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

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Appendix B: Evaluations of Equilibrium Computer Codes

MELTS

We evaluated the MELTS computer algorithm (Ghiorso and Sack, 1995; Ghiorso et al., 2002), as the Rhyolite-MELTS v1.02 package, which is suggested as appropriate for volatile free systems at low pressure (Gualda et al., 2012). The MELTS programs have been used extensively to help explain igneous petrogenesis, both terrestrial (e.g., Lee and Bachmann (2014), Dauphas et al. (2014)) and extraterrestrial (e.g., Balta and McSween (2013), Stockstill-Cahill et al. (2012)). We found that the MELTS code works adequately (i.e., reproduces experimentally determined temperatures and equilibria) for compositions rich in olivine and pyroxene components, but not for compositions rich in anorthite component. Specifically, the calculated liquidus field(s) for spinel are too small, and the liquidus fields for anorthite are too small and of an incorrect shape. None the less, we use and present liquidus and subliquidus T-X phase equilibria from MELTS for the more complex compositions here where experimental data are sparse.

For compositions on and near the forsterite-anorthite join, Fo-An (Mg_2SiO_4 – $CaAl_2Si_2O_8$), results from Rhyolite-MELTS are significantly discrepant from experimental determinations. We were unable to calculate in Fo-An, using ideal compositions for forsterite and anorthite, because the quadratic minimization algorithm in Rhyolite-MELTS v1.02 failed to converge. The program did run successfully for compositions along a slightly non-end-member join; instead of pure Fo, we use instead a mix of 39 parts Mg_2SiO_4 and 1 part of the picritic Apollo 15C green glass (Table 1 of main text), see Figure B1. With this change, MELTS did reproduce the location of the olivine-liquidus surface successfully (albeit ~20°C too hot). However, the spinel-liquidus surface is modeled at too low a temperature range, and at higher An proportion than found in experiments, Figure B1 (Andersen, 1915; Osborn and Tait, 1952;

Irvine, 1974). Similarly, the anorthite-liquidus surface is at temperatures below that determined in experiments (Richet and Bottinga, 1984).

For the more complex compositions of mixtures between Perid14B (Table 1 of main text) and anorthite, Rhyolite-MELTS v1.02 gave satisfactory results except for the extent of the spinel-liquidus field. For the Perid14B composition, the code gave the reasonable liquidus temperature of 1721°C (1 bar pressure), which compares well with the estimate of ~1740°C in Bowen (1914), see Figures 4a, 4c of main text. Similarly, a mix of 40% Perid14B and 60% An is similar to the composition C93 of (Soulard et al., 1994); MELTS gives this a liquidus of 1335°C (M+Ol+Opx+Aug+Pl), while experiments place the liquidus between 1341 and 1323°C (Longhi, 1987; Libourel et al., 1989). Thus, we adopt those liquidus locations (see main text, Figure 4a) for peridotite-rich compositions on that join. However, MELTS does not predict spinel as a liquidus phase on the Perid14B-An join (Figures 4a, 4c), although it should have appeared based on the simple CMAS liquidus diagram (Figs. 3a, 3b). Thus, as for the Fo-An system, Rhyolite-MELTS v1.02 does not model the spinel field adequately; again, this should not be counted as a fault of the model, merely that the application here is outside its range of calibration.

FactSage

Although the FactSage© program and databases are "…fully optimized from 25°C to above the liquidus temperatures at all compositions and oxygen partial pressures" (Bale et al., 2009), we found that its treatments of alumina-rich phases and pyroxenes are partially inconsistent with experimental results.

For alumina-rich phases, FactSage tends to over-estimate their stabilities. For the simple system Fo-An, FactSage's predicted liquidus surface is similar but slightly larger (in temperature range) with that determined experimentally, compare Figures 2a & 2b of main text. In the sub-liquidus region of Fo-An, FactSage predicts fields of cordierite (Cd) and sapphirine stability, Figure B2, although these have not been found in experiments, see Figure 2a of main text and Osborn and Tait (1952). To generate the main text Figure 2b by FactSage, sapphirine and cordierite were suppressed.

The stability of sapphirine and cordierite extends to FactSage's calculated phase relations for more complex systems. For example, sapphirine and cordierite appear as liquidus phases in its calculation of the Fo-An-Sil liquidus surface, Figure A3. Neither phase is reported in

experiments on the system, see Figure D1a of Appendix D (Andersen, 1915; Irvine, 1975), and they were suppressed in the calculations and phase diagrams reported in the main text (Figures 3 & 4).

