Pliniusite, $\text{Ca}_5(\text{VO}_4)_3\text{F}$, a new apatite-group mineral and the novel natural ternary solid-solution system pliniusite–svabite–fluorapatite

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ABSTRACT

The new apatite-group mineral pliniusite, ideally $\text{Ca}_5(\text{VO}_4)_3\text{F}$, was found in fumaroles at the Tolbachik volcano, Kamchatka, Russia, and in a pyrometamorphic rock of the Hatrurim Complex, Israel. Pliniusite, together with fluorapatite and svabite, forms a novel and almost continuous ternary solid-solution system characterized by wide variations of $T^{V} = \text{P}, \text{As}, \text{and} \text{V}$. In paleo-fumarolic deposits at Mountain 1004 (Tolbachik), members of this system, including the holotype pliniusite, are associated with hematite, tenorite, diopside, andradite, kainotropite, baryte and supergene volborthite, brochantite, gypsum and opal. In sublimates of the active Arsenatnaya fumarole (Tolbachik), pliniusite–svabite–fluorapatite minerals coexist with anhydrite, diopside, hematite, berzelite, schäferite, calciogollhiterite, forsterite, enstatite, magnesiostilite, ludwigite, rhodoborite-group fluoroborates, powellite, baryte, udnaitina, arsenduitina, parabrunellite, and spinel. At Nahal Morag, Negev Desert, Israel, the pliniusite cotype and V-bearing fluorapatite occur in schorlomite-gehlenite paralava with rankinite, walstromite, zadovite-aradite series minerals, magnesiostilite, hematite, kinesite, barioferrite, perovskite, gurinite, baryte, tenorite, delafosite, wollastonite, and cupidine. Pliniusite forms hexagonal prismatic crystals up to 0.3 mm across (Mountain 1004) or grains up to 0.02 mm across (Nahal Morag and Arsenatnaya fumarole). Pliniusite is transparent to semitransparent, colorless or whitish, with a vitreous luster. The calculated density is 3.402 g/cm$^3$. Pliniusite is optically uniaxial (–), $\omega = 1.763(5)$, $\varepsilon = 1.738(5)$. The empirical formulas of pliniusite type specimens calculated based on 13 anions (O+F+Cl) per formula unit are (Ca$^{4.87}$Ba$^{0.12}$Na$^{0.06}$Sr$^{0.08}$Fe$^{0.02}$)$_3$$(V^{3+}$Fe$^{3+}$)$_2$(Si$^{4+}$O$^{12}$)F$^{1.03}$ (Mountain 1004) and (Ca$^{4.94}$Ba$^{0.08}$Sr$^{0.08}$Fe$^{0.02}$)$_3$$(V^{3+}$Fe$^{3+}$)$_2$(Si$^{4+}$O$^{12}$)F$^{1.03}$ (Nahal Morag). Pliniusite has a hexagonal structure with space group $P6_3/m$, $a = b = 9.5777(7)$ Å, $c = 6.9659(5)$ Å. $V = 553.39(7)$ Å$^3$, and $Z = 2$. The structure was solved using single-crystal (holotype) X-ray diffraction, $R = 0.0254$. The mineral was named in honor of the famous Roman naturalist Pliny the Elder, born Gaius Plinius Secundus (AD 23–79). It is suggested that the combination of high temperature, low pressure, and high oxygen fugacity favors the incorporation of $V^{5+}$ into calcium apatite-type compounds, leading to the formation of fluorovanadates.

Keywords: Pliniusite, apatite group, new mineral, calcium fluoride vanadate, fluorapatite, svabite, crystal structure, X-ray diffraction, Raman spectroscopy, electron microprobe analysis

INTRODUCTION

The family of apatite-type compounds (apatites, in the common chemical terminology) is huge. It includes more than 40 natural members, valid mineral species belonging to the apatite supergroup, and several hundred synthetic phases. This family is well-known due to its importance in natural sciences, modern technologies, and human life in general (Kohn et al. 2002).

The general simplified formula of apatites is $M_6(TO_4)_3X$ and the crystal-chemical formula is $\text{i}^{\text{i}}X\text{M}^{\text{ii}}\text{M}^{\text{iii}}\text{M}^{\text{iv}}(\text{VO}_4)_3\text{X}$ ($Z = 2$), where the Roman numerals indicate the ideal coordination numbers. Apatite-type compounds are hexagonal or pseudo-hexagonal. The space group of the archetype structure of apatite is $P6_3/m$. In minerals of the apatite supergroup, the following components are now known as the species-defining ones: $M = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Mn}^{2+}, \text{Cd}^{2+}, \text{Na}^{+}, \text{Y}^{3+}, \text{La}^{3+}, \text{Ce}^{3+}, \text{Nd}^{3+}, \text{Bi}^{3+}; T = \text{P}^{5+}, \text{As}^{5+}, \text{V}^{5+}, \text{Si}^{4+}, \text{S}^{4+}, \text{B}^{3+}, X = \text{F}^-, \text{OH}^-, \text{Cl}^-, \text{O}_2^-$ (Pasero et al. 2010; IMA 2021). Based on both chemical and crystal chemical (first of all, ordering of metal cations between different $M$