Yakubovichite, CaNi$_2$Fe$_{3+}$$(PO_4)_3$, a new nickel phosphate mineral of non-meteoritic origin

SERGEY N. BRITVIN$^{1,2,*}$, MIKHAIL N. MURASHKO$^1$, MARIA G. KRZHIZHANOVS’KAYA$^1$, YEVRGENY VAPNIK$^3$, NATALIA S. VLASENKO$^4$, OLEG S. VERESHCHAGIN$^1$†, DMITRII V. PANKIN$^6$, ANATOLY N. ZAITSEV$^1$, and ANATOLY A. ZOLOTAREV$^1$

$^1$Institute of Earth Sciences, Saint-Petersburg State University, Universitetskaya Nab. 7/9, St. Petersburg, 199034, Russia
$^2$Nanomaterials Research Center, Kola Science Center, Russian Academy of Sciences, Fersman Str. 14, Apatity, 184200, Russia
$^3$Department of Geological and Environmental Sciences, Ben-Gurion University of the Negev, POB 653, Beer-Sheva, 84105, Israel
$^4$Geomodel Resource Center, Saint-Petersburg State University, Ulyanovskaya Str. 1, St. Petersburg, 198504, Russia
$^5$Center for Optical and Laser Materials Research, St. Petersburg State University, Ulyanovskaya Str. 5, St. Petersburg, 199034, Russia

**Abstract**

Yakubovichite, CaNi$_2$Fe$_{3+}$(PO$_4$)$_3$, a new mineral containing up to 20 wt% NiO, represents a novel type of terrestrial phosphate mineralization featuring an extreme enrichment in Ni. The mineral was discovered in the Hatrurim Formation (Mottled Zone)—pyrometamorphic complex whose outcrops are exposed in Israel and Jordan in the area coincident with the Dead Sea Transform fault system. Nickel-rich minerals in these assemblages also include Ni phosphates: halamishite Ni$_2$P$_2$, negevite NiF$_2$, transjordanite and orishchininite—two polymorphs of NiF$_2$P$_3$, nazarovite Ni$_3$P$_3$, polekhovskite MoNiP$_2$; Ni-spinel trevorite NiFe$_{2-}$O$_3$, bunsenite NiO, and nickelferrous members of the hematite-eskolaite series, Fe$_3$O$_4$–Cr$_2$O$_3$ containing up to 2 wt% NiO. Yakubovichite forms polycrystalline segregations up to 0.2 mm in size composed of equant crystal grains, in association with crocobelonite, hematite, other phosphates, and phosphidites. It has a deep yellow to lemon-yellow color, is transparent to translucent with vitreous luster, and has no cleavage. Mohs hardness = 4. Yakubovichite is orthorhombic, *Imma*, unit-cell parameters of the holotype material: $a = 10.3878(10)$, $b = 13.0884(10)$, $c = 6.4794(6)$, $\AA$, $V = 880.94(2)$ $\AA^3$, $Z = 4$. Chemical composition of holotype material (electron microprobe, wt%): Na$_2$O 1.82, K$_2$O 1.76, CaO 6.37, SrO 0.49, BaO 1.37, MgO 2.13, NiO 21.39, CuO 0.16, Fe$_2$O$_3$ 18.80, Al$_2$O$_3$ 1.06, V$_2$O$_5$ 0.44, Cr$_2$O$_3$ 0.15, P$_2$O$_5$ 44.15, total 100.09. The empirical formula calculated on the basis of 12 O atoms per formula unit is (Ca$_{0.05}$Na$_{0.25}$K$_{0.15}$Ba$_{0.04}$Sr$_{0.02}$)$_{1.94}$Ni$_{1.39}$Mg$_{0.02}$Fe$_{0.24}$V$_{0.01}$Cr$_{0.01}$Si$_{0.01}$Al$_{0.10}$P$_{3.02}$O$_{12}$: $D_{an}$ = 3.657 g cm$^{-3}$. The strongest lines of powder XRD pattern [d(Å)/I(hkl)]: 5.82(44)(101), 5.51(73)(101), 5.21(32)(200), 4.21(34)(121), 2.77(97)(240), 2.74(100)(202), 2.59(38)(400). Yakubovichite is the first mineral that crystallizes in the $\alpha$-CrPO$_4$ structure type. It has a direct synthetic analog, CaNi$_2$Fe$_{3+}$(PO$_4$)$_3$. Since yakubovichite is the first natural Ni-phosphate of non-meteoritic origin, the possible sources of Ni in the reported mineral assemblages are discussed. Pyrometamorphic rocks of the Hatrurim Formation were formed at the expense of the sediments belonging to a Cretaceous-Paleogene (Cretaceous-Tertiary) boundary (∼66 Ma ago). This geological frame marks the event of mass extinction of biological species on Earth that was likely caused by the Chicxulub impact event. The anomalous enrichment of pyrometamorphic assemblages in Ni may be related to metamorphic assimilation of Ni-rich minerals accumulated in the Cretaceous-Paleogene layer, which was formed due to a Chicxulub collision.

**Keywords:** Nickel, phosphate, phospide, trevorite, bunsenite, eskolaite, crystal structure, pyrometamorphism, Dead Sea Transform Fault, Hatrurim Formation, Cretaceous-Paleogene boundary

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**Introduction**

Nickel in metallogenic provinces on Earth behaves as a typical chalcophile element, with a strong affinity to sulfide and arsenide ores (Meyer 1968). The world largest Cu-Ni-PGE sulfide deposits that are confined to ultrabasic complexes, such as Norilsk-Talnakh in Russia (Barnes et al. 2020), Sudbury in Canada (Hawley 1962), Cu-Ni ore fields in Australia (Hoatson et al. 2006), as well as Ni-laterites formed by the weathering of sulfide-bearing ultramafites (Thorne et al. 2012) provide ~90% of Ni world production (Meyer 1968). In the 21st–20th centuries, Ni deposits belonging to the so-called five-element, i.e., Ag-Bi-Co-Ni-U, formation, with a predominance of Ni-Co arsenide ores, were very important. The ore fields of this type are widespread in Canada (Petruk 1971). However, the most famous and best-studied five-element mining district is an Erzgebirge area, which encompasses numerous now abandoned shafts in Saxony (Germany) and Jáchymov (St. Joachimsthal) in the Czech Republic (Ondruš et al. 2003; Guichler et al. 2021).

The speciation of secondary minerals in the oxidation zones of ore deposits is largely determined by the composition of primary ores. Therefore, it is not surprising that the most diverse group