As noted above, FactSage calculates larger fields of spinel stability than are reported in experiments. Although this is barely noticeable for the simple system Fo-An (main text Figure 2a, 2b), the difference is petrologically more significant in complex systems. In Fo-An-Sil (Appendix D), the liquidus field of spinel is so extensive that it eliminates the Ol+Pl liquidus line, which is known to obtain at low pressure (Andersen, 1915; Irvine, 1975). Instead, there is a small field of liquidus Sp+Opx, which should be present only at high pressures. In Fo-An-Di-Sil (main text, Figures 3a, 3b) and Fo-An-Di-Sil-FeO, the spinel liquidus field calculated by FactSage is larger than in experiments, but without a Sp+Opx liquidus.

FactSage includes data for many species of pyroxenes, including diopside (augite), pigeonite, orthopyroxene, and protopyroxene, and calculates phase boundaries as these species react and replace each other. Some of these reaction boundaries seem peculiar, for instance in Figure B4 here and in the main text's Figure 4c in which protopyroxene appears at lower temperatures than pigeonite. However peculiar these may seem, they have no significance for our purpose here.

Table B1. Compositions used in Modeling

Wt%	Ideal Anorthite	Ideal Forsterite	Apollo 15C Green Glass[a]
SiO_2	43.19	42.71	46.0
TiO_2	0.00	0.00	0.4
Al_2O_3	36.65	0.00	7.7
Cr_2O_3	0.00	0.00	0.4
FeO	0.00	0.00	18.9
MnO	0.00	0.00	--
MgO	0.00	57.29	17.5
CaO	20.16	0.00	8.4
Na_2O	0.00	0.00	0.1
K_2O	0.00	0.00	0.
sum	100.	100.	99.5
Norm	Wt%		
Pl	100	0	21.6
Ol	0	100	25.7
Hy	0	0	33.8
Di	0	0	17.3
Or	0	0	0.0
Il	0	0	0.8
Chr	0	0	0.9
Mg*	--	100	62.3
An*	100	--	95.8

[a] Elkins-Tanton et al. (2003)

