A calorimetric study of zoisite and clinozoisite solid solutions

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ABSTRACT

Enthalpies of drop solution in molten lead borate have been measured for a series of four zoisite and 12 clinozoisite samples, spanning both epidote solid solutions. Mixing within the zoisite series between 0.0 and 0.2 X_{Al_2Fe} appears to be ideal. The enthalpy of drop solution varies between 493.0 ± 3.2 and 496.0 ± 3.6 kJ/mol with a slight increase with increasing Fe content, based on a linear fit to the data. The clinozoisite solid solution shows more complex behavior. The enthalpy of drop-solution for samples between 0.28 and 0.65 X_{Al_2Fe} varies between 491.7 ± 4.2 and 500.7 ± 3.0 kJ/mol and shows significant scatter. For samples between 0.65 and 0.95 $X_{Al_2Fe,}$ the drop solution enthalpies increase abruptly, going from 494.3 ± 3.4 to 521.1 ± 5.4 kJ/mol. End-member drop solution values for Fe-free zoisite were estimated by the linear fit and for clinozoisite by assuming a fictive Fe-free end-member, taking into account the estimated energy of the monoclinic-orthorhombic transition, and by extrapolation of the Fe-rich data to $X_{Al_2Fe} = 1$. Standard enthalpies of formation from the elements for Fe-free zoisite, Al-clinozoisite, and Fe-clinozoisite have been calculated based on the present data and data from the literature. The values are $\Delta H_{f,298.15}^{0,zoi} = -6878.5 \pm 6.8$ kJ/mol; $\Delta H_{f,298.15}^{0,Al-czoi} = -6882.5 \pm 6.9$ kJ/mol; $\Delta H_{f,298.15}^{0,Fe-czo} = -6461.9 \pm 6.8$ kJ/mol. The overall trend in the drop solution data reflects an apparent positive enthalpy of mixing for the clinozoisite series, consistent with the presence of a miscibility gap in the series between about 0.5 and 0.8 X_{Al_2Fe}. An attempt to fit the highly asymmetric enthalpy of mixing data with a two-parameter asymmetric Margules mixing model, however, failed to yield realistic values for the interaction parameters and the solvus closure temperature. The significant scatter in the data, between $X_{Al_2Fe} = 0.0$ and 0.65, may be due to short-range ordering, suggested by Fehr and Heuss-Assbichler (1997), or could be due to different states of metastable disorder in the samples. The steep increase in enthalpy going from $X_{Al_2Fe} = 0.65$ to 1.0 the may be due to the effect of possible increasing Fe^{3+}-Al^{3+} disorder among the M1 and M3 octahedral sites. The break in slope of the enthalpy data occurs at or near the composition where the onset of Fe^{3+} disorder had been observed previously in clinozoisite.