**VISIBLE TO NEAR-INFRARED SPECTRA OF IRON-BEARING SPINEL WITH APPLICATION TO SINUS AESTUUM AND LUNAR SPINEL ANORTHOSITE.** C.R.M. Jackson[1], L.C. Cheek[2], K.B. Williams[1], K. Donaldson Hanna[3], C.M. Pieters[1], S.W. Parman[1], R.F. Cooper[1], M.D. Dyar[4], M. Nelms[4], M.R. Salvatore[5]. colin_jackson@brown.edu, [1]Department of Geological Sciences, Brown University, Providence, RI 02912, USA [2]Department of Astronomy, University of Maryland, College Park, MD, 20742, USA [3]Department of Physics, Oxford University, Oxford, UK, [4]Department of Astronomy, Mount Holyoke College, South Hadley, MA, 01075, USA, [5]School of Earth and Space Exploration, Arizona State University, Tempe, AZ, 85287, USA

Introduction: Remote sensing observations now identify spinel, in the absence of measureable olivine and pyroxene, as a globally distributed component of the lunar crust [1-8]. A wide range of formation hypotheses have been advanced, including both exogenic and endogenic processes [9-12]. Evaluating these hypotheses requires a detailed understanding of how the spectrum of spinel is affected by changes in the crystal structure caused by variations in composition (Fe and Cr contents, fO$_2$) and physical parameters (cooling rate, inter-mineral mixing, space weathering).

Here, we report visible to near-infrared (V-NIR) reflectance (300-3500 nm) and Mössbauer spectra of $(Mg,Fe^{+2})(Al,Fe^{+3})_2O_4$ spinel, synthesized at lunar-like fO$_2$ with systematic variation in Fe abundance. Spectral results to show that the Fe# of the remotely observed lunar spinel anorthosite is likely very low (very high Mg#) and the spectra of pyroclastic spinel remotely observed at Sinus Aestuum are consistent with extremely rapid cooling rates.
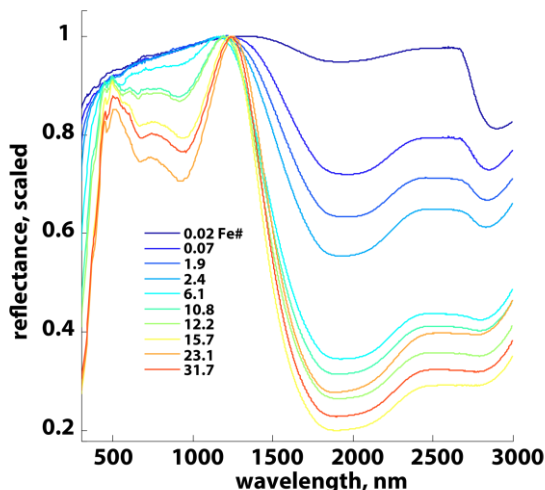
Figure 1: Scaled reflectance spectra of stoichiometric spinel color-coded for Fe#. Spectra were scaled by fitting a polynomial to the reflectance maximum centered near 1400 nm and dividing by the polynomial maximum.

Methods: Reagent grade oxides were mixed in stoichiometric proportions to form $(Mg,Fe^{+2})(Al,Fe^{+3})_2O_4$ spinel with variable Fe# (~0 to 32). Oxides were homogenized using an agate mortar and pestle under ethanol and then pressed into 1 cm diameter compacts (~1 cm height). Compacts were then placed on a bed of zirconia ~1 mm beads contained in an alumina boat and loaded into a horizontal gas-mixing furnace. Samples were sintered for 72 hours at 1450°C. Oxygen fugacity was fixed (IW-1) by streaming a CO-CO$_2$ mixture through the furnace. The necessary CO/CO$_2$ ratio for IW-1 was determined using a yttrium-doped zirconia fO$_2$ sensor, but fO$_2$ was not actively monitored for the duration of sintering. After sintering, the temperature was ramped down to ~20°C over approximately 6 hours. A second series of spinel was synthesized with excess-Al$_2$O$_3$ using similar methods to explore the spectral effects of the point defects associated with Al-rich non-stoichiometry. As discussed below, the point defect effects associated with excess-Al$_2$O$_3$ are similar to those expected for extremely slow cooling. V-NIR and Mössbauer spectra were aquired on dry-sieved particulates (<45 μm) at RELAB and Mount Holyoke College, respectively.

Spectral Results: Reflectance spectra of particulate (<45 μm), nominally stoichiometric spinel display systematic behavior, with bands at 700, 1000, 2000, and 2800 nm increasing in strength with increasing bulk Fe content (Fig. 1). The especially strong bands at 2000 and 2800 are discernible for all spinel compositions and saturate at <15 Fe#. Absorption bands at 700 and 1000 nm, collectively referred to as the ~1000 nm bands, are weaker and become observable at >6 Fe#. The 2000 and 2800 nm bands are nominally assigned to $^{IV}Fe^{+2}$ electronic transitions following previous interpretations [e.g. 13]. Spectra of spinel with excess Al$_2$O$_3$ (non-stoichiometric, Al$_2$O$_3$-rich) have severely weakened ~1000 nm bands and strengthened 2000 and 2800 nm bands (Fig. 2). We interpret this effect to be related to the coupling of the spinel inversion reaction (i.e. $^{IV}(Fe^{+2},Mg) + {}^{VI}Al = {}^{VI}(Fe^{+2},Mg) + {}^{IV}Al$) and the generation of ^{IV}Al via the incorporation of excess Al$_2$O$_3$. In effect, the incorporation of excess Al$_2$O$_3$ forces Fe to become less disordered in spinel. Importantly, this provides evidence that the strength of ~1000 nm bands in spinel depends on $^{VI}Fe^{+2}$ concentration.