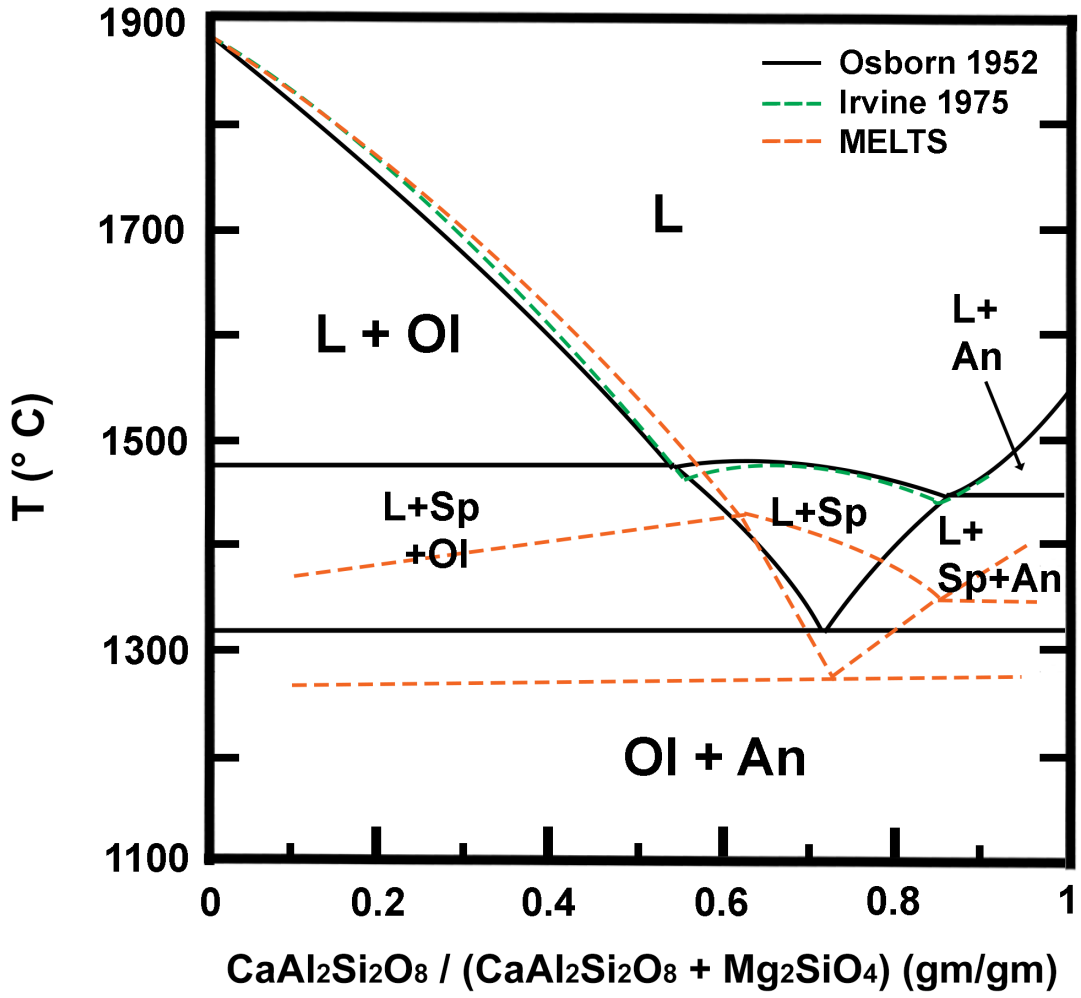

Figure B1. Liquidus location in Fo-An (Mg_2SiO_4 – $CaAl_2Si_2O_8$). Comparison of liquidus locations from experimental studies by Osborn and Tait (1952) in black, and by Irvine (1975) in green, and as calculated by Rhyolite-MELTS 1.02 Gualda et al. (2012) in orange. See also Figures 2a & 2b of the main text. Note that the experiments are consistent with each other, and that the MELTS model is inconsistent with the location of the L+Sp and L+An fields

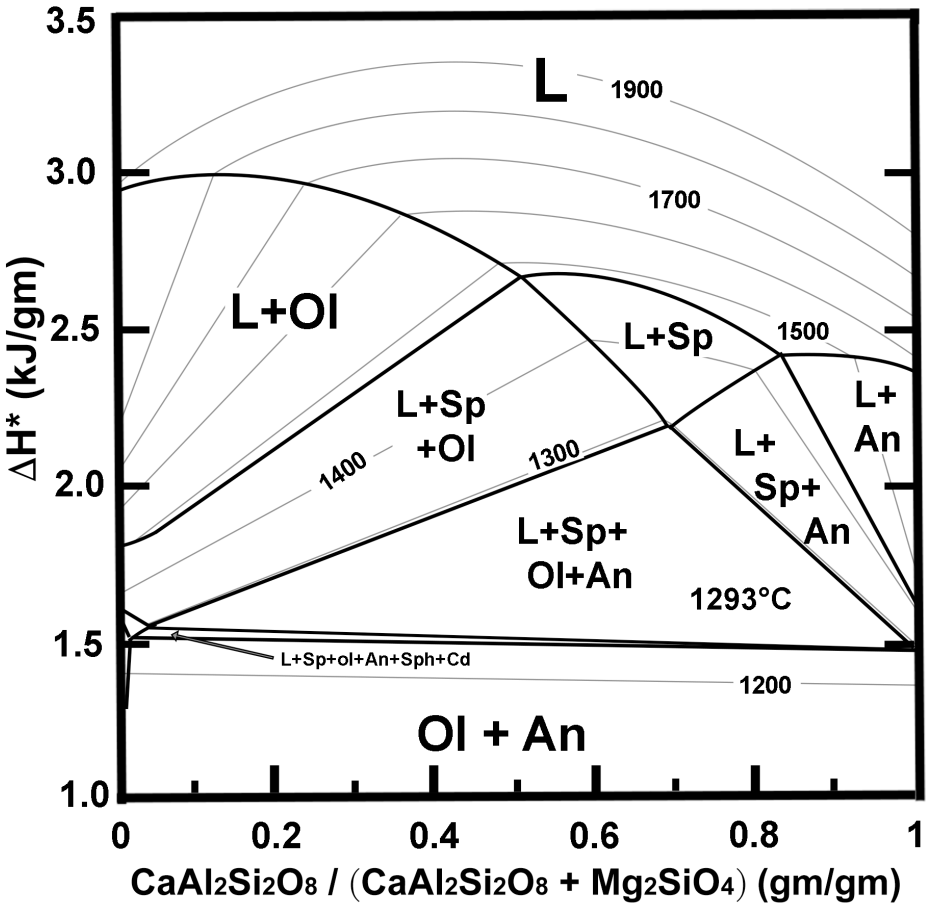

Figure B2. ΔH*-X phase diagram for the Fo-An join, calculated by FactSage, excluding no phases.

