

Spinel-Anorthosites on the Moon: Impact Melt Origins Suggested by Enthalpy Constraints

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Appendix A: Standard States and the Graphical Method of Ussler and Glazner (1992)

Following Ussler and Glazner (1992), the enthalpy ΔH^* of a substance ‘y’ is defined as the difference between the enthalpy of formation of the substance at T and P, and the enthalpy of formation of the crystalline equivalent of that substance at the reference temperature $T_0 = 25^\circ\text{C}$ and 1 bar:

$$\Delta H^*(T)_y = \Delta_{\text{fm}}H(T)_y - \Delta_{\text{fm}}H(T_0)_{\text{Solids}}.$$

The substance ‘y’ could be a solid, a mix of solids, a melt, or a mixture of solids and melt. For a system consisting of melt + crystals,

$$\Delta H^*(T) = X_{\text{melt}} \cdot \Delta_{\text{fm}}H(T)_{\text{melt}} + \sum_i [X_i \cdot \Delta_{\text{fm}}H(T)_{\text{crystal-i}}] - \sum_i [X_i \cdot \Delta_{\text{fm}}H(T_0)_{\text{solid-i}}],$$

where “X” indicates the mass fraction of a phase, “ \sum_i ” indicates a summation of all the crystals (for the former) and all the solid equivalents of the melt composition (for the latter). All calculated enthalpies, and graphs thereof, are in kJ/gram. This equation implicitly assumes ideal mixing of melt and solid components, i.e. there are no heat effect from liquid or solid solution. This assumption is not correct, but measured heats of mixing in complex naturalistic systems are relatively small compared to the heats of melting of the mineral components, see for example Sugawara and Akaogi (2003) and Green et al. (2012).

Following Ussler and Glazner (1992), the standard state enthalpies of melts [$\Delta_{\text{fm}}H(T_0)_{\text{Solids}}$] are calculated in terms of their CIPW normative mineralogies, with the exceptions that normative albite is recast as nepheline + 2 quartz (molar), and that normative enstatite is recast as $\frac{1}{2}$ forsterite + $\frac{1}{2}$ quartz, and normative ferrosilite is recast as $\frac{1}{2}$ fayalite + $\frac{1}{2}$ quartz. This modification obviates the need to consider enthalpies of these mineral-mineral reactions, and permits comparisons across a broad range of natural and synthetic magma compositions. In effect, the standard state here is taken as selected igneous minerals at $T_0 = 25^\circ\text{C}$ and 1 bar.

Thermochemical data, enthalpies of formation at 25°C and heat capacity functions, are

taken where possible from the self-consistent compilation of Holland and Powell (2011), Table A1. Enthalpy values are calculated, following Nicholls and Stout (1982), by integrating the heat capacity functions for minerals and melts from 25°C to the temperature of interest and adding enthalpies of fusion. For melt components in magmas (e.g., Mg_2SiO_4 component in basalt) the heat capacity function of the melt was extrapolated down from each component's melting temperature to the temperature of interest. Sources of thermochemical data used here, including melting temperatures, heat capacity functions, and standard state enthalpies, are given below.

Table A1: Thermochemical Data Used in Graphical Construction of ΔH^* -X Phase Diagrams.

component		Anorthite	Forsterite	Fayalite	Quartz*	Wollastonite	Spinel	Hercynite	Diopside
formula		CaAl ₂ Si ₂ O ₈	Mg ₂ SiO ₄	Fe ₂ SiO ₄	SiO ₂	CaSiO ₃	MgAl ₂ O ₄	FeAl ₂ O ₄	CaMgSi ₂ O ₆
molar mass	daltons	278.21	140.69	203.778	60.08	116.16	142.27	173.81	216.55
$\Delta H_f^0(298)^a$	kJ/gm	-15.214	-15.442	-7.252	-15.158	-14.064	-16.175	-13.24	-14.786
Cp Coefficients ^b solid	k ₀	3.71	0.233	0.2011	0.0929	0.1593	0.2229	0.2167	0.3145
	k ₁ /10 ²	1	0.1494	1.73	-0.0642	0	0.613	0.587	0.0041
	k ₂ /10 ⁵	-4340	-604	-1960	-715	-967	-1690	-2430	-2750
	k ₃ /10 ⁷	-1.96	-1.87	-0.901	-0.716	-1.08	-1.55	-1.18	-2.02
T _{melt}	K	1830	2163	1490 ^c	1700	1821 ^c	2408 ^d	2372	1668
ΔH_{melt}	kJ/gm	0.482	0.81	0.438 ^c	0.156	0.493	0.745 ^d	0.546 ^e	0.636
Cp Coefficient ^b melt	k ₀	0.43	0.269	0.244	0.0825	0.1674	0.21966 ^f	0.173766 ^g	0.334

^a Unless otherwise noted, data from Holland and Powell (2011). $\Delta H_f^0(298)$ is the heat of formation of the compound from the elements at 298.15K, 1 bar pressure.

^b Heat capacity polynomial coefficients from Holland and Powell (2011): C_p (J/mol-K) = $k_0 + k_1 \cdot T + k_2 \cdot T^{-2} + k_3 \cdot T^{-1/2}$.

^c Robie and Hemingway (1995)

^d Richet and Bottinga (1984)

^e Estimated by corresponding states as $\Delta H_{melt}(\text{MgAl}_2\text{O}_4) - \frac{1}{2} \Delta H_{melt}(\text{Mg}_2\text{SiO}_4) + \frac{1}{2} \Delta H_{melt}(\text{Fe}_2\text{SiO}_4)$.

^f Chase (1998).

^g Estimate of Besmann et al. (2005); hercynite melts incongruently to corundum + liquid.

* Extra enthalpy of 0.0104 kJ/gm from alpha-beta transition (Robie et al. 1972).

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