Crocobelonite, CaFe$_3$+(PO$_4$)$_2$O, a new oxyphosphate mineral, the product of pyrolytic oxidation of natural phosphides

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**ABSTRACT**

Crocobelonite, CaFe$_3$+(PO$_4$)$_2$O, 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 FeP, transjordanite Ni$_3$P, murashkoite FeP$_2$, halamishite Ni$_3$P$_4$, and negevite Ni$_5$P$_3$. 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-2O 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 isotopic with synthetic oxyphosphate $AV_3$($PO_4$)$_2$O where $A = Ca$, Sr, Cd. The crystal structure has been refined to R$_p = 0.71\%$ 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$_2$O$_3$ 43.37, Al$_2$O$_3$ 0.33, SiO$_2$ 0.32, P$_2$O$_5$ 39.45, Total 100.06. The empirical formula based on O = 9 apfu is Ca$_{2+}$Fe$^{3+}$(Mg$_{0.05}$Al$_{0.02}$)$_{2.01}$(P$_{0.01}$Si$_{0.02}$)$_{2.00}$O$_{10.00}$ with $D_{calc} = 3.555$ g/cm$^3$. The strongest lines of powder XRD pattern $[d(\AA)l/(hk\ell)]$ 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-1M is monoclinic, $P2_1/m$, $a = 7.2447(2)$, $b = 6.3832(1)$, $c = 7.3993(2)$ Å, $\beta = 106.401(2)$°, $V = 328.252(14)$ 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. $R_p = 1.81\%$. Chemical composition is: CaO 15.56, MgO 0.16, NiO 0.78, Fe$_2$O$_3$ 41.28, Al$_2$O$_3$ 0.45, V$_2$O$_5$ 0.42, Cr$_2$O$_3$ 0.23, TiO$_2$ 0.79, P$_2$O$_5$ 39.94, Total 99.61, corresponding to the empirical formula (O = 9 apfu) Ca$_{2+}$Fe$^{3+}$(Ni$_{0.06}$Ti$_{0.01}$Al$_{0.02}$)$_{2.00}$V$_{0.02}$Cr$_{0.02}$P$_{2.00}$O$_{10.00}$ with $D_{calc} = 3.604$ g/cm$^3$. The strongest lines of powder XRD pattern $[d(\AA)l/(hk\ell)]$ are 6.98(17)(100), 4.40(22)(101), 3.547(100)(301), 3.485(21)(200), 3.195(50)(020), 2.855(38)(102), 2.389(33)(T22). Crocobelonite represents a novel type of phosphate mineral formed by oxidation of phosphate 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

**INTRODUCTION**

Since the discovery of combusted sedimentary beds in the Judean Desert (Picard 1931) and the recognition of similar rocks elsewhere in Israel, Palestinian Authority and Jordan (Bentor et al. 1963; Gross 1977; Khoury and Nassir 1982a, 1982b; Burg et al. 1992), pyrometamorphic complex known as the Hatrurim Formation or the Mottled Zone (Fig. 1) has attracted substantial mineralogical interest. A combination of high-temperature combustion processes, intense hydrothermal activity and weathering in a desert climate has led to the emergence of dozens of exotic mineral species (e.g., Sokol et al. 2014, 2019; Britvin et al. 2015, 2022a; Khoury 2020). As an example, the anomalous chromium mineralization is represented by a suite of Cr$^{3+}$ species, such as bentorite Ca$_3$Cr$_2$(SO$_4$)$_3$(OH)$_2$·2H$_2$O (Gross 1980) and ellinaite CaCrO$_4$ (Eckhardt and Heimbach 1963), hashemite BaCrO$_4$ (Hauff et al. 1979), perovskite-supergroup chondrites (Weber and Bischoff 1994); perovskite-supergroup minerals: vapnikite, the double perovskite Ca$_{10}$Ca$_5$UO$_{24}$ (Sharygin et al. 2013);...