions
347 $(\text{VO}_4)^{3-}$ and F^- , after aradite $\text{BaCa}_6[(\text{SiO}_4)(\text{VO}_4)](\text{VO}_4)_2\text{F}$ which was also found in paralavas of the
348 Hatrurim Complex (Galuskin et al. 2015).

349 ~~We believe that~~ The temperature of crystallization of pliniusite in the Hatrurim paralava was
350 significantly higher than Tolbachik fumaroles whereas low pressure and high oxidizing potential are
351 common for both mineral-forming systems. We suggest that such conditions are favorable for the
352 incorporation of significant amount of V^{5+} into the *T* site of calcium apatite-type compounds and in
353 general for the formation of fluorovanadate minerals.

354

355

IMPLICATIONS

356 Our structural data on the fluorapatite–svabite–pliniusite solid-solution system are potentially
357 important for understanding apatite crystal chemistry in both natural and synthetic systems. Ionic
358 radii of tetrahedrally coordinated V^{5+} (0.355 Å) and As^{5+} (0.335 Å) are about twice larger than that
359 of P^{5+} (0.17 Å) (Shannon, 1976). It is recognized that this difference hampers the formation of solid
360 solutions between fluorapatite $Ca_5(PO_4)_3F$ and svabite $Ca_5(AsO_4)_3F$ or pliniusite $Ca_5(VO_4)_3F$.
361 Moreover, the significant difference in the electron structure between vanadium (metal) and
362 phosphorus (non-metal) atoms prevents the formation of the fluorapatite–pliniusite solid solution.
363 Indeed, pliniusite and V-enriched Ca phosphates of the apatite group are extremely rare in nature:
364 they were unknown before the present work. On the other hand, the apatite-type structure is
365 relatively flexible, and the substitution of P^{5+} for larger As^{5+} or V^{5+} in the tetrahedral T sites can be
366 compensated by the distortion of the basic structural unit, a hexagonal ring formed by TO_4 tetrahedra
367 and slightly distorted $Ca1$ -centred tricapped trigonal prisms (White et al. 2005, Fig. 6). In synthetic
368 apatites, incorporation of V^{5+} can cause rotation and tilting of tetrahedra accompanied by the
369 twisting of $Ca1$ -centred prisms (via changing the so-called "twist angle") (Fang et al. 2018).
370 Besides, Boechat et al. (2020) reported the simultaneous expansion of phosphate ions and
371 contraction of vanadate ions in the solid solution which may minimize the crystallographic disorder
372 symmetry distortion and allow more stability to the structure in the whole composition range of
373 solid solution.

374 Pliniusite was formed in two different geological formations characterized by similar
375 physical and chemical conditions (high temperature, low pressure and high oxidizing potential) but
376 with different mechanisms of crystallization. In paralava belonging to the pyrometamorphic
377 Hatrurim Complex, fluorapatite containing $<0.2 (VO_4)^{3-}$ *pfu* crystallized at early stage while
378 pliniusite with $(PO_4)^{3-} < 0.3$ *pfu* crystallized later, probably from the residual V-enriched melt.
379 Temperatures of crystallization of both minerals were not lower than 1100°C, i.e., the temperatures
380 favorable to the formation of the continuous solid solution $Ca_5[(P_{1-x}V_x)O_4]_3F$, with $0 \leq x \leq 1$ (Deng

381 [et al. 2015](#)). The significant gap between phosphate and vanadate from Hatrurim paralavas (Fig. 4)
382 is caused by their crystallization from chemically different melts. In contrast, pliniusite of fumarolic
383 origin, though crystallized at definitely lower temperatures (500–800°C), forms a continuous solid-
384 solution system with fluorapatite and svabite in which, however, samples close to the $\text{Ca}_5(\text{VO}_4)_3\text{F}$
385 end member were not found (Fig. 4).

386 Kinetic factors, fluctuations in gas composition and non-equilibrium conditions of
387 crystallization of the fluorapatite–svabite–pliniusite phases in fumaroles (where gas transports some
388 essential constituents) determine the formation of the (metastable?) solid solution with wide
389 compositional variations in tetrahedrally coordinated components. Fluctuations in chemical
390 composition of volcanic gas can be the major factor which determines the chemistry of this solid-
391 solution system. Taking into account this, justly fumarolic systems can be considered as an
392 excellent, probably the best "natural laboratory" for studies of chemical variations and mechanisms
393 of isomorphous substitutions in high-temperature apatites.

