American Mineralogist, Volume 82, pages 165–181, 1997

A statistical model of thermodynamic mixing properties of Ca-Mg-Fe^{2+} garnets

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Abstract

At present the most widely used models of thermodynamic mixing properties of garnet are those that are optimized to fit the experimental phase-equilibrium data along various binary garnet joins using the method of mathematical programming. We conducted a thorough weighted regression analysis of the available volumetric, calorimetric, and phase-equilibrium data. This resulted in a much improved set of a-X relationships with the following Margules parameters (in joules, kelvins, bars). $W^G_{FeMg} = -24166 + 22.09T - 0.034P$, $W^G_{MgFe} = 22265 - 12.40T + 0.050P$, $W^G_{FeCa} = 17526 - 14.51T + 0.135P$, $W^G_{CaFe} = -18113 + 15.51T + 0.040P$, $W^G_{MgCa} = 14306 - 2.49T + 0.140P$, $W^G_{CaMg} = 65182 - 20.82T + 0.068P$ (all pfu containing 12 O atoms). The robust regression analyses allowed us to obtain the uncertainties associated with each of the parameters, quantities not available by mathematical programming analysis of phase-equilibrium data. Uncertainty estimates are essential for rigorous quantification of errors associated with mineralogic thermobarometers. From the probabilistic model developed here, we present detailed formulations for ascertaining errors of activity coefficients of the end-member components in any garnet solid solution. This provides an opportunity to evaluate the uncertainties in mineralogic thermobarometers involving garnets of compositions dissimilar to those used in the experiments on which the garnet mixing models are based. The results of this study elicit several significant points. The analysis strongly suggests that there is an excess entropy of mixing along the Fe-Mg join because Fe-Mg mixing in garnet is substantially nonideal. The excess entropy of mixing along the Ca-Mg and Ca-Fe joins is asymmetric and therefore assumption of a large symmetric entropy parameter or no entropy along these joins is an oversimplification. Large uncertainty in the mixing properties exists for Ca-rich garnets. There should be a Ca-Mg-Fe ternary interaction parameter (7110 J/mol).