Crystal structure and chemistry of skarn-associated bismuthian vesuvianite

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ABSTRACT

Due to its strong chalcophile character and the influence of its s2 lone-pair electrons on the crystal structure trivalent bismuth is extremely rare in silicate minerals, with Bi-contents in common silicates typically below 1 ppm. In the present paper, we report on an exceptionally Bi-rich variety of the rock-forming mineral vesuvianite with up to ca. 20 wt% Bi2O3, occasionally in combination with enhanced Pb contents up to ca. 5 wt% PbO. The mineral occurs as small (≤300 μm) idiomorphic, black crystals in a sulfide-free silicate skarn in the Långban Mn-Fe deposit, central Sweden. The major skarn minerals comprise Ba-rich potassium feldspar, albite plagioclase, Pb-rich scapolite, and phlogopite, while Pb-rich epidote, vesuvianite, and calcic garnets are minor phases. The vesuvianite grains are intensely zoned displaying Bi-rich cores surrounded by thinner Bi-poor rims. Although generally high in bismuth, the crystal cores invariably show oscillatory zoning. In addition to high Bi- and Pb-contents, the crystals are occasionally enriched in copper, cerium, antimony, and arsenic, thus reflecting the complex chemistry and evolution of the Långban mineralization.

Chemical analyses demonstrate a strong negative correlation between Ca and Bi, hence confirming that Bi replaces Ca at X sites of the vesuvianite structure. Concentrations of Si and Al are lower, while Fe and Ti contents are somewhat enhanced in the Bi-rich cores. Maximum Bi and Pb contents analyzed in the present vesuvianite crystals correspond to 3.19 and 0.87 atoms per formula unit, respectively. This exceeds by far previous reports in the literature. X-ray single-crystal diffraction studies of a crystal splinter with intermediate Bi-content (1.08 apfu) show that the space group P4/nnc is the most appropriate to describe the crystal structure; the refinement converged to an R1 index of 0.0493. The recorded unit-cell parameters, a = 15.7018(6), c = 11.8648(6) Å, and V = 2925.2(2) Å3, are to our knowledge the largest ones observed so far for P4/nnc vesuvianite. Bismuth was demonstrated to order at the X3′(Bi) site that is only 0.46 Å distant from the nearest X3(Ca) site. Consequently, the X3 and X3′ sites cannot be simultaneously fully occupied.

Keywords: Vesuvianite, bismuth, crystal structure, Långban, Sweden, skarn, crystal chemistry

INTRODUCTION

The ionic radii of sixfold- to eightfold-coordinated Bi3+ (1.03–1.17 Å) are very similar to those of Na+ (1.02–1.18 Å), Ca2+ (1.00–1.12 Å), and trivalent cations of the light rare earth elements, as, e.g., Ce3+ (1.01–1.14 Å) (Shannon 1976). This suggests that cases of Bi3+ substitution in rock-forming Na- and/or Ca-silicates should not be uncommon. However, Bi-contents are generally very low (<1 ppm) in silicate minerals and only two extremely rare silicate minerals with nominal Bi-contents are known; eulytine [Bi4(SiO4)3] and bismutoferrite [Fe2Bi(SiO4)3(OH)]. In contrast, Bi-contents may reach high levels in common sulfide minerals and a large number of Bi-sulfide mineral species are known. Main reasons for this are the affinity for Bi3+ to form covalent bonds to sulfur (chalcophile character) and the 6s2 lone-pair electronic configuration of Bi3+ that prefers highly unsymmetrical coordination in oxygen-based structures. However, the stereochemical effects of the lone-pair configuration weaken with increasing coordination number of the Bi-centered polyhedra (Galy et al. 1975) and this creates possibilities for Bi-incorporation in certain silicate structures when formed in environments poor in sulfur. In the present paper, we report on the crystal chemistry of an extremely Bi-rich vesuvianite that represents an exceptional example of Bi3+ substitution in a rock-forming silicate mineral.

The simplified formula of boron-free vesuvianite can be written as XaYbZcO8Wd where X represents four independent sevenfold- to ninefold-coordinated sites, Y represents one five-fold-coordinated (Y1) and two independent sixfold-coordinated sites (Y2 and Y3), Z denotes three distinct fourfold-coordinated sites, and W represents the sites (O10 and O11) occupied by monovalent and divalent anions such as (OH), F, and O (Groat et al. 1992a, 1992b). Vesuvianites with empty T sites, 01T1 and 01T2, have 10 W sites in the structural formula, whereas vesuvianites with three-fold-coordinated B at T2 have 11 W sites due to the substitution 12B + 24O → 17O + 19(OH) (Groat et al. 1996). The general formula for vesuvianite group minerals may therefore be formalized as XaXYbYTcZdO8(W)e, where “O” and “D” denote ortho- and dicyclic groups and W represents sites

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0003-004X/13/0004-566$5.00/DOI: http://dx.doi.org/10.2138/am.2013.4310

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American Mineralogist, Volume 98, pages 566–573, 2013