394

395

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403

404

405

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501 **Figure captions**

502

503 **Figure 1.** SEM/BSE image of crystals of pliniusite (1) on hematite crystal crust (2) with baryte (3).

504 The holotype specimen is from Mountain 1004, Tolbachik volcano, Kamchatka, Russia.

505

506 **Figure 2.** Whitish open-work aggregates of prismatic pliniusite crystals with yellow diopside on

507 crust consisting of iron-black hematite which covers basalt scoria. The holotype specimen is from

508 Mountain 1004, Tolbachik volcano. FOV width: 2.15 mm. Photo: I.V. Pekov and A.V. Kasatkin.

509

510 **Figure 3.** Pliniusite in the cotype specimen from Nahal Morag, Hatrurim Basin, Israel. A – general

511 view of coarse-grained paralava: reddish-brown – andradite-schrolomite series garnet, light yellow-

512 brown – melilite, colourless – rankinite, wollastonite and cuspidine. B – inclusion of Ba- and V⁵⁺-

513 bearing minerals in rankinite (Rnk); fragment magnified in C is shown in the frame. C – elongated

514 crystals of pliniusite (Pls) in association with walstromite (Wls), gurimite (Gur), tenorite (Tnr),

515 cuspidine (Cus), rankinite (Rnk), wollastonite (Wo), and secondary Ca-hydrosilicates (HSi). B and

516 C are SEM/BSE images of polished sections.

517

518 **Figure 4.** Ratios of major tetrahedrally coordinated constituents (*T*) in minerals of the pliniusite–

519 svabite–fluorapatite solid-solution system.

520

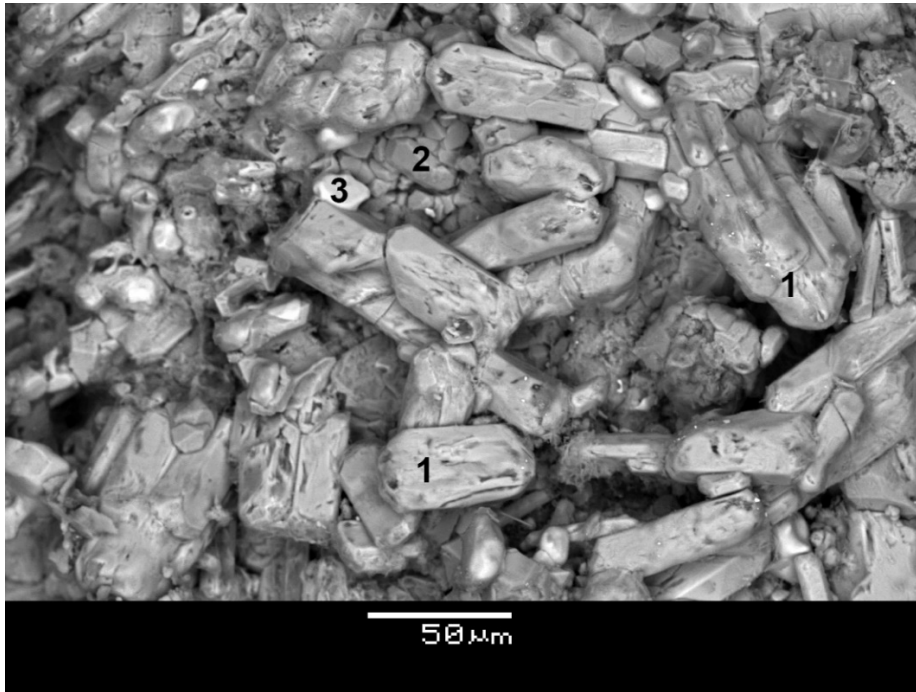
521 **Figure 5.** Raman spectra of pliniusite from (a) Nahal Morag, Hatrurim Basin (cotype) and (b)

522 Mountain 1004, Tolbachik volcano (holotype).

523

524 **Figure 6.** Crystal structure of pliniusite (space group $P6_3/m$) projected down the *c*-axis. Black lines

