LUNAR ROCKS RICH IN Mg-Al SPINEL: ENTHALPY CONSTRAINTS SUGGEST ORIGINS BY IMPACT MELTING.

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Introduction: VNIR reflectance spectra from the M[3] instrument on Chandraya'an-1 show that spinel-rich rock, without detectable olivine or pyroxene, is widespread across the moon [1], especially in the walls and peaks of impact craters. Such spinel-rich rocks are commonly explained as products of assimilation of anorthosite into picritic magmas [1-5]. However, large amounts of energy are required for assimilation, which means it can only have limited effects (in terms of bulk chemistry) in normal igneous processes [6-9].

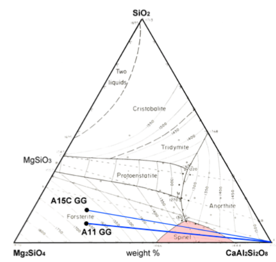
Assimilation or mixing at constant pressure is isenthalpic – enthalpy (H) being the expression of the energy changes in system at constant pressure – no energy (enthalpy) is added or removed. Assimilation need not be isothermal, so it is best visualized on H – composition (X) diagrams [10], which we use here to understand formation of Mg-Al spinel as picrite magma assimilates anorthosite.

Methods: Isothermal, isobaric phase diagrams of enthalpy versus composition, were generated [10] from temperature (T)-X phase diagrams for relevant systems [11,12], other phase equilibria that allow extrapolation [5,13], and published thermochemical data (mostly from [14]). Enthalpies are expressed as H*, the enthalpy needed to bring the material from 25°C to the temperature of interest; H* values are calculated by integrating heat capacity functions and adding enthalpies of phase changes (e.g., melting). Heats of mixing in solids and silicate liquid are small compared to heats of melting [10], and thus can be ignored. Isotherms in the sub-liquidus, supersolidus fields are approximate, because mineral proportions and melt compositions there are poorly constrained.

Lunar anorthosite was modeled as pure An_{100} anorthite. Picritic magma was modeled successively from pure Fo_{100} olivine as the simplest, to Apollo 15C green glass as the most realistic composition.

Forsterite–Anorthite. This is the simplest join in basalt petrogenesis in which Mg-Al spinel appears as a liquidus phase, Fig. 1 [11,12]. In the H*-X phase diagram for the join (Fig. 2), the isothermal olivine-anorthite-spinel-melt peritectic [11] appears as a large field because it represents significant crystallization and enthalpy changes. The field of spinel+melt is small because little spinel is produced before olivine or anorthite come on the liquidus – the extent of that field is uncertain because there is little experimental data available [16].

Fig. 1. Liquidus surface in forsterite-anorthite-silica [12]. Mg-Al spinel liquidus surface in pink. Bottom edge, forsterite-anorthite, is the simplest system to produce Mg-Al spinel [11]. Dots are projections of A15C & A11 Green Glasses (GG) [15]; tie lines between Green Glasses and anorthite (Fig. 3) in blue.



Isenthalpic mixing is not isothermal. For example, the green line on Fig. 2 shows isenthalpic mixing of forsterite at 1550°C with anorthite at 1550°C. All mixtures along that line have temperatures <1550°C!

Model A11 Green Glass – Anorthite. We investigated a model of the Apollo 11 green glass composition, the most olivine-normative of the Apollo picrites [15] and thus most likely to produce abundant spinel (Fig. 1). The A11 green glass is projected into forsterite-anorthite-silica [12] by ignoring wollastonite and other components (~10% by mass) and converting its Fe to Mg (atomic basis). Phase equilibria on the join between this A11(Mg) picrite and anorthite were calculated as above. An inferred composition of a lunar Mg-suite magma [5,17] falls near this join.

In this H*-X diagram, Fig. 3a, the geometry of the forsterite-anorthite system (Fig. 2) is preserved near the

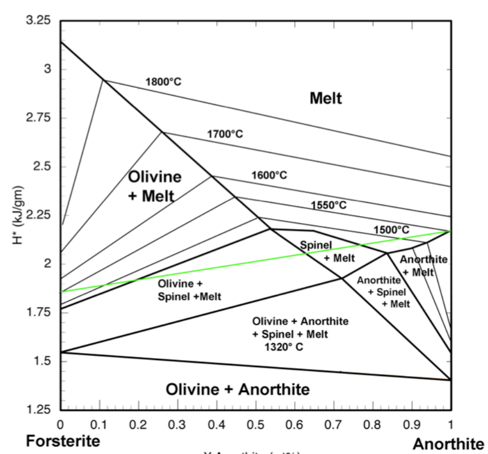


Fig. 2. Enthalpy-composition diagram for forsterite-anorthite [11]. Dark lines are phase boundaries, light lines are iostherms, lower triangle field is peritectic: melt+spinel⇔olivine+anorthite. Green line shows mixing of olivine + anorthite at 1550°C.

liquidus; at lower T, spinel is lost and melts evolve along the olivine-plagioclase cotectic to the olivine-orthopyroxene-plagioclase peritectic (Fig. 1).

