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Crocobelonite, $CaFe^{3+}_2(PO_4)_2O$, a new oxyphosphate mineral, the product of pyrolytic oxidation of natural phosphides

Sergey N. Britvin[1,2,*], Mikhail N. Murashko[1], Maria G. Krzhizhanovskaya[1], Natalia S. Vlasenko[3], Oleg S. Vereshchagin[1,†], Yevgeny Vapnik[4], and Vladimir N. Bocharov[3]

[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]Geomodel Resource Center, Saint-Petersburg State University, Ulyanovskaya Str. 1, St. Petersburg, 198504, Russia
[4]Department of Geological and Environmental Sciences, Ben-Gurion University of the Negev, POB 653, Beer-Sheva, 84105, Israel

Abstract

Crocobelonite, $CaFe^{3+}_2(PO_4)_2O$, is a new natural oxyphosphate discovered in the pyrometamorphic complexes of the Hatrurim Formation in Israel and Jordan. Crocobelonite-bearing assemblages contain a series of anhydrous Fe-Ni phosphates, hematite, diopside, anorthite, and phosphides—barringerite Fe_2P, transjordanite Ni_2P, murashkoite FeP, halamishite Ni_5P_4, and negevite NiP_2. Crocobelonite forms submillimeter-sized aggregates of prismatic to acicular crystals of saffron-red to pinkish-red color. There are two polymorphic modifications of the mineral whose structures are interrelated by the unit-cell twinning. Crocobelonite-2*O* is orthorhombic, *Pnma*, a = 14.2757(1), b = 6.3832(1), c = 7.3169(1) Å, V 666.76(1) Å^3, Z = 4. This polymorphic modification is isotypic with synthetic oxyphosphates $AV^{3+}_2(PO_4)_2O$ where A = Ca, Sr, Cd. The crystal structure has been refined to R_B = 0.71% based on powder XRD data, using the Rietveld method and the input structural model obtained from the single-crystal study. Chemical composition (electron microprobe, wt%) is: CaO 16.03, MgO 0.56, Fe_2O_3 43.37, Al_2O_3 0.33, SiO_2 0.32, P_2O_5 39.45, Total 100.06. The empirical formula based on O = 9 apfu is $Ca_{1.02}(Fe^{3+}_{1.94}Mg_{0.05}Al_{0.02})_{2.01}(P_{1.98}Si_{0.02})_{2.00}O_{9.00}$ with D_{calc} = 3.555 g/cm^3. The strongest lines of powder XRD pattern [d(Å)(I)(hkl)] are: 6.54(16)(200), 5.12(26)(201), 3.549(100)(102), 3.200(50)(401), 2.912(19)(220), 2.869(40)(411), 2.662(21)(501). Crocobelonite-1*M* is monoclinic, $P2_1/m$, a = 7.2447(2), b = 6.3832(1), c = 7.3993(2) Å, β = 106.401(2)°, V = 328.252(14) Å^3, Z = 2. This polymorphic modification does not have direct structural analogs. Its crystal structure has been solved and refined based on the single-crystal data to R_1 = 1.81%. Chemical composition is: CaO 15.56, MgO 0.16, NiO 0.78, Fe_2O_3 41.28, Al_2O_3 0.45, V_2O_3 0.42, Cr_2O_3 0.23, TiO_2 0.79, P_2O_5 39.94, Total 99.61, corresponding to the empirical formula (O = 9 apfu) $Ca_{0.99}(Fe^{3+}_{1.85}Ni_{0.04}Ti_{0.04}Al_{0.03}V^{3+}_{0.02}Cr_{0.01}Mg_{0.01})_{2.00}P_{2.01}O_{9.00}$ with D_{calc} = 3.604 g/cm^3. The strongest lines of powder XRD pattern [d(Å)(I)(hkl)] are 6.98(17)(100), 4.40(22)(101), 3.547(100)($\bar{2}01$), 3.485(21)(200), 3.195(50)(020), 2.855(38)(102), 2.389(33)($\bar{1}22$). Crocobelonite represents a novel type of phosphate mineral formed by oxidation of phosphide minerals at temperatures higher than 1000 °C and near-atmospheric pressure (pyrolytic oxidation).

Keywords: Phosphate, oxyphosphate, oxophosphate, phosphide, pyrolytic oxidation, crystal structure, new mineral, pyrometamorphism, Dead Sea, Middle East, Hatrurim Formation