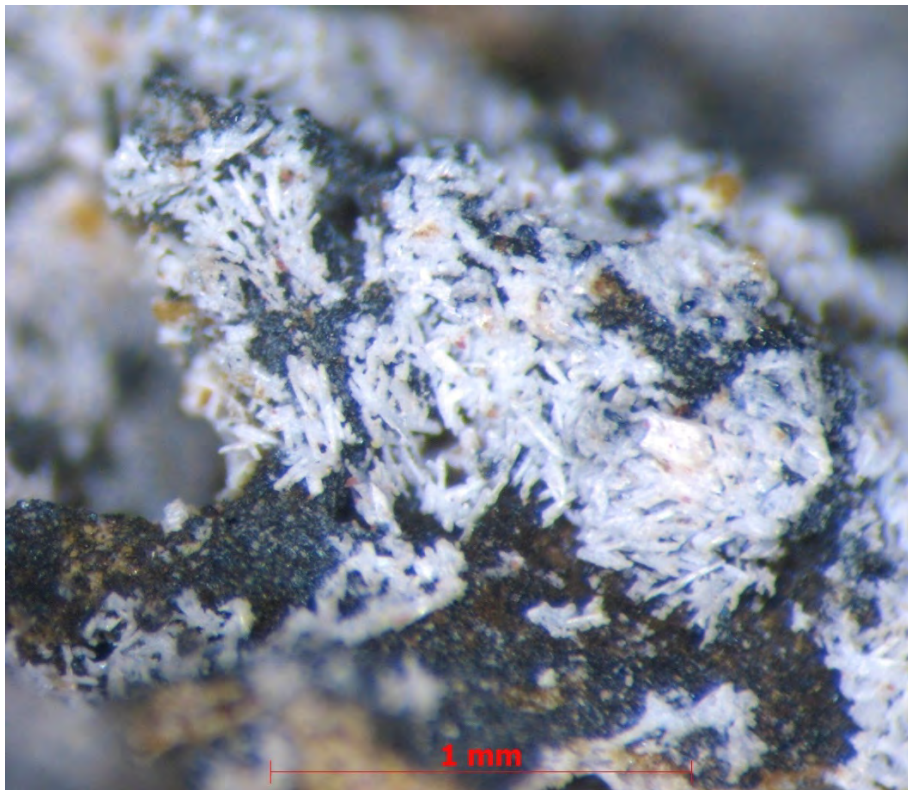
525 outline the unit cell.



527

528 **Figure 1**

529



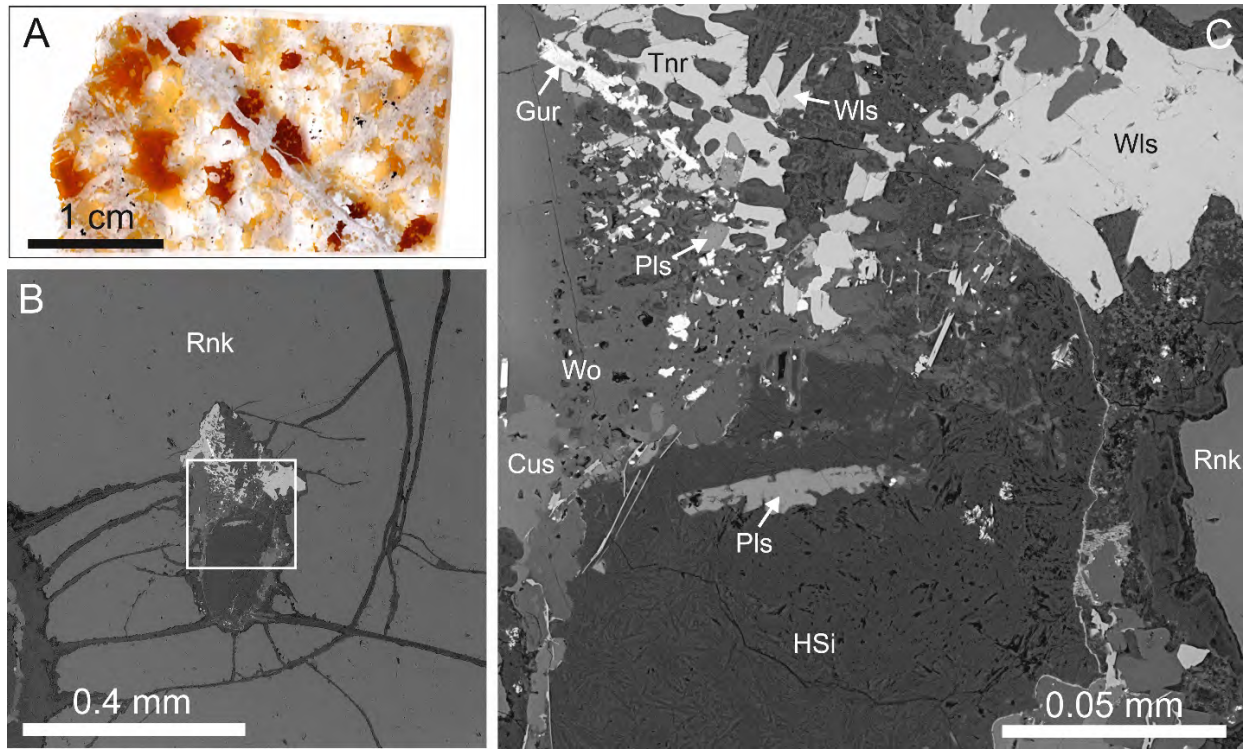
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531 **Figure 2**

