

# Waipouaite, $\text{Ca}_3(\text{V}_{4.5}^{4+}\text{V}_{0.5}^{5+})\text{O}_9[(\text{Si}_2\text{O}_5(\text{OH})_2)[[\text{Si}_3\text{O}_{7.5}(\text{OH})_{1.5}]] \cdot 11\text{H}_2\text{O}$ , a new polyoxovanadate mineral from the Aranga Quarry, New Zealand

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## ABSTRACT

Waipouaite,  $\text{Ca}_3(\text{V}_{4.5}^{4+}\text{V}_{0.5}^{5+})\text{O}_9[(\text{Si}_2\text{O}_5(\text{OH})_2)[[\text{Si}_3\text{O}_{7.5}(\text{OH})_{1.5}]] \cdot 11\text{H}_2\text{O}$ , is a new mineral from the Aranga Quarry, Northland Region, New Zealand. It occurs in basalt as overgrowths on thompsonite-Ca and chabazite-Ca and as inclusions within calcite and okenite. It forms dark olive green to almost black prismatic crystals to 0.3 mm in length. Crystals are transparent to translucent with a vitreous luster. The Mohs hardness is  $\sim 2$ , and the measured density is  $2.24(2) \text{ g/cm}^3$ . The new mineral is biaxial (+), with  $\alpha = 1.620(5)$ ,  $\beta = 1.622(5)$ ,  $\gamma = 1.628(5)$  (white light). The calculated  $2V$  is  $60.2^\circ$ . Dispersion could not be observed. The optical orientation is  $Z = \mathbf{b}$ . Pleochroism is  $X$  blue-green,  $Y$  olive green,  $Z$  olive;  $X > Y \gg Z$ . Electron microprobe analyses gave the empirical formula (based on 36 O apfu)  $(\text{Ca}_{2.90}\text{Na}_{0.05}\text{K}_{0.04}\text{Sr}_{0.01})_{\Sigma 3.00}(\text{V}_{4.60}^{4+}\text{V}_{0.44}^{5+})_{\Sigma 5.04}(\text{Si}_{4.97}\text{Al}_{0.02})_{\Sigma 4.99}\text{O}_{21.45}\text{OH}_{3.55} \cdot \text{H}_2\text{O}_{11.00}$ .

Waipouaite is monoclinic,  $P2_1/c$ ,  $a = 12.843(3)$ ,  $b = 23.589(5)$ ,  $c = 11.560(2) \text{ \AA}$ ,  $\beta = 115.54(3)^\circ$ ,  $V = 3160.0(13) \text{ \AA}^3$ , and  $Z = 4$ . The eight strongest reflections in the X-ray powder diffraction pattern are [ $d_{\text{obs}}$  in  $\text{Å}$  ( $I$ ) ( $hkl$ ): 11.78 (100) (020, 100), 9.54 (16) (011), 7.85 (19) (021), 6.29 (32) (031), 5.92 (31) (040), 5.22 (21) ( $\bar{1}22$ ), 3.140 (18) ( $\bar{3}33$ ), 2.850 (17) (180, 242). The crystal structure was refined using synchrotron single-crystal X-ray data to  $R_1 = 6.85\%$  for 6594 reflections with  $I > 2\sigma I$ . Waipouaite is the first natural polyoxovanadosilicate and has a novel structure based on  $[(\text{V}^{4+}, \text{V}^{5+})_5\text{O}_{17}]$  polyoxovanadate units, which are unique in natural and synthetic phases. Synthesis of polyoxovanadosilicates has proved to be a great challenge, and the discovery of waipouaite demonstrates that these compounds can form under natural conditions.

**Keywords:** Waipouaite, new mineral species, calcium vanadyl silicate, crystal structure, polyoxovanadate, Aranga Quarry, New Zealand, synchrotron