Crystal-chemical reinvestigation of probertite, CaNa[B$_2$O$_4$(OH)$_4$]·3H$_2$O, a mineral commodity of boron

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ABSTRACT

The crystal chemistry of probertite, a mineral commodity of B (B$_2$O$_3$ ~ 50 wt%) with ideal formula CaNa[B$_2$O$_4$(OH)$_4$]·3H$_2$O from the Kramer Deposit (Kern County, California, type locality), was investigated by a multi-methodological approach [i.e., single-crystal X-ray (at 293 K) and neutron (at 20 K) diffraction, EPMA-WDS, LA-ICP-MS, and LA-MC-ICP-MS]. As recently determined for other hydrous borates, the real chemical formula of probertite from the Kramer Deposit is virtually ideal, i.e., the fractions of other elements are insignificant. Therefore, excluding B, probertite does not act as a geochemical trap of other industrially relevant elements (e.g., Li, Be, or REE). Our experimental results confirm that the structure of probertite is built up by the so-called pentaborate polyanion [B$_5$O$_{10}$(OH)$_6$]$^3-$ (topology: 5(2Δ + 3T)), which consists of oxygen-sharing B-tetrahedra and B-triangular units. The five (geometrical) components of the polyanion are BO$_3$, BO$_2$OH, BO$_2$O, BO$_2$OH, and BO$_2$(OH)$_2$ groups. The pentaborate building units are connected to form chains running along [100]. Clusters of distorted Ca-polyhedra [Ca$_2$O$_3$(OH)$_2$(OH)$_2$]$_n$, CN = 9] and Na-polyhedra [Na$_2$O(OH)$_2$(OH)$_2$]$_n$, CN = 6] are mutually connected by edge-sharing and, in turn, connected to the pentaborate chains by edge-sharing (with the Ca-polyhedron) and corner-sharing (with the Na-polyhedron). The hydrogen-bonding scheme of the probertite structure is complex and pervasive, with 10 independent H sites (belonging to hydroxyl groups or H$_2$O molecules) and 11 of the 14 oxygen sites being involved in H-bonds as donor or acceptors. Hence, the H-bonding network likely plays an important role in the stability of probertite. In addition, the potential utilizations of probertite are discussed.

Keywords: Probertite, borates, mineral commodity, X-ray diffraction, neutron diffraction, crystal chemistry, hydrogen bonding

INTRODUCTION

Proberrite is a hydrous borate, with the ideal formula CaNa[B$_2$O$_4$(OH)$_4$]·3H$_2$O, usually found in sedimentary borate deposits along with the more common borax [ideal composition (i.e.), Na$_2$[B$_2$O$_4$(OH)$_4$]·8H$_2$O], colemanite (i.e., Ca[B$_2$O$_4$(OH)$_4$]·H$_2$O), ulexite (i.e., NaCa[B$_2$O$_4$(OH)$_4$]·5H$_2$O), kernite and tincalconite (i.e., Na$_2$[B$_2$O$_4$(OH)$_4$]·8H$_2$O). Borates from this kind of deposit represent more than 90% of the borate minerals utilized by industry worldwide (USGS 2019 and references therein). On the basis of its high economic importance and supply risk, boron is considered one of the “critical elements” (or “critical raw materials,” according to the European Commission 2017). The worldwide production of borates has been tripled in the last 20 years (ca. 3 Mt in 1998; ca. 10 Mt in 2019), and the forecast predicts the market to grow, in response to the rising request of B for several technologically relevant products (e.g., heat-resistant glasses and ceramics, B-treated low-alloy steels, radiation-shielding materials, pharmaceutical, and agricultural compounds). Among those, the radiation-shielding materials represent a market segment referred to as nuclear reactors for energy production or scientific research, along with neutron sources for medical applications (i.e., B neutron-capture therapy). B-bearing materials can offer an efficient radiation-shielding capacity, as $^{10}$B shows a high capacity to absorb thermal neutrons due to its high cross-section for the $^{10}$B(n,α)$^7$Li reaction (~3840 barns; Carter et al. 1953; Sears 1986; Palmer and Swihart 1996; Rauch and Waschkowski 2002). On the other hand, the neutron absorption capacity of $^{11}$B is modest (cross section ~0.006 barns). In nature, about 20% of boron occurs as $^8$B.

In the last years, we have investigated the crystal chemistry and the physical and chemical stability (at high/low temperature and high pressure, or leaching) of colemanite (Lotti et al. 2017, 2018, 2019), kurnakovite (ideally Mg[B$_2$O$_4$(OH)$_4$]·5H$_2$O (Gatta et al. 2019; Pagliaro et al. 2021)), kernite (Comboni et al. 2020a; Gatta et al. 2020), and meyerhoffierite (ideally Ca$_2$[B$_2$O$_4$(OH)$_4$]·2H$_2$O (Comboni et al. 2020b)), using a multi-methodological approach. The aim of this paper is to extend our crystal-chemical investigation on borates to probertite, as one of the naturally occurring borates with the highest B-content (~50 wt% B$_2$O$_3$), by a multi-methodological approach based on single-crystal X-ray (at room conditions) and neutron diffraction (at low temperature: 20 K), electron microprobe analysis in wavelength-dispersive mode (EPMA-WDS) along with laser