Discreditation of bobdownsite and the establishment of criteria for the identification of minerals with essential monofluorophosphate (PO$_3$F$_2^-$)

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ABSTRACT

Bobdownsite, IMA number 2008-037, was approved as a new mineral by the Commission on New Minerals, Nomenclature and Classification (CNMNC) as the fluoride end-member of the mineral whitlockite. The type locality of bobdownsite is in Big Fish River, Yukon, Canada, and bobdownsite was reported to be the first mineral with essential monofluorophosphate (PO$_3$F$_2^-$). The type specimen of bobdownsite has been reinvestigated by electron probe microanalysis (EPMA), and our data indicate that fluorine abundances are below detection in the mineral. In addition, we conducted detailed analysis of bobdownsite from the type locality by gas chromatography isotope ratio mass spectrometry, Raman spectroscopy, EPMA, and NMR spectroscopy. These data were compared with previously published data on synthetic monofluorophosphate salts. Collectively, these data indicate that bobdownsite is indistinguishable from whitlockite with a composition along the whitlockite-merrillite solid solution. Bobdownsite is therefore discredited as a valid mineral species. An additional mineral, krásnoite, has been purported to have monofluorophosphate components in its structure, but reexamination of those data indicate that F$^-$ in krásnoite forms bonds with Al, similar to OH$^-$ bonded to Al in perhamite. Consequently, krásnoite also lacks monofluorophosphate groups, and there are currently no valid mineral species with monofluorophosphate in their structure. We recommend that any future reports of new minerals that contain essential monofluorophosphate anions be vetted by abundance measurements of fluorine, vibrational spectroscopy (both Raman and FTIR), and where paramagnetic components are permisibly low, NMR spectroscopy. Furthermore, we emphasize the importance of using synthetic compounds containing monofluorophosphate anions as a point of comparison in the identification of minerals with essential monofluorophosphate. Structural data that yield satisfactory P-F bond lengths determined by X-ray crystallography, coupled with direct chemical analyses of fluorine in a material do not constitute sufficient evidence alone to identify a new mineral with essential monofluorophosphate.

Keywords: Merrillite, whitlockite, apatite, krásnoite, fluorine, SIMS standard, NMR spectroscopy, hydrogen isotopes

INTRODUCTION

Phosphate minerals such as apatite, merrillite, and whitlockite are of importance to a wide variety of fields from Earth science to life science, material science, and planetary science (Chew and Spikings 2015; Harlov 2015; Hawthorne 1998; Hughes et al. 2006, 2008; Hughes and Rakovan 2015; Jolliff et al. 2006; McCubbin and Jones 2015; McCubbin et al. 2014; Rakovan and Pasteris 2015; Shearer et al. 2015; Webster and Piccoli 2015). Phosphates are the major source of P on Earth and their uses range from fertilizers to detergents to insecticides. Synthetic phosphates have been used for ceramics and coatings, and have even been used for the production of fuel cells (i.e., Kendrick et al. 2007; Lin et al. 2007; Pietak et al. 2007). Phosphates have a propensity for concentrating rare earth elements (Jolliff et al. 1993; Prowatke and Klemme 2006; Shearer et al. 2011) that are used pervasively for deciphering sedimentary, igneous, and metamorphic petrogenesis. Furthermore, their ability to accommodate the radios isotopes used for dating makes them important to geochronological studies of rocks (Chew and Spikings 2015). At present, there are 586 unique phosphate mineral spec-