

Experimental study along the magnesio-hornblende–glaucophane join

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ABSTRACT

Amphiboles have played a leading role in metamorphic petrology, from helping to define several metamorphic facies to forming the basis of geothermobarometry, if their thermodynamic mixing properties can be calibrated to the temperature and pressure of formation. Compositional variations of sodium- and sodium-calcium-amphiboles may reveal important information about paleo-subduction zones but have not been studied as much as the more common calcium-amphiboles. In this study we investigate the mixing properties of amphibole solid solutions between magnesio-hornblende and glaucophane [${}^B\text{Ca}_2{}^C(\text{Mg}_4\text{Al})^T(\text{AlSi}_7)\text{O}_{22}(\text{OH})_2 - {}^B\text{Na}_2{}^C(\text{Mg}_3\text{Al}_2)^T(\text{Si}_8)\text{O}_{22}(\text{OH})_2$] as a binary sub-join within the ternary amphibole system tremolite–glaucophane–tschermakite where the principal substitutions are Ca for Na at the B, Al for Mg at the C, and Al for Si at the T crystallographic sites. Amphiboles were made from mixtures of reagent oxides at 10 mol% increments between magnesio-hornblende and glaucophane, formed in a piston-cylinder press at 735–860 °C and 1.3–2.5 GPa for 72–216 h giving good yields (92–100 wt%). A positive deviation is present in the volume-composition plot, even after correcting volumes for non-binary components, supporting the presence of a positive deviation in the enthalpy of mixing (ΔH^{mix}) along this join. Fourier transform infrared spectra (FTIR) were obtained in the range of 350–4000 cm⁻¹ for the mid-infrared spectra (MIR) for the purpose of estimating the extent of short-range ordering and for autocorrelation analysis, and, in the 650–50 cm⁻¹, for far-infrared spectra (FIR) for autocorrelation analysis. Autocorrelation analysis gave $\delta\Delta\text{Corr}$ values, which further support a positive deviation in the ΔH^{mix} along the magnesio-hornblende–glaucophane join, although the $\delta\Delta\text{Corr}$ maximum did not occur at the calcium-poor (i.e., glaucophane-rich) portion of the join as expected. Synthetic end-member glaucophane and magnesio-hornblende were mixed in a molar ratio of 1:1 and allowed to equilibrate by homogenization for variable durations in the range of 600–800 °C at 2.0 GPa to determine the maximum-width of the miscibility gap. These compositional re-equilibration experiments suggested the presence of an asymmetric miscibility gap (steeper toward glaucophane) with a critical-point below 700 °C. Combining the results of this study with previously published results on the tremolite–glaucophane join allowed refinement of several asymmetric formalism mixing parameters (i.e., $W_{\text{Gt,Ts}} = 20 \text{ kJ}$, $\alpha_{\text{Ts}} = 1.2$) and modeling of the miscibility gap within the tremolite–glaucophane–tschermakite ternary system. The results showed that the composition of the critical point is very close to the maximum in the autocorrelation parameter $\delta\Delta\text{Corr}$, as one would predict. An important implication of this study is that low-temperature immiscibility between calcium- and sodium-rich amphiboles may be more important than the role of pressure, as proposed by Brown (1977), in accounting for the change in B-site Na contents of metamorphic amphiboles.

Keywords: Magnesio-hornblende, glaucophane, miscibility-gap, autocorrelation, infrared spectra, thermodynamic modeling