532

533

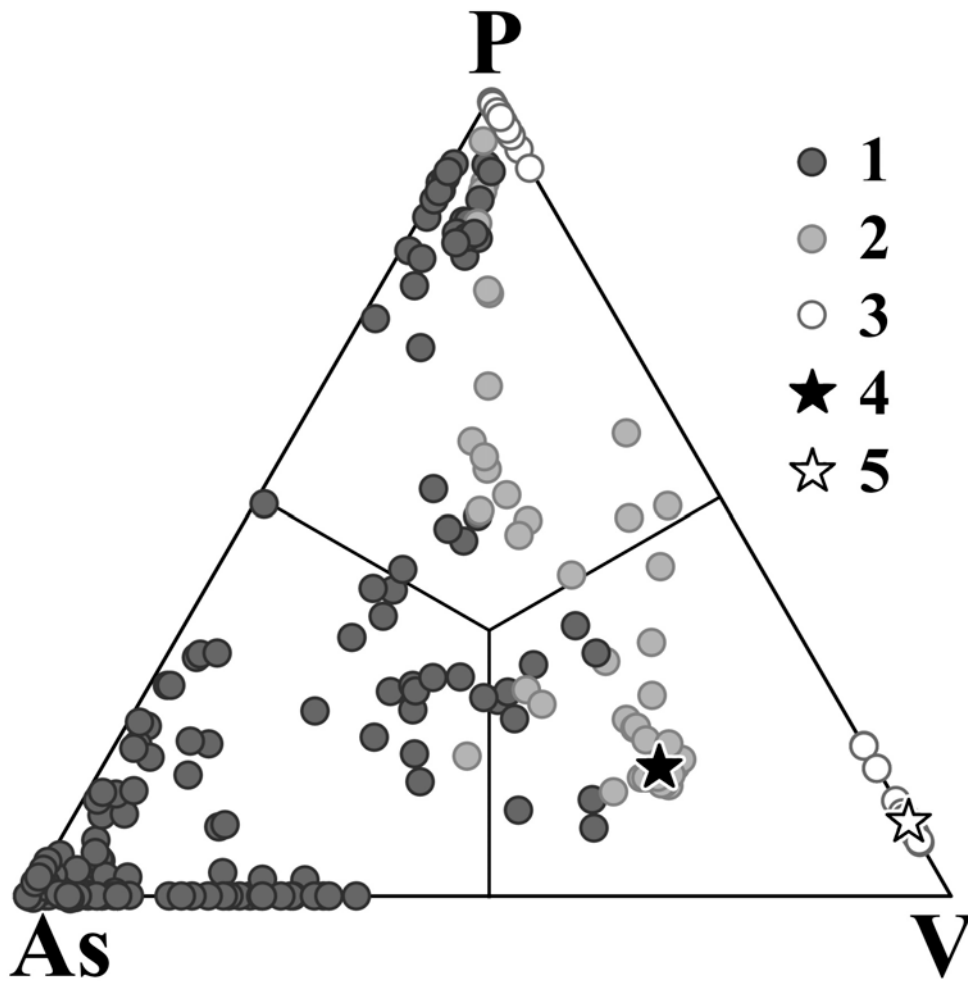
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536 **Figure 3**

