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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 Svratkou, Svratka Crystalline Complex) in the Czech Republic. The average electron microprobe composition of the vesuvianite shows 12.10 wt% Fe_2O_3 (4.66 Fe pfu), 2.77 wt% B_2O_3 (2.45 B pfu), 1.71 wt% As_2O_5 (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) Å] was refined in space group $P4/nnc$ to an R_1 value of 0.0221. The site refinement and Mössbauer spectroscopy results show Fe^{2+} 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 Z2 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