Fields in which spinel is present are in pink on Fig. 3a; the darker pink fields would appear to contain only spinel in VNIR spectra [1]. These 'VNIR spinel-only' fields are at high H*, i.e. high T; at lower H*, spinel reacts out to yield olivine±anorthite. To access the 'VNIR spinel-only' fields, the A11(Mg) melt at its liquidus would have to mix with anorthite at H*>1.4 kJ/gm (blue line), i.e., at T>1300°C. This H* value is also a proxy for how much energy (enthalpy) must be added for assimilation to produce spinel.

A15C Green Glass – Anorthite. A more realistic system considers Fe and other melt components, like

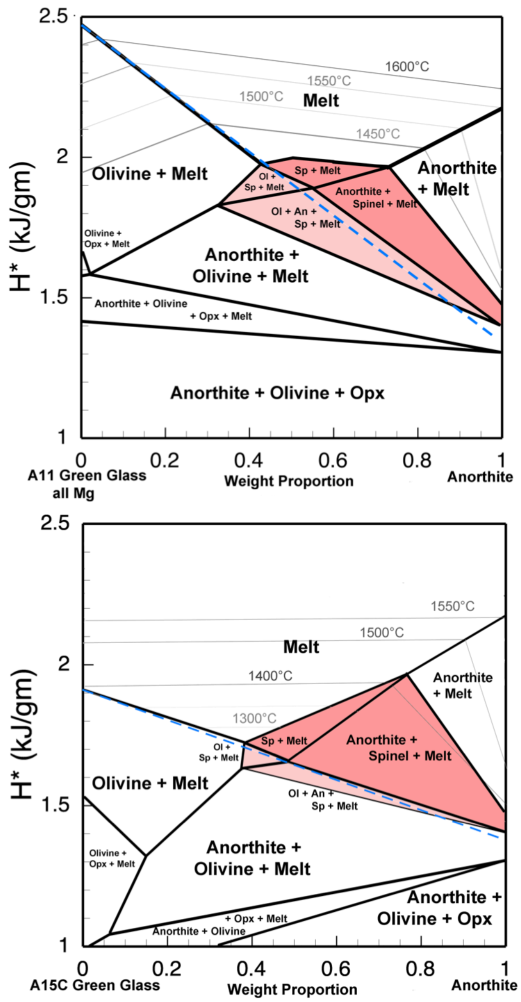


Fig. 3. H*-X phase diagrams: top, simplified A11 picrite green glass (see text); and bottom, A15C picrite green glass [13,15q,r]. Phase boundaries at H*<1.5 are approximate. Fields with spinel are pink; darker pink fields do not contain olivine or pyroxene, as required by VNIR observations of lunar spinel-rich rocks [1j]. Blue dashed lines show mixing between picrite at liquidus and anorthite at the lower limit of H* that permits formation of "VNIR spinel-only' material.

assimilation of anorthosite into picrite like the Apollo 15C green glass [5]. Magmatic evolution of the A15C glass is known [13], but compositions between it and anorthite have not been explored. The H*-X diagram is approximated here (Fig. 3b) from those end-members by warping T-X relations from Fig. 1 to fit the liquidus of the A15C glass (~1400°C [13]) and experiments of [5]. Formation of 'VNIR spinel-only' material from A15C melt at its liquidus again requires anorthite with H*>1.4 kJ/gm (blue line), i.e., at T>1300°C.

Conclusions: Lunar spinel-rich rocks ('VNIR spinel-only) can form by assimilation of anorthosite into picrite magmas (at their liquidi), but only if the anorthosite is hot, T>1300°C (Fig. 3). This constraint arises because spinel is stable only near the liquidi of relevant compositions (Fig. 3) [11,12], and because a significant amount of enthalpy is needed to dissolve anorthite into magma [6,7]. The needed enthalpy could come from olivine crystallization (~0.5 kJ/gm at 1300°C), but nearly 3 gm of olivine must crystallize to heat 1 gm of anorthite from 25 to 1300°C from the picrite, and there is no evidence for so much olivine near the 'VNIR spinel-only' deposits. However, such hot anorthosite is conceivable in the model of [18], in which the early lunar crust undergoes extensive tidal flexure.

Given these issues with spinel formation via assimilation, it seems more likely that the 'VNIR spinel-only' deposits formed via impact melting. Impacts can provide the needed enthalpy (and more) to bring target rocks and melt to conditions appropriate for spinel formation. Impact melts can easily be emplaced into circumstances where they cool rapidly, and so avoid having spinel replaced by ol+an. However, an impactor's target must include material rich in olivine (picritic or troctolitic), because mixtures of mare basalt and anorthite do not evolve to spinel saturation (Fig. 1).

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