

Appendix A. Re-evaluation of the enthalpy of fusion of anorthite at 1 bar

Accurate determination of the enthalpy of fusion of anorthite and its temperature dependence, $\Delta H_{fusion}(T)$, depends on accurate information on the heat capacity of anorthite crystal, liquid and glass. In previous studies, Lange (2007) and Tenner et al. (2007) show that a re-evaluation of thermodynamic data used to calculate the enthalpy of fusion of sanidine and albite led to improved estimates. Therefore, a similar exercise is provided in this study for the enthalpy of fusion of anorthite.

Because $\text{CaAl}_2\text{Si}_2\text{O}_8$ liquid quenches to a glass (and not 100% crystals) during a drop calorimetric experiment, direct determination of the enthalpy of fusion of anorthite is not possible. Instead, $\Delta H_{fusion}(T_f)$ is calculated from measurements of the heat of vitrification, $\Delta H_{vit}(T_s)$, the difference in enthalpy between glass and crystal by solution calorimetry at the temperature of the solution (T_s), and then taken to high temperature by integration of the heat capacity functions for crystal, glass and liquid as shown in the following equation:

$$\Delta H_{fusion,T_f} = \Delta H_{vit,T_s} + \int_{T_s}^{T_g} [C_P^{glass}(T) - C_P^{crystal}(T)]dT + \int_{T_g}^{T_f} [C_P^{liquid}(T) - C_P^{crystal}(T)]dT \quad (\text{A1})$$

Thus, the data required to calculate the enthalpy of fusion of anorthite are: (1) the enthalpy of vitrification for $\text{CaAl}_2\text{Si}_2\text{O}_8$ by solution calorimetry, $\Delta H_{vit}(T_s)$; (2) the glass transition temperature of the glass used in the solution calorimetry experiments (T_g); (3) the melting temperature of anorthite at one bar (T_f); and (4) the heat capacity equations for $\text{CaAl}_2\text{Si}_2\text{O}_8$ crystal, glass and liquid as a function of temperature.

Following Richet and Bottinga (1984), we use the heat of vitrification for anorthite of 77.8 kJ/mol at 985 K reported by Navrotsky et al. (1980) in Equation A1, and the reported T_g for that glass of 1130 K. We additionally use the one-bar melting temperature of 1830 K determined by

Rankin and Wright (1915). Where we differ from the analysis of Richet and Bottinga (1984) is in the heat capacity equations for $\text{CaAl}_2\text{Si}_2\text{O}_8$ crystal, glass and liquid, as illustrated in Figure A1. First, we use the Berman (1988) heat capacity equation for crystalline anorthite, because the form of that equation extrapolates to high temperatures in a more realistic manner than the equation given in Krupka et al. (1987). Second, we use the model of Richet (1987) to calculate the heat capacity of $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass, which recovers heat capacity glass measurements more accurately than the equation used in Richet and Bottinga (1984). Third, we use the combined drop calorimetric enthalpy data of both Richet and Bottinga (1984) and Stebbins et al. (1984) on $\text{CaAl}_2\text{Si}_2\text{O}_8$ liquid to obtain the best estimate of the liquid heat capacity. As illustrated in Figure A2, there is excellent inter-laboratory agreement between the measurements from both studies. A linear fit to the data from both studies leads to a temperature-independent liquid heat capacity value of 433.6 J/mol-K, which recovers the enthalpy data from both studies within reported experimental error ($<0.1\%$).

When the revised heat capacity equations for $\text{CaAl}_2\text{Si}_2\text{O}_8$ crystal, glass and liquid are input into the Equation A1, the resulting enthalpy of fusion for anorthite at 1830 K is 142.4 kJ/mole, which is 9.4 kJ/mol larger than the value of 133.0 reported in Richet and Bottinga (1984). This 7% increase in the calculated value for the enthalpy of fusion for anorthite at 1830 K is due entirely to the improved heat capacity equations in Figure A1.

This exercise to re-evaluate the best value for the enthalpy of fusion of anorthite was conducted by the second author at the time that the model of Lange et al. (2009) was being developed; it was included into their calibration model and yet not recorded in Table 1 of that study inadvertently. Fortunately, this error did not affect the application of the Lange et al. (2009) Basic Visual excel program, which contained all the standard-state terms used in the calibration.