The abundance of $^{VI}Fe^{+2}$ depends on bulk Fe content as well as factors that control the degree of ordering (distribution of Fe between the A and B sites in AB$_2$O$_4$), such as cooling rate. Faster cooling locks in lower degrees of ordering, leading to greater amounts of $^{VI}Fe^{+2}$ at the expense of $^{IV}Fe^{+2}$. Consequently the strength of the ~1000 nm bands is a proxy for both the Fe content and cooling rate of remotely sensed spinel.

Mössbauer spectra of the nominally stoichiometric, synthetic spinel indicate very low Fe^{+3}/Fe_{tot} (0.03-0.1, neglecting the two lowest Fe# spinel), consistent with the reducing conditions imposed during sintering (IW-1). Further, Mössbauer spectra indicate the ordering parameter, Q ($Q = {}^{VI}X_B - {}^{IV}X_B$, for AB_2O_4 spinel), is 0.80±0.17 (95% confidence), consistent with the ordering parameter predicted for the laboratory cooling rate ($\sim 10^{-2}$ °C s^{-1} at 500 °C) using the Ginzburg-Landau rate law model [e.g.14] and kinetic parameters from [15] ($Q_{model} = 0.82$).
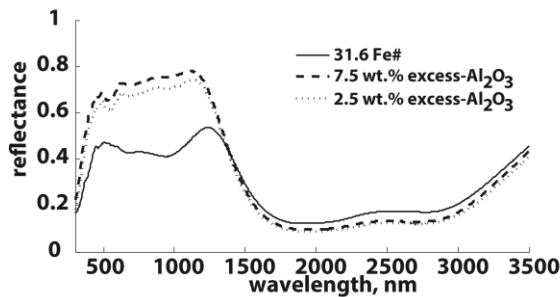
Figure 2: Reflectance spectra of spinel (solid line) and spinel with excess Al_2O_3 (dotted and dashed lines). Compared to the stoichiometric spinel, spinel with excess Al_2O_3 have substantially weakened absorptions at 700 and 1000 nm and strengthened 2000 and 2800 nm bands. All spinel in Figure 2 have the same Fe#.

Petrologic Implications: Remotely sensed lunar spinel can be divided into two groups based on their spectra and geologic context. One group (Group 1) occurs as small (~100 m in diameter) exposures within highland terrains and lack ~1000 nm bands while displaying strong bands centered ~2000 nm (see [6] for a review). A second group (Group 2) is associated with a subset of pyroclastic deposits at Sinus Aestuum and display relatively weak ~1000 nm bands and relatively strong ~2000 nm bands [7, 8]. Both Groups 1 and 2 show evidence for a second long wavelength absorption centered beyond 2500 nm, consistent with the known spectrum of $(Mg,Fe^{+2})(Al,Fe^{+3})_2O_4$ (Fig. 1).

Spinel Anorthosite, Group 1: Spinel synthesized at IW-1 and cooled at $\sim 10^{-2}$ °C s^{-1} at 500 °C have observable ~1000 nm bands at >6 Fe#. Accounting for lunar-applicable cooling rates, grain size, and fO_2, we estimate spinel with >12 Fe# (<88 Mg#) have observable 1000 nm bands under ambient lunar conditions. This suggests spinel that lack ~1000 nm bands are nearly pure $MgAl_2O_4$, provided $^{VI}Cr^{+3}$ causes an absorption in spinel at ~550 nm [e.g. 13,16], and suggests a link between spinel anorthosite and Mg-Suite magmatism [12]. However, the effects of Fe oxidation state, Fe ordering due to Cr, mixing with plagioclase, and space weathering must also be considered to strengthen this constraint.

Pyroclastic Spinel, Sinus Aestuum, Group 2: Given the dependence of the 1000 nm band strength on $^{VI}Fe^{+2}$ and the 2000 nm band strength on $^{IV}Fe^{+2}$, the ln(1000 nm)/ln(2000 nm) reflectance minimum ratio for a $(Mg,Fe^{2+})(Al,Fe^{3+})_2O_4$ spinel should provide information

regarding cooling rate. The average continuum-corrected ln(1000 nm)/ln(2000 nm) reflectance minimum ratio of the pyroclastic spinel at Sinus Aestuum is 0.109 ± 0.011 (95% confidence), and the ln(1000 nm)/ln(2000 nm) reflectance minimum ratio of the stoichiometric, synthetic spinel is 0.0347 ± 0.0088 (95% confidence). This difference in relative band minima between Group 2 and the synthetic spinel is large (216±59 % higher), suggesting very rapid cooling for the pyroclastic spinel at Sinus Aestuum compared to the laboratory cooling rate. The vacuum cooling rate for a 0.5 mm diameter mare basalt bead at 1000 °C is ~1000 °C s^{-1} [17]. The Ginzburg-Landau rate law model predicts a cooling rate of 1000 °C s^{-1} results in a 90% increase in ln(1000 nm)/ln(2000 nm) reflectance minimum values compared to cooling at 10^{-2} °C s^{-1} [14, 15]. Thus, the large offset between experimental and Sinus Aestuum spinel ln(1000 nm)/ln(2000 nm) band minimum ratios is consistent with extremely rapid cooling, which would require the absence of an extensive vapor cloud and small bead size. There is experimental evidence that $^{VI}Fe^{+3}$ also contributes to the strength of ~1000 nm bands in spinel [18], and consequently the large ln(1000/2000 nm) band minimum ratio at Sinