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Multi-analytical approach to solve the puzzle of an allanite-subgroup mineral from Kesebol, Västra Götaland, Sweden

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ABSTRACT

Dark-brownish, euhedral crystals of an "allanite-like" mineral occur in a hematite-impregnated Mn-silicate rock at Kesebol, Västra Götaland, Sweden, associated with gasparite-(Ce), chernovite-(Y), rhodonite, andradite, manganoan calcite, and quartz. A structural study was carried out on single crystals—untreated, heated in air, and heated under inert atmosphere—combined with Mössbauer spectroscopy and TEM investigation. In all the untreated crystals the mean <M3-O> distance indicates that Me^{2+}(Me = Mn, Fe) prevails at this site (<M3-O> in the range 2.169–2.180 Å), in contrast with chemical data obtained by EPMA that yield a simplified formula $Ca(REE^{3+}_{2/3}\square_{1/3})Me^{3+}_3(SiO_4)(Si_2O_7)O(OH)$, when normalized to Si = 3.00 apfu. Moreover, when a crystal is heated in air, all geometrical and structural variations indicate the development of an oxidation-dehydrogenation reaction, thus confirming that M3 is occupied by divalent cations before heating. The corresponding dehydrogenation is confirmed by a dramatic lengthening of the donor-acceptor distance. A crystal was annealed under inert atmosphere to verify possible effects of radiation damage on the polyhedral volumes. After prolonged annealing at 700 °C, a slight decrease of the unit-cell parameters is observed, suggesting restoring of crystallinity from a "partially metamict" state. Nonetheless, even in the annealed crystal, the <M3-O> distance is still consistent with a dominance of divalent cations at the M3 site. For all the examined crystals, structural data point to an octahedral cation population as follows: M1 = (Me^{3+}, Al); M2 = (Al, Me^{3+}); M3 = (Me^{2+}, Me^{3+}). This assumption is also in agreement with the Mössbauer spectrum, which was fitted to two Lorentzian quadrupole doublets for Fe^{3+} and one for Fe^{2+}. Values of the isomer shifts (0.36 and 0.37 mm/s for Fe^{3+}; 1.11 mm/s for Fe^{2+}) and the quadrupole splitting (1.96 and 1.02 for Fe^{3+}; 1.90 for Fe^{2+}) show that Fe^{2+} (~12% of the total iron) is located in M3, while Fe^{3+} occupies M1 and, to lesser extent, M2. TEM-EDS investigations have revealed chemical heterogeneities related to different degree of radiation damage. In particular, areas showing poor crystallinity are relatively enriched in Si and O with respect to the highly crystalline areas, thus suggesting that EPMA chemical data are biased by the presence of metamict areas enriched in SiO_2 and likely in H_2O. EPMA data were therefore corrected for the excess of silica. The cation population after correction is in keeping with the structural and spectroscopic data. Disregarding minor substitutions, the ideal chemical formula for the epidote-group mineral from Kesebol is $CaREEFe^{3+}AlMn^{2+}(Si_2O_7)(SiO_4)O(OH)$, which is related to ferriallanite-(Ce) by the substitutional vector $^{M3}(Mn^{2+}) \rightarrow {}^{M3}(Fe^{2+})$.

Keywords: Epidote-group, allanite-subgroup, single-crystal X-ray diffraction, Mössbauer spectroscopy, transmission electron microscopy, metamictization