Fe-rich and As-bearing vesuvianite and wiluite from Kozlov, Czech Republic

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ABSTRACT

Green vesuvianite crystals occur with garnet and calcite in a hand specimen from the Nedvědice marble near Kozlov (near Štěpánov nad Svatkou, Svatka Crystalline Complex) in the Czech Republic. The average electron microprobe composition of the vesuvianite shows 12.10 wt% Fe₂O₃ (4.66 Fe pfu), 2.77 wt% B₂O₃ (2.45 B pfu), 1.71 wt% As₂O₃ (0.46 As pfu), and 1.40 wt% F (2.26 F pfu). The Fe concentration is the highest ever recorded for a vesuvianite-group mineral. The boron contents are extremely variable and two of the five compositions show more than the 2.50 B pfu needed for wiluite, and the average is only slightly less than this. The crystal structure \[ \{a = 15.7250(4), c = 11.7736(3) \text{ Å}\] was refined in space group \(P4/nnc\) to an \(R_I\) value of 0.0221. The site refinement and Mössbauer spectroscopy results show Fe\(^{3+}\) substituting for Ca at the X3 site and filling the Y1 position, and Fe\(^{3+}\) substituting for Al at the Y3 position. Most of the Fe (70% from the site refinements and 78% from the Mössbauer interpretation) is ferric. The main effect of the high-Fe concentration is to increase the mean Y3-O distance to an unusually large 2.018 Å. Boron occurs at the T1 site, where it is coordinated by oxygen atoms at two O7B and two O11 positions, and at the T2 sites where it is coordinated by O atoms at one O10 and two O12A sites. When the nearby X3 site contains Fe, the T2 position is either vacant or [3]-coordinated by some combination involving an O10 site and two O12B positions, in which case the B atom is likely offset from the T2 site to reduce the B-O12B distance.

Fluorine and OH occupy the O11 positions when there is a vacancy at the adjacent T1 position. Pentavalent As substitutes for Si at the ZZ site and Al at the Y2 site. The \(P4/nnc\) symmetry indicates that this vesuvianite formed at high temperatures (400–800 °C) and the predominance of Fe\(^{3+}\) and As\(^{5+}\) suggests under oxidizing conditions.

The results showing Fe at three different sites with three different coordinations attests to the flexibility of the vesuvianite crystal structure. The incorporation of As at two different sites in the structure shows that rock-forming silicate minerals such as vesuvianite can be a reservoir for this heavy element.

Keywords: Vesuvianite, wiluite, iron, Czech Republic, arsenic, crystal structure

INTRODUCTION

Vesuvianite is a rock-forming or accessory silicate mineral found in metamorphic rocks, rodoliths, and altered alkaline rocks. From a crystal-chemical point of view the formula of vesuvianite may be written as \(X_{10}Y_{11}Z_{27}O_{35}(OH,F)_6\), where X are seven- to ninefold-coordinated, Y has octahedral or square pyramidal coordination, and Z represents tetrahedral coordination. The X positions are commonly occupied by Ca; the Y sites by Al, Mg, and Fe; and the Z positions by Si. The vesuvianite structure (Fig. 1) is closely related to that of grossular, but differs from it by having additional X4 and Y1 sites (site nomenclature from Groat et al. 1992a), the latter with square pyramidal coordination, at various levels along the fourfold axes. It is assumed that the X4 and Y1 periodicity is preserved within a single channel, but adjacent channels may have X4 and Y1 at different z levels (e.g., Giuseppetti and Mazzi 1983; Fitzgerald et al. 1986; Allen and Burnham 1992; Pavese et al. 1998; Armbruster and Gnos 2000a, 2000b). The different X4 and Y1 arrangements lead to various tetragonal space groups. Allen and Burnham (1992) showed that ordered channel arrangements are favored in vesuvianites grown at <300 °C, and such crystals exhibit either \(P4/n\) or \(P4nc\) symmetry. In addition, a crystal might be assembled of domains representing both space groups, in which case the resulting space group becomes \(P4\). Vesuvianites grown at 400–800 °C exhibit disordered channel arrangements and the resulting symmetry is \(P4/nnc\) (Allen and Burnham 1992), Galuskin et al. (2003) suggested that the degree of order is also influenced by substitutions at the channel sites.

Groat et al. (1994, 1996) reported that some vesuvianite samples contain B at the T1 (0.055, 0.055, ¼) and T2 (¼, ¼, ¼, ¼) sites and Groat et al. (1998) described the new vesuvianite-group mineral wiluite defined as having more than 2.5 B atoms per formula unit (apfu). Groat et al. (1992b) showed that F substitutes for OH at both the O10 and O11 sites in the vesuvianite structure and Britvin et al. (2003) described the new vesuvianite-group mineral fluorvesuvianite defined as containing more than 4.5 F apfu.