Phosphovanadylite-Ca, Ca[V₄⁺P₂O₈(OH)₈]⋅12H₂O, the Ca analogue of phosphovanadylite-Ba

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ABSTRACT

Phosphovanadylite-Ca, Ca[V₄⁺P₂O₈(OH)₈]⋅12H₂O, is a new mineral from the South Rasmussen (or South Rasmussen Ridge) phosphate mine, Soda Springs, Caribou County, Idaho. It is named as the Ca analog of phosphovanadylite, which is now renamed as phosphovanadylite-Ba. The new mineral grows on matrix containing fine-grained quartz, massive, porous fluorapatite and hydroxylapatite, framboidal pyrite, and tiny, euhedral sphalerite crystals. Other minerals directly associated with the new mineral are sincosite and native Se. Phosphovanadylite-Ca crystallized at ambient temperatures from late-stage aqueous solutions of near neutral pH under relatively reducing conditions. The mineral is cubic, space group $\bar{A}3m$, $a = 15.441(11)$ Å, $V = 3682(5)$ Å³, and $Z = 6$. Crystals occur as small, greenish-blue simple cubes (to 0.1 mm on edge) intergrown to form thin crusts. Penetration twinning on {111} is common. The color is bright greenish blue, the streak is very pale greenish blue, and the luster is vitreous. The Mohs hardness is estimated at 2. The new mineral is brittle with irregular fracture and no cleavage. The measured density is 2.02(3) g/cm³ and the calculated density based on the empirical formula is 2.038 g/cm³. Phosphovanadylite-Ca is isotropic with $n = 1.559(2)$. The normalized electron microprobe analysis based upon sufficient H for charge balance and 12 molecules of zeolitic H₂O is: Na₂O 0.22, K₂O 0.55, CaO 5.58, SrO 0.10, BaO 0.21, Al₂O₃ 3.27, VO$_2$ 35.85, P₂O₅ 18.78, H₂O 35.44, Total 100.00. The empirical formula (based on 2 P and 28 O apfu) is: (Ca$_{0.75}$K$_{0.09}$Na$_{0.05}$Ba$_{0.01}$Sr$_{0.01}$)$_{23}$O$_{89}$[(V$_{4+}$Al$_{0.75}$)$_{23}$P$_{28}$O$_{105}$(OH)$_{3.87}$]⋅12H₂O. The eight strongest powder X-ray diffraction lines are $d_{	ext{obs}}$ in Å (hkil): 11.04 (110) 97, 7.7881 (200) 100, 4.487 (222) 14, 3.1706 (422) 46, 2.749 (440) 32, 2.4576 (440) 32, 2.2343 (620) 14, and 1.8295 (822) 16. The crystal structure of phosphovanadylite-Ca ($R_1 = 0.027$ for 171 reflections with $F_o > 4\sigma(F)$) contains V$_{4+}$O$_8$ polyvanadate clusters of four edge-sharing V$_4$O$_8$ octahedra. The polyvanadate clusters are linked into a three-dimensional zeolite-like framework by sharing corners with PO$_4$ tetrahedra. The open space in the framework is dominated by H₂O with the equivalent of one large cation pfu sharing one of the H₂O sites. The framework is identical to that in phosphovanadylite-Ba; however, in phosphovanadylite-Ba, the dominant extra-framework cation is Ba, while in phosphovanadylite-Ca, it is Ca.

Keywords: Phosphovanadylite-Ca, new mineral, crystal structure, zeolite-type structure, phosphovanadylite-Ba, South Rasmussen phosphate mine, Idaho

INTRODUCTION

Phosphovanadylite, Ba[V₄⁺P₂O₈(OH)₈]⋅12H₂O, was described in 1998 by Medrano et al. from the Enoch Valley phosphate mine, Soda Springs, Caribou County, Idaho. This mine was operated by the Monsanto Company from 1986 to 2004 and is now reclaimed. The mining of phosphates in southeastern Idaho has come under intensive scrutiny in recent years because of contamination of the water system, especially by Se. Nevertheless, mines continue to be operated by several companies, including Monsanto (through its wholly owned subsidiary, P4 Production LLC). Development of the South Rasmussen (or South Rasmussen Ridge) mine began with the issuance of a lease to Monsanto in 2001 by the Bureau of Land Management (BLM). Specimen collecting at the South Rasmussen mine in 2010 by then mine geologist John Keefner and one of the authors (T.A.L.) yielded crystals of the new mineral Phosphovanadylite-Ca, described herein. Interestingly, the new mineral occurs in association with native Se.

Phosphovanadylite-Ca is named as the Ca-dominant analog of phosphovanadylite. The new mineral and name has been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2011-101). The description of the mineral is based upon material from five co-type specimens now deposited in the collections of the Natural History Museum of Los Angeles County, California, U.S.A., catalog numbers 63578, 63579, 63580, 63581, and 63582. The CNMNC has also approved the name change for the original phosphovanadylite to phosphovanadylite-Ba.

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