

An unusual epidote supergroup mineral: A solid solution containing the new (OH)-analogue of dollaseite-(Ce)

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In a fragment of a skarn rock from the Malmkärra iron mine, Norberg, Västmanland (Sweden) containing the fluorbritholite-(Nd) holotype (Holtstam et al. 2023), an unusual mineral belonging to the allanite group has been found. Besides fluorbritholite-(Nd), the associated minerals are calcite, dolomite, magnetite, lizardite, talc, fluorite, baryte, scheelite and gadolinite-(Nd). The mineral was investigated with electron microprobe, single crystal X-ray diffraction, vibrational (Raman and FT-IR) and Mössbauer spectroscopy. One crystal was annealed at different temperatures from 500 to 700°C, in 50°C steps. Structural refinements, along with quantitative chemical data, suggest the following cationic populations for the structural sites: $A1 = \text{Ca}_{0.96}\text{REE}^{3+}_{0.03}\text{Mn}_{0.01}$; $A2 = \text{REE}^{3+}_{0.99}\text{Ca}_{0.01}$; $M1 = \text{Mg}_{0.40}\text{Al}_{0.32}\text{Fe}^{3+}_{0.26}\text{Fe}^{2+}_{0.02}$; $M2 = \text{Al}_{0.98}\text{Fe}^{3+}_{0.02}$; $M3 = \text{Mg}_{0.72}\text{Fe}^{2+}_{0.18}\text{Fe}^{3+}_{0.10}$; $T1,2,3 = \text{Si}_{2.93}\text{Al}_{0.07}$, leading to a total positive charge of 24.63. The presence of divalent iron is in fairly good agreement with Mössbauer data, and it is confirmed by a significant shortening of the $\langle M3\text{-O} \rangle$ distance, compatible with Fe^{2+} oxidation induced by heating in air (Bonazzi & Menchetti 1994). The occurrence of a considerable amount of divalent cations at both $M1$ and $M3$ sites requires more than one monovalent anion per formula unit. In the dollaseite group minerals, where $M1$ and $M3$ are dominated by divalent cations (Armbruster et al. 2006), charge balance is achieved through the $\text{F}^- \rightarrow \text{O}^{2-}$ substitution at the O4 site. The lack of fluorine in the present mineral suggests that charge neutrality could be achieved through the presence of additional H^+ (about 0.4 atoms per formula unit, apfu), which could also explain unusual peaks observed at 3580 and 3594 cm^{-1} in Raman and FT-IR spectra, respectively. Another $\text{O}\cdots\text{O}$ contact suitable for a hydrogen bond could occur between O10 and O2 (Gatta et al. 2012); however, only one independent proton site could be located, with O10 as donor and O4 as acceptor. According to Varlamov et al. (2019), a number of epidote minerals seem to have more than one hydroxyl group pfu, although Raman spectra of the studied samples did not allow them to estimate the exact content of OH groups due to strong luminescence and background noise at wavenumbers $> 2000 \text{ cm}^{-1}$. In conclusion, it is reasonable to describe the composition of the mineral from Malmkärra as a solid solution between three members, *i.e.*, dissakisite-(Ce) (32%), ferriallanite-(Ce) (28%), and the (OH)-analogue of dollaseite-(Ce) (40%), a still undescribed end-member.

References

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