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Pliniusite, $Ca_5(VO_4)_3F$, 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 $Ca_5(VO_4)_3F$, was found in fumarole deposits 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^{5+} = P, As, and 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, berzeliite, schäferite, calciojohillerite, forsterite, enstatite, magnesioferrite, ludwigite, rhabdoborite-group fluoroborates, powellite, baryte, udinaite, arsenudinaite, paraberzeliite, 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, magnesioferrite, hematite, khesinite, barioferrite, perovskite, gurimite, baryte, tenorite, delafossite, wollastonite, and cuspidine. Pliniusite forms hexagonal prismatic crystals up to 0.3 × 0.1 mm and open-work aggregates up to 2 mm across (Mountain 1004) or grains up to 0.02 mm (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 (–), ω = 1.763(5), ε = 1.738(5). The empirical formulas of pliniusite type specimens calculated based on 13 anions (O+F+Cl) per formula unit are $(Ca_{4.87}Na_{0.06}Sr_{0.03}Fe_{0.02})_{\Sigma 4.98}(V_{1.69}As_{0.66}P_{0.45}S_{0.12}Si_{0.09})_{\Sigma 3.01}O_{11.97}F_{1.03}$ (Mountain 1004) and $(Ca_{4.81}Sr_{0.12}Ba_{0.08}Na_{0.05})_{\Sigma 5.06}(V_{2.64}P_{0.27}S_{0.07}Si_{0.03})_{\Sigma 3.01}O_{12.15}F_{0.51}Cl_{0.34}$ (Nahal Morag). Pliniusite has a hexagonal structure with space group $P6_3/m$, $a = b = 9.5777(7)$, $c = 6.9659(5)$ 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