Orthovanadate wakefieldite-(Ce) in syenite 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 (Ce0.279Ca0.271Y0.267Gd0.057Nd0.055Dy0.025Sm0.027La0.020Th0.027Sr0.015)(V5+0.98Ca0.13Fe0.031As0.005O4)nH2O has been found in metacherts from Praborna (Italian Alps) as micrometer-sized euhedral crystals in clinopyroxene + plagioclase symplectites replacing eugonite-facies vanadium-bearing omphacite (AegirineAs4.46Fe2Si2.13Al2.57Diopside0.8 with V2O5 ≤ 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 isosstructural with zircon, with a = 7.2233(12) Å, c = 6.3949(18) Å, V = 333.66(13) Å3, Z = 4, space group I4/mmm, and it has been therefore identified as Ca- and Y-bearing wakefieldite-(Ce) (ideally CeV5+O4). Cell parameters are in agreement with those of synthetic Ce0.7Ca0.3VO4. 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 (AFMQ ≥ +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

INTRODUCTION

Rare-earth (REE) orthovanadates are known in materials science because of their uncommon properties. Neodymium-doped YVO4, GdVO4, and LuVO4 are very efficient laser host crystal (vanadate lasers: e.g., O’Connor 1966). CeVO4 is a semiconductor, showing outstanding redox and optical properties, which is used as a biological safeguard against inflammation and radiation injury because of its oxidation resistance, and could serve as a potential solar-driven photocatalyst and anticancer agent (Chang et al. 2019, and references therein). Surface V5+ species are known to closely interact with Ce4+, which unlike other lanthanides, can be stable in water (e.g., Yu and O’Keefe 2006), reducing it to Ce3+-forming insoluble Ce3+V5+O4 (Martínez-Huerta et al. 2004). Moreover, Ca-bearing CeVO4 could incorporate even some Ce4+ in a stable solid form (Petit et al. 2011).

Wakefieldite, a natural REE orthovanadate of the xenotime group with the ideal formula REEV5+O4 and zircon-type structure, is rare but known to occur preferentially in highly oxidized rocks, in particular in Mn-oxide ores (Baudracco-Grittì et al. 1987; Cadoni et al. 2011; Gröbner et al. 2011; Moriyama et al. 2011; Walter et al. 2018). Wakefieldite was discovered first as wakefieldite-(Y) in an hematite- and goethite-bearing pegmatite at Wakefield Lake, Quebec (Canada) (Miles et al. 1971), followed by wakefieldite-(Ce) found in the oxidation zone of silicified limestones at Kusu (Zaire) and known formerly as kusüite (Deliens and Piret 1977), wakefieldite-(La) from the manganese and iron Glückstern Mine associated with hausmannite Mn2+Mn3+O4 (Thuringia, Germany) (Witzke et al. 2008) and wakefieldite-(Nd) in the Arase stratiform hematite-bearing ferromanganese deposit (Kochi prefecture, Japan) (Moriyama et al. 2011). Wakefieldite-(La), along with a series of vanadium- and REE-bearing minerals, has also been reported in low-grade obducted manganese-rich radiolarites covering the Ligurian