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A Monte Carlo study of short- and long-range order of tetrahedral cations in sapphirine and khmaralite

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Abstract

The open-branched tetrahedral chain of sapphirine-group minerals contains tetrahedra with 1–3 bridging O atoms (Q^1, Q^2, and Q^3). The topology implies that short-range order (SRO) driven by bonding enthalpies forces some long-range order (LRO). This is an ideal system to investigate the interplay between SRO, LRO, and configurational entropy. Results are presented of Monte Carlo simulations of ordering patterns involving Be, Al, and Si on the branched chain.

The "Loewenstein's Rule" enthalpy term favoring AlOSi links is insufficient to obtain the experimental LRO occupancies. Additional site-dependent potentials repelling Si from Q^1 and Q^2 and driving asymmetry between the two Q^3 sites are needed. All enthalpy terms are close to 2 RT in magnitude, so the observed LRO cannot be regarded as arising dominantly from Si-avoidance.

A "Markov Braid" method is presented of calculating configurational entropies for the simulations. The substantial SRO present is shown to reduce S_{config} by only 17–18%.

Khmaralite is related to sapphirine but contains ca. 1.5 Be per 12 tetrahedra and shows different LRO of {Be, Al, Si}. The minority cation Be is concentrated in Q^3 sites. If the exchange enthalpy $\Delta H_{AlSi} = -2$ RT, then ΔH_{BeAl} and ΔH_{BeSi} must be –6.5 to –7.5 RT to reproduce the observed mean Q for Be, Al, and Si. Khmaralite has a doubled chain period relative to sapphirine. This superstructure enables the formation of tetrahedral Be–octahedral Fe^{2+} clusters in the structure. A small number of site-specific potentials allows the LRO of the khmaralite chain to be reproduced, but "Be-avoidance" remains by far the dominant interaction.

Site occupancies were extrapolated to Be-rich compositions. More than 1.7 Be atoms per 12 tetrahedra is predicted to drive Be into new sites and create unfavorable BeOBe links, and to drive Si from Q^3 into the Q^1 sites. This is likely to be why the related mineral welshite, which can incorporate higher Be contents, has a quite different Be ordering pattern and symmetry.

Keywords: Branched tetrahedral chain, khmaralite, sapphirine, welshite, aluminum, beryllium, silicon, aluminum avoidance, beryllium avoidance, configurational entropy, long-range order, Markov braid, short-range order, silicon avoidance