

Orthovanadate wakefieldite-(Ce) in symplectites replacing vanadium-bearing omphacite in the ultra-oxidized manganese deposit of Praborna (Aosta Valley, Western Italian Alps)

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ABSTRACT

Because of their unique structure and properties, rare-earth (REE) orthovanadates have been extensively employed for decades in advanced ceramics, in particular in the laser industry in replacement of Nd:YAG. A Ca-bearing REE orthovanadate with the empirical formula $(\text{Ce}_{0.279}\text{Ca}_{0.271}\text{Y}_{0.267}\text{Gd}_{0.057}\text{Nd}_{0.055}\text{Dy}_{0.032}\text{Sm}_{0.027}\text{La}_{0.020}\text{Th}_{0.027}\text{Sr}_{0.002})(\text{V}_{0.908}^{5+}\text{Cr}_{0.067}^{3+}\text{Fe}_{0.017}^{3+}\text{As}_{0.005}^{5+})\text{O}_4 \cdot n\text{H}_2\text{O}$ has been found in metacherts from Praborna (Italian Alps) as micrometer-sized euhedral crystals in clinopyroxene + plagioclase symplectites replacing eclogite-facies vanadium-bearing omphacite (Aegirine_{55–48}Jadeite_{42–33}Diopside_{10–8} with $\text{V}_2\text{O}_3 \leq 1.39$ wt%). We applied the synchrotron radiation, single crystal, micro-diffraction technique, recently optimized at ID09A beamline (ESRF, France), to determine the crystal structure of this mineral. It is tetragonal and isostructural with zircon, with $a = 7.2233(12)$ Å, $c = 6.3949(18)$ Å, $V = 333.66(13)$ Å³, $Z = 4$, space group $I4_1/amd$, and it has been therefore identified as Ca- and Y-bearing wakefieldite-(Ce) (ideally $\text{CeV}^{5+}\text{O}_4$). Cell parameters are in agreement with those of synthetic $\text{Ce}_{0.7}\text{Ca}_{0.3}\text{VO}_4$. Raman spectra of the studied wakefieldite-(Ce) are comparable with natural and synthetic wakefieldite-(Ce) spectra and revealed the presence of OH groups and/or water of hydration, which is also suggested by the low totals in microprobe analyses. Mass balance indicates that wakefieldite-(Ce) is a by-product of the omphacite breakdown; omphacite and Mn-rich epidote, a minor reactant, provided vanadium and REE, respectively. Petrological observations and thermodynamic modeling suggest that the mineral, coexisting with hematite, Mn-rich epidote, and braunite, formed during retrogression to greenschist-facies conditions at ultra-oxidized conditions ($\Delta\text{FMQ} \geq +16$ log units), which are often observed in Mn-oxide ores. Wakefieldite is an effective scavenger of REE in oxidized geological environments at P - T conditions that range from sedimentary to medium-grade metamorphic settings, even where the REE bulk concentration is negligible. Its rarity reflects both the overall low abundance of vanadium and the need for ultra-oxidized conditions that are rarely achieved in metamorphic rocks, where REE phosphates (i.e., monazite, xenotime) are commonly found instead.

Keywords: Vanadate, wakefieldite, manganese, Alps