Figure A1

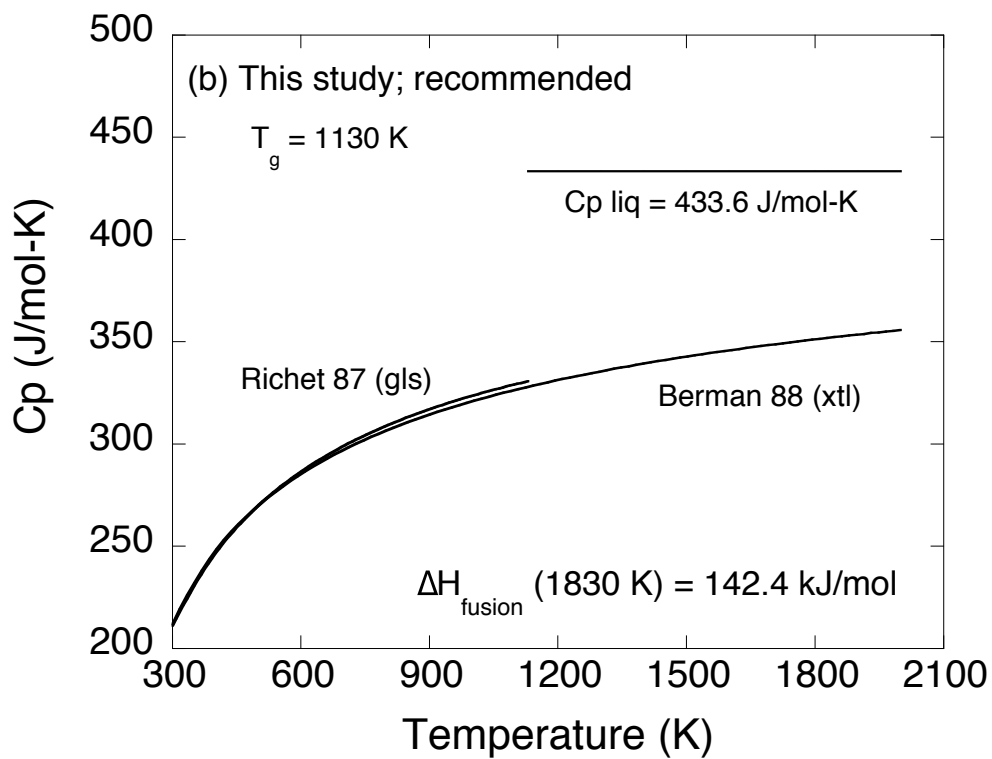
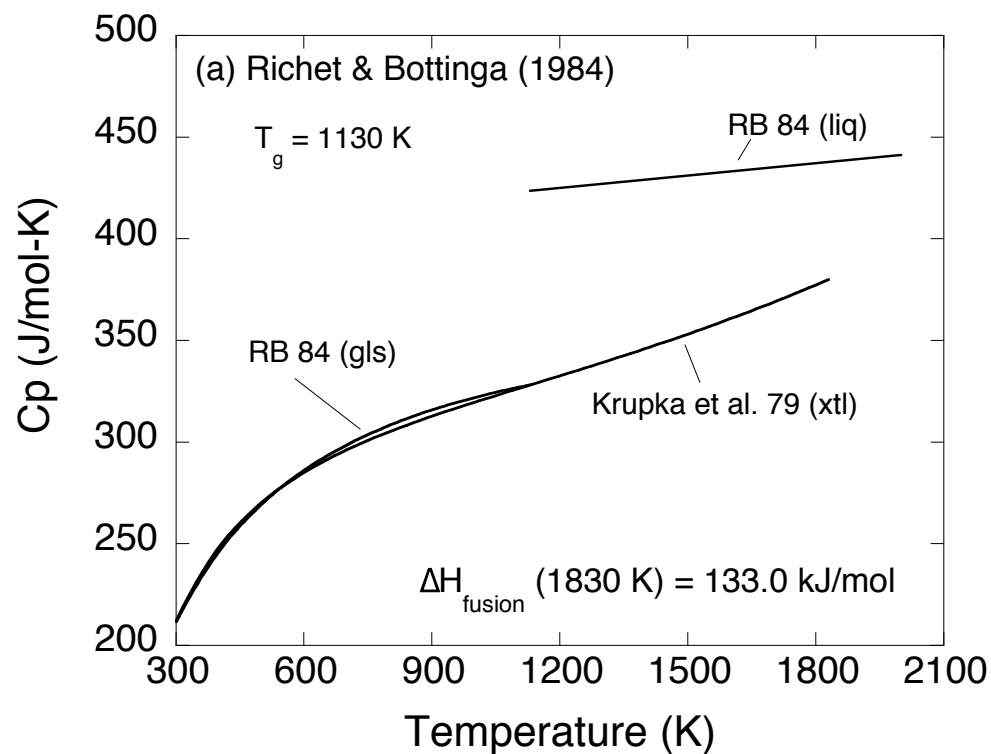


Figure A2