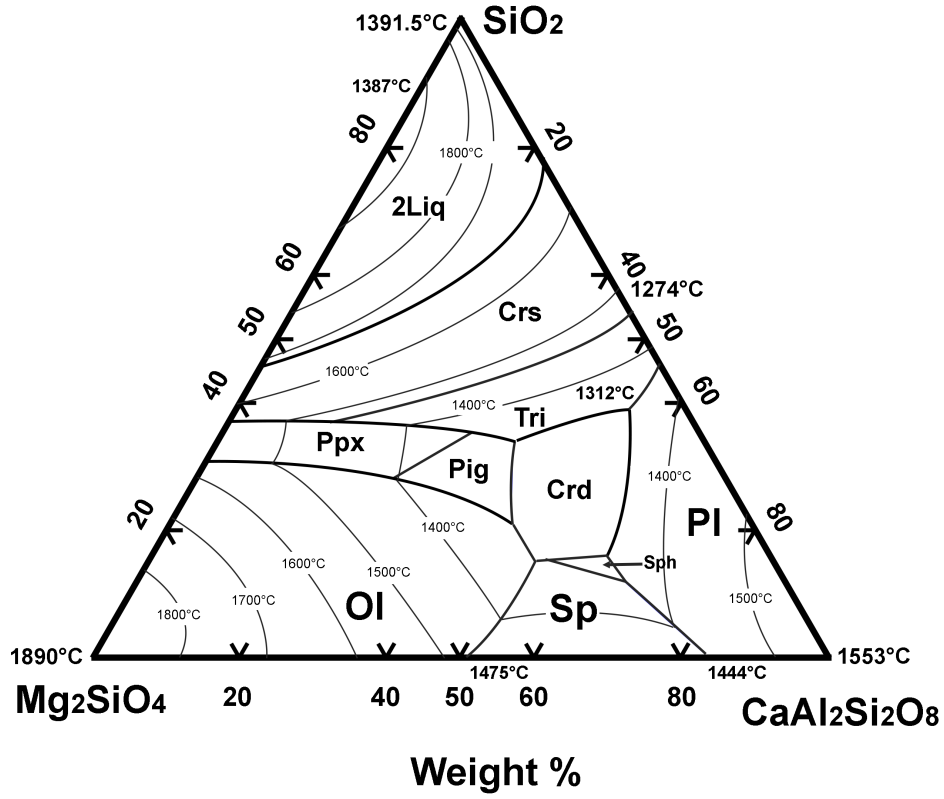

Figure B3. Liquidus equilibria in An-Fo-Sil (anorthite-forsterite-silica) calculated with FactSage, and including the phases cordierite (Crd) and sapphirine (Sph). Neither cordierite nor sapphirine has been observed in experiments at 1 bar in the system (Andersen, 1915; Irvine, 1974; Longhi, 1987; Soulard et al., 1994). Compare with Figure 3b of the main text, in which Crd and Sph were suppressed.

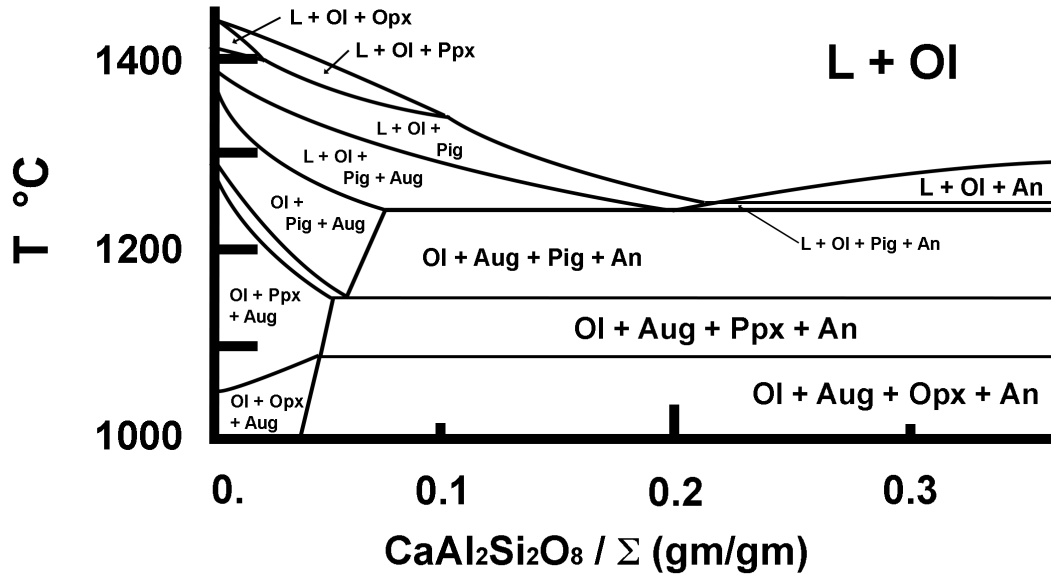

Figure B4. Details of the phase equilibria calculated by FactSage for lower temperatures and An contents on the join Perid14B-An (main text, Figure 4c) in the system Fo-An-Di-Sil-FeO (Bale et al., 2009; Bale et al., 2016). The calculated relations among pryoxenes in the sub-solidus are complex, and possible inconsistent with experimental determinations. They are presented here for completeness, and without judgement or comment. See Figure 4c of main text for context of this figure. Phase relations in the Fe-free system are inferred to be similar, see Figure 3d of main text.

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