The crystal structure of cascandite, CaScSi$_5$O$_8$(OH)

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Abstract

A new pyroxenoid mineral, cascandite, with the ideal formula CaScSi$_5$O$_8$(OH), is triclinic with $a = 9.791(8)$ Å, $b = 10.420(9)$ Å, $c = 7.076(6)$ Å, $\alpha = 98.91(8)^\circ$, $\beta = 102.63(8)^\circ$, $\gamma = 84.17(8)^\circ$; $Z = 4$ for the $C\overline{1}$ unit cell setting. The crystal structure of cascandite is similar to those of pectolite and serandite and is composed of two main structural units: octahedral chains and three repeat tetrahedral chains. Cascandite, unlike pectolite and serandite, has only two octahedral cations per formula unit, and the octahedral chains are formed by two strands of edge-sharing octahedra occupied by calcium and scandium cations.

Cascandite is a member of the hydrous pyroxenoid series, whose peculiarities are related to the presence of intrachain hydrogen bonding.

Introduction

Cascandite, a new scandium silicate, was found in a geode from the granite of Baveno, Italy, together with quartz, orthoclase, albite and jervisite, another new scandium silicate with ideal formula NaScSi$_5$O$_6$. The descriptions of these new minerals are given by Mellini et al. (1982). The chemical, physical and crystallographic properties indicate that cascandite is a three-repeat pyroxenoid.

The present structural study was undertaken to give a better description of the new scandium mineral and to acquire a deeper insight into the crystal chemistry of pyroxenoids.

Structure determination

A small crystal of cascandite was selected and examined first by X-ray film methods. Triclinic cell parameters (Table I) were obtained by least squares refinement using 25 reflections centered on a Philips PW 1100 single-crystal diffractometer with graphite monochromated MoKα radiation. A total of 1526 non-zero reflections were measured from 3 to 30° 2θ, using a 2θ/2θ scan and scan width 1.20°. The data were corrected for Lorentz and polarization factors. No absorption correction was made because of the small dimensions of the crystal.

Only qualitative energy dispersive analytical data were available when the structure determination was undertaken. The solution of the structure was obtained starting from the atomic coordinates of wollastonite based on $P\overline{1}$ setting, as given by Buerger and Prewitt (1961). However the $E$ statistics indicated a non-centrosymmetric structure, and thus we removed the symmetry constraints on the octahedral cations. We assumed that one of the six octahedral sites in the unit cell of the trial structure was vacant and the site that had been centrosymmetrically related was occupied by a scandium cation, as suggested by the preliminary analytical data. Four refinement cycles were calculated, each followed by a Fourier synthesis. The behavior of the thermal parameters and the heights of the various peaks in the Fourier maps strongly indicated that one more octahedral site had to be considered vacant and that two silicon atoms had to be shifted from their positions in the trial structure. The new structural arrangement smoothly refined to an $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o| = 0.08$.

We then realized that the arrangement was indeed a centrosymmetric one, closely related to that in minerals of the pectolite-serandite series. The false indication of the absence of a symmetry center most probably resulted from not having taken into account the "unobserved" reflections. The refinement was then continued in the $P\overline{1}$ space group. The introduction of anisotropic thermal parameters for all atoms led to $R_1 = 0.042$ and $R_2 = (\Sigma w |F_o| - |F_c| / \Sigma |F_o|^2)^{1/2} = 0.046$, where $w$ was the reciprocal of the variance on $F_o$ as estimated from
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