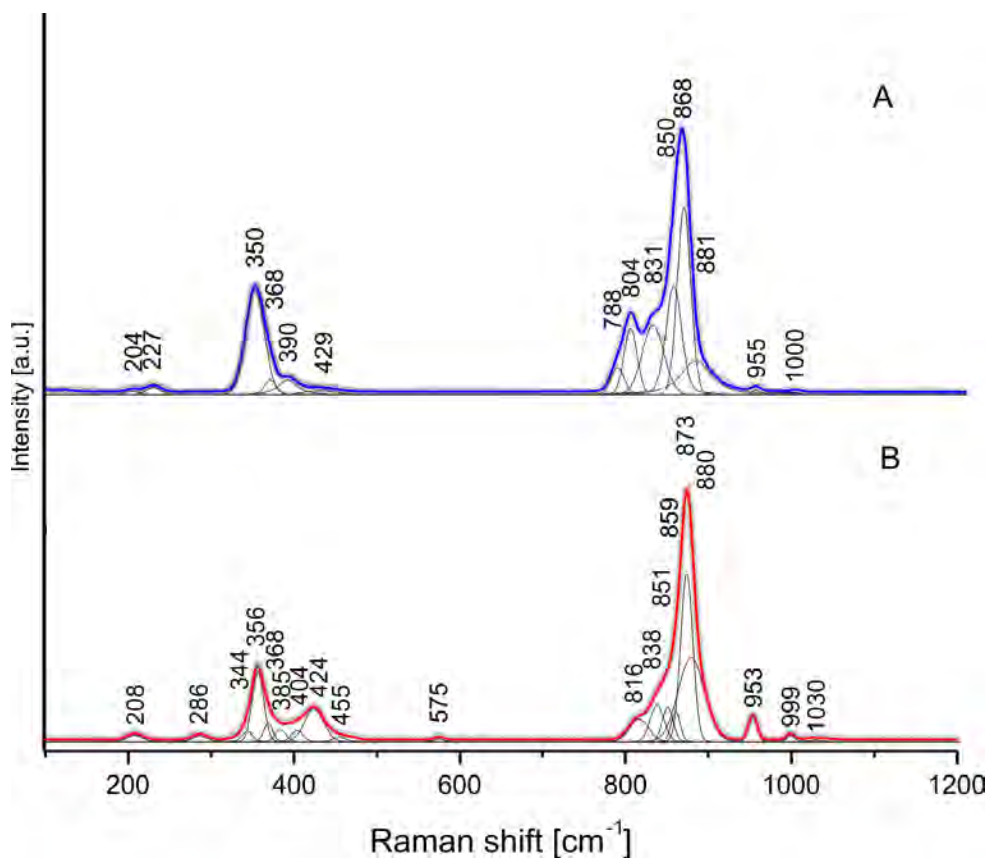
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539 **Figure 4**

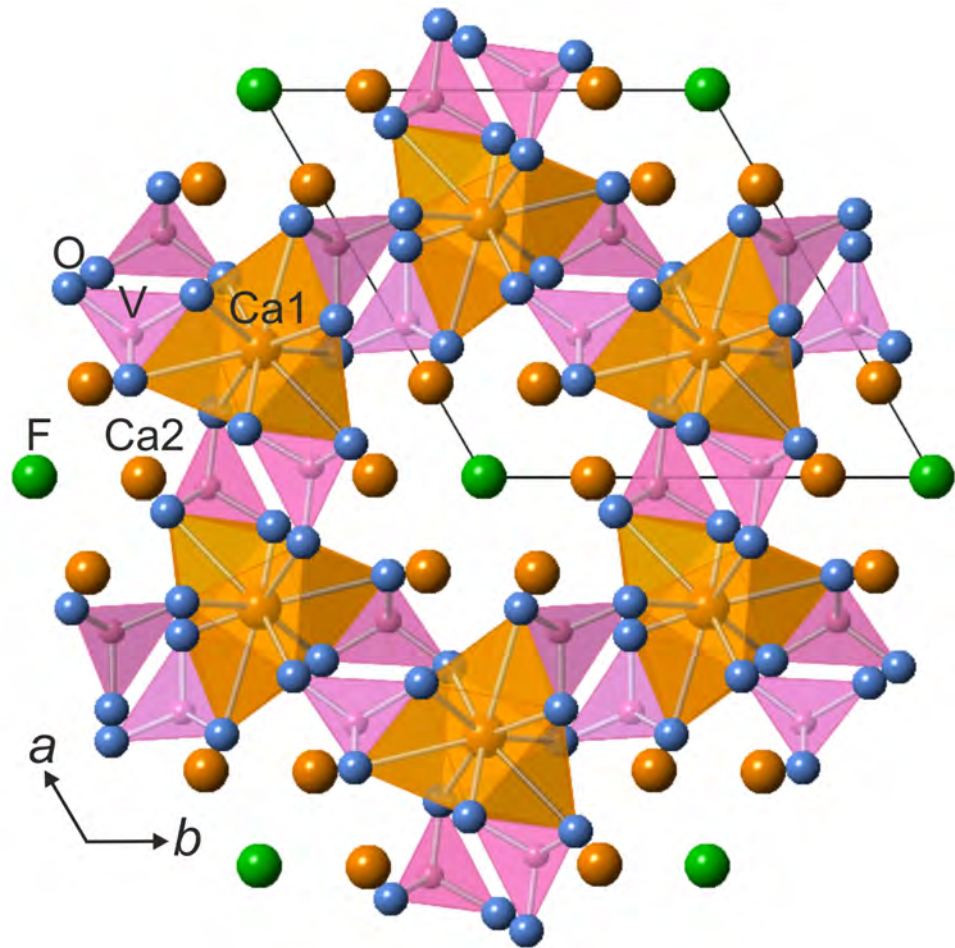
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541

