Monte Carlo study of short- and long-range order of Be, Al and Si on a branched tetrahedral chain, with implications for mixing behaviour

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

The preference of Si for Q^3 sites in sapphirine *sensu strictu* is traditionally believed to be a consequence of maximising the proportion of enthalpically favourable Si-O-Al linkages. This 'Loewenstein's Rule' enthalpy does indeed tend to drive the minority component onto Q^3 sites. However, for a composition with 1.91 Si per 6 tetrahedra for which neutron diffraction site occupancies are available, even extreme values of $\Delta H_{AlSi} = \Delta H$ ($^1/_2$(SiOSi) + $^1/_2$(AlOAl) $\rightarrow$ SiOAl) raise the mean Q of Si to only 2.45, rather than the 2.64 observed. A realistic value for ΔH_{AlSi} of -1.5 *RT* gives $\langle Q \rangle_{Si}$ = 2.31. Simulations with this energy term alone also have $x_{Si,Q2} > x_{Si,Q1}$ in contradiction to structure refinements. The site occupancies can be simulated well if additional energy terms repelling Si from Q^1 and Q^2 sites, and a term that drives difference in long-range occupancy between the two distinct Q^3 sites, are included. These site-specific terms reflect interaction between the chain and the walls of edge-sharing octahedra that complete the structure.

Khmaralite contains essential Be, and shows a distinctive LRO scheme of the three cations Be, Al and Si. Be competes with Si for Q^3 sites. If ΔH_{BeSi} = -1.5 *RT*, the enthalpies ΔH_{BeAl}, ΔH_{BeSi} must be more negative: -5.2 *RT* and -6.6 *RT* to obtain the structure refinement <Q> values of 2.98, 2.05 and 1.70 for Be, Si, Al respectively. This is consistent with larger charge imbalance making "Be avoidance" a much stronger effect than "Al avoidance". Four small additional site-specific terms including a term generating the doubled chain periodicity of khmaralite replicate 20 out of the 24 independent Be and Si occupancies well.

The simulations can redistribute cations to give maximal SRO for fixed LRO occupancies. Configurational entropies can also be calculated using a "Markov braid" algorithm. SRO reduces both H_{mix} and S_{mix} relative to those predicted from LRO occupancies.