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Relating formulations of the thermodynamics of mineral solid solutions: Activity modeling of pyroxenes, amphiboles, and micas

ROGER POWELL[1,*] AND **TIM HOLLAND**[2]

[1]School of Earth Sciences, University of Melbourne, Parkville, Victoria 3052 Australia
[2]Department of Earth Sciences, University of Cambridge, Cambridge, U.K.

ABSTRACT

In a thermodynamic description of a mineral solid solution, it is customary to select a minimal group of end-members that constitutes an independent set, and yet in practical calculations it commonly occurs that a different independent set or subset is required. Given the simplification of the symmetric formalism, it is straightforward to derive the enthalpies of formation of dependent end-members as well as the interaction energies between the end-members in the new independent set, in terms of those in the original set. For example, a simplified ternary solid solution of Fe-free Ca-amphiboles might be described with independent end-members tremolite, tschermakite, and pargasite, and yet some calculations may require the use of end-members such as edenite or hornblende. Not only are their end-member properties dependent on those of the first three, but the mixing properties of any of the binary joins involving edenite or hornblende are dependent on those in the original independent set. Examples drawn from pyroxenes, amphiboles, and biotite micas show that such dependencies may prove invaluable in using experimental information or heuristics to help constrain the mixing properties of complex solid solutions. In particular, it is found that in non-ideal solid solutions that involve Fe and Mg distributed over two or more non-equivalent sites, equipartition of Fe and Mg implies extreme restrictions on the ratios of the interaction parameters and the magnitude of the Fe-Mg exchange energy. The thermodynamics can only be formulated generally and consistently when Fe-Mg ordering is explicitly included, and this is done most simply via ordered Fe-Mg end-members.