542 **Figure 5**

543



544

545 **Figure 6**

546 **Tables**

547

548 **Table 1.** Chemical composition of minerals of the pliniusite–fluorapatite–svabite solid-solution system.

No.	1	2	3	4	5	6	7	8	9
Locality	Mt. 1004	N. M.	N. M.	Mt. 1004	Mt. 1004	Arsen.	Mt. 1004	Mt. 1004	Mt. 1004
Mineral	Pln (holotype)	Pln (cotype)	Pln	Pln	Pln	Pln	FAp	FAp	FAp
	wt. %								
Na ₂ O	0.33 (0.00 – 0.41)	0.26 (0.13 – 0.37)	0.20	0.37	0.04	0.32	0.34	0.39	0.23
K ₂ O	0.01 (0.00 – 0.02)		0.05						
CaO	48.04 (47.57 – 48.50)	45.92 (45.25 – 46.67)	45.10	48.21	47.81	46.40	48.13	49.79	48.81
SrO	0.58 (0.49 – 0.69)	2.05 (1.94 – 2.16)	2.01	0.50	0.45	0.69	0.49	0.61	0.38
BaO		2.14 (1.81 – 2.48)	2.36						
FeO	0.26 (0.00 – 0.52)		0.18	0.25	0.12		0.19	0.12	0.35
SiO ₂	0.94 (0.67 – 1.19)	0.34 (0.22 – 0.65)	0.22	0.85	1.18	1.05	0.78	0.46	0.96
P ₂ O ₅	5.63 (4.84 – 7.44)	3.13 (2.57 – 4.28)	2.75	5.28	8.93	8.56	7.44	18.52	14.31
V ₂ O ₅	27.04 (25.01 – 27.90)	41.03 (40.20 – 41.54)	42.22	27.59	18.16	17.23	25.00	21.73	17.61
As ₂ O ₅	13.26 (11.67 – 14.97)			12.77	18.48	20.76	13.57	3.82	12.02
SO ₃	1.73 (1.48 – 1.93)	0.95 (0.62 – 1.36)	0.75	1.73	1.22	1.81	1.66	1.19	1.62
F	3.46 (3.18 – 3.67)	1.65 (1.48 – 1.80)	1.58	3.18	3.01	2.82	3.33	3.53	3.41
Cl		2.07 (1.79 – 2.26)	2.28		0.07	1.13			
–O=F+Cl	1.46	1.16	1.18	1.34	1.28	1.44	1.40	1.49	1.44
Total	99.82	98.38	98.52	99.39	98.19	99.33	99.53	98.67	98.26

549

550

551

552 **Table 1** (continued).

