

Atomistic processes in actinolite and tremolite at elevated temperatures

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Elucidating the atomistic mechanism of high-temperature transformations of iron-containing amphiboles ($AB_2C_5T_8O_{22}W_2$, with $C_5 = M(1)_2M(2)_2M(3)$) may have important implications in several fields, including metamorphic petrology, geophysics, and environmental sciences. Here the effect of octahedrally coordinated Fe^{2+} on the temperature-driven dehydrogenation/dehydroxylation in Mg-rich amphiboles is analysed by a comparative study of tremolite and actinolite via *in situ* high-temperature Raman spectroscopy, thermogravimetric/mass-spectrometry analyses, and X-ray diffraction (Rösche et al. 2022).

We show that similar to Fe-rich amphiboles (Mihailova et al. 2021, 2022, Bernardini et al. 2023) thermally activated delocalized e^- and H^+ are also formed in Fe-bearing magnesian amphiboles, but at much higher temperatures than in ferrous (e.g. grunerite) and mixed-valence iron-rich amphiboles (e.g. riebeckite). The delocalized electrons in actinolite couple with polar FeO_6 phonons to form polarons. However, the polaronic dipoles in actinolite are not mutually aligned as in the case of Fe-rich amphiboles, because iron cations are present in the actinolite structure as isolated octahedra or dimers of octahedra, while the majority of MO_6 octahedra in the strips are occupied by Mg. The final product of the thermally-induced decomposition of both actinolite and tremolite is a single phase of monoclinic pyroxene with an intermediate chemical composition between diopside and clinoenstatite, having vacancies at the octahedral sites and, for actinolite, also Fe^{3+} . Cristobalite occurs only as a minor phase in amounts less than 1% and ~5% for tremolite and actinolite, respectively. The dehydroxylation of tremolite causes immediate collapse of the silicate double chain into SiO_4 single chains, which is followed up by a rearrangement of the amphibole B-type and C-type cations into pyroxene octahedral sheets. The actinolite-to-pyroxene breakdown is preceded by a state of "oxo-actinolite" in which all Fe^{2+} are exchanged to Fe^{3+} , all ${}^W(OH)^-$ groups next to Fe-containing $M(1)M(1)M(3)$ configurations are exchanged to ${}^W O^{2-}$, and all H^+ , including those from W -site anions next to MgMgMg triads, are delocalized, but still in the bulk of the crystal grain.

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