No.	1	2	3	4	5	6	7	8	9
Locality	Mt. 1004	Nahal Morag	N. M.	Mt. 1004	Mt. 1004	Arsen.	Mt. 1004	Mt. 1004	Mt. 1004
Mineral	Pln (holotype)	Pln (cotype)	Pln	Pln	Pln	Pln	FAp	FAp	FAp
formula calculated on the basis of 13 anions (O+F+Cl)									
Na	0.06	0.05	0.04	0.07	-	0.06	0.06	0.07	0.04
K	-		-						
Ca	4.87	4.77	4.72	4.90	4.94	4.82	4.88	4.85	4.90
Sr	0.03	0.11	0.11	0.03	0.03	0.04	0.03	0.03	0.02
Ba		0.08	0.09						
Fe	0.02		0.01	0.02	-		0.01	-	0.03
Si	0.09	0.03	0.02	0.08	0.11	0.10	0.07	0.04	0.09
P	0.45	0.26	0.23	0.42	0.73	0.70	0.60	1.43	1.13
V	1.69	2.63	2.72	1.73	1.16	1.10	1.56	1.31	1.09
As	0.66			0.63	0.93	1.05	0.67	0.18	0.59
S	0.12	0.07	0.05	0.12	0.09	0.13	0.12	0.08	0.11
F	1.04	0.51	0.49	0.95	0.92	0.86	1.00	1.01	1.01
Cl		0.34	0.38		0.01	0.19			
O	11.99	12.05	12.11	12.01	12.05	12.10	12.03	12.04	12.02
ΣM	4.98	5.01	4.97	5.02	4.97	4.92	4.98	4.95	4.99
ΣT	3.01	2.99	3.02	2.98	3.02	3.08	3.02	3.04	3.01
$\Sigma F+Cl$	1.04	0.85	0.87	0.95	0.93	1.05	1.00	1.01	1.01

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556 **Table 1** (continued).

No.	10	11	12	13	14	15	16	17	18	19
Locality	Mt. 1004	N. M.	N. M.	Arsen.	Arsen.	Arsen.	Arsen.	Arsen.	Arsen.	Arsen.
Mineral	FAp	FAp	FAp	FAp	Svb	Svb	Svb	Svb	Svb	Svb
	wt. %									
Na ₂ O	0.27	0.01		0.59		0.68	0.40	0.66	0.40	0.78
CaO	49.59	53.83	53.52	53.16	44.78	42.67	45.47	46.06	44.40	43.80
SrO	0.35	0.95	1.02	0.09		0.19	0.27	0.18		
BaO		0.15	0.83							
MnO		0.04				0.29	0.16			
FeO	0.37	0.13								0.16
SiO ₂	1.17	0.85	2.60	0.22		0.25	3.51	0.24	0.17	0.10
P ₂ O ₅	19.18	39.39	36.19	37.20		0.18	4.17	9.36	4.04	0.55
V ₂ O ₅	10.60	2.02	0.80	0.06	13.94	3.88	3.45	1.03	0.66	0.49
As ₂ O ₅	13.61			5.96	37.29	47.71	33.38	40.80	47.00	51.63
SO ₃	1.99	0.40	1.38	0.49	0.91	1.48	5.05	1.16	0.80	1.86
CrO ₃		0.38	0.03							
F	3.89	3.28	4.00	4.02	2.00	2.22	2.33	3.05	3.01	3.22
Cl		0.01		0.20	2.41	1.53	1.71	0.44	0.48	0.06
-O=F+Cl	1.64	1.38	1.68	1.74	1.38	1.28	1.36	1.38	1.38	1.37
Total	99.38	100.06	98.69	100.25	99.95	99.80	98.54	101.60	99.58	101.28

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560 **Table 1** (continued).

No.	10	11	12	13	14	15	16	17	18	19
Locality	Mt. 1004	N. M.	N. M.	Arsen.	Arsen.	Arsen.	Arsen.	Arsen.	Arsen.	Arsen.
Mineral	FAp	FAp	FAp	FAp	Svb	Svb	Svb	Svb	Svb	Svb
formula calculated on the basis of 13 anions (O+F+Cl)										
Na	0.05	-		0.10		0.14	0.08	0.13	0.08	0.16
Ca	4.88	4.88	4.93	4.88	4.96	4.79	4.85	4.83	4.91	4.82
Sr	0.02	0.05	0.05	-		0.01	0.01	0.01		
Ba		-	0.03							
Mn		-				0.03	0.01			
Fe	0.03	-								0.01
Si	0.11	0.07	0.22	0.02		0.03	0.35	0.02	0.02	0.01
P	1.49	2.82	2.63	2.70		0.02	0.35	0.78	0.35	0.05
V	0.64	0.11	0.05	-	0.95	0.27	0.23	0.07	0.04	0.03
As	0.65			0.27	2.02	2.61	1.74	2.09	2.54	2.77
S	0.14	0.03	0.09	0.03	0.07	0.12	0.38	0.08	0.06	0.14
Cr		0.03	-							
F	1.13	0.88	1.09	1.09	0.65	0.73	0.73	0.94	0.98	1.05
Cl		-		0.03	0.42	0.27	0.29	0.07	0.08	0.01
O	11.98	12.10	11.87	11.92	12.05	12.03	12.03	12.01	11.97	11.98
ΣM	4.98	4.93	5.01	4.98	4.96	4.97	4.95	4.97	4.99	4.99
ΣT	3.03	3.06	2.99	3.02	3.04	3.05	3.05	3.04	3.01	3.00
$\Sigma F+Cl$	1.13	0.88	1.09	1.12	1.07	1.00	1.02	1.01	1.06	1.06

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562 Pliniusite, fluorapatite and svabite are labeled as Pln, FAp and Svb, respectively. The localities are labeled as: Mt. 1004 – Southern fumarole
 563 field at Mountain 1004, Tolbachik volcano (Nos. 1, 4–7, 9, 10, 12); N. M. – Nahal Morag, Hatrurim Basin (Nos. 2, 3, 15, 17); Arsen. –
 564 fumarole Arsenatnaya, Tolbachik (Nos. 8, 11, 13, 14, 16, 18, 19).

565 $\Sigma M = Na+K+Ca+Sr+Ba+Mn+Fe$, $\Sigma T = Si+P+V+As+S+Cr$. Empty cell means that the content of a constituent is below the detection limit
 566 and dash means 0.00 *apfu* (for minor admixtures). Nos. 1 and 2: average values for eight and five spot analyses, respectively; ranges are
 567 given in parentheses.

568 **Table 2.** Powder X-ray diffraction data (d in Å) of the holotype pliniusite.

I_{obs}	d_{obs}	I_{calc}^*	d_{calc}^{**}	hkl
11	8.32	10	8.295	100
5	5.347	4	5.334	101
7	4.807	4	4.789	110
3	4.163	2	4.147	200
27	3.958	20	3.946	111
4	3.575	3	3.564	201
33	3.488	40	3.483	002
7	3.217	7	3.211	102
14	3.148	13	3.135	210
100	2.869	100	2.859	211
35	2.823	42	2.817	112
58	2.776	55	2.765	300
25	2.674	27	2.667	202
6	2.579	5	2.570	301
3	2.337	3	2.330	212
16	2.310	15	2.300	130
7	2.274	8	2.264	221
8	2.194	9	2.184	311
1	2.082	1	2.074	400
2	2.031	2	2.026	203
19	1.980	28	1.973	222
4	1.926	6	1.920	132
3	1.912	3	1.903	230
23	1.871	38	1.866	213
16	1.844	15	1.836	321
7	1.818	10	1.810	140
6	1.788	9	1.782	402
2	1.759	2	1.752	141
6	1.745	18	1.741	004
9	1.676	15	1.670	232
2	1.665	2	1.659	500
3	1.639	6	1.634	133
1	1.619	1	1.614	501
1	1.606	1	1.606	142
4	1.575	6	1.568	240
3	1.563	5	1.556	331
4	1.536	6	1.529	421
2	1.526	3	1.522	124
9	1.504	17	1.498	502
2	1.489	2	1.490	150
8	1.477	12, 6	1.474, 1.472	304, 233
5	1.463	8	1.457	511
2	1.433	2, 3	1.429, 1.428	242, 413
1	1.392	1	1.388	134

2	1.375	4	1.370	152
4	1.344	8, 1	1.338, 1.338	341, 115
2	1.335	4	1.328	250
3	1.304	3, 7	1.305, 1.299	521, 243
1	1.289	2	1.285	234
4	1.276	8	1.273	125
3	1.272	3, 4	1.270, 1.265	342, 610
5	1.259	7, 5	1.255, 1.254	144, 513
3	1.247	7	1.241	252
2	1.204	2, 3	1.204, 1.201	225, 504

569 *For the calculated pattern, only reflections with intensities ≥ 1 are given; **calculated with the unit-
 570 cell parameters from single-crystal XRD data. The strongest reflections are marked in bold.
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Table 3. Selected bond lengths (Å) of the holotype pliniusite.

<i>T</i> – O(3)	1.625(2) x 2	Ca2 – F	2.3248(8)
- O(2)	1.627(3)	- O(3)	2.347(2) x 2
- O(1)	1.647(3)	- O(1)	2.398(3)
< <i>T</i> -O>	1.631	- O(3)	2.497(2) x 2
		- O(2)	2.744(3)
Ca1 – O(2)	2.395(2) x 3	<Ca-F/O>	2.451
- O(1)	2.482(2) x 3		
- O(3)	2.874(2) x 3		
<Ca-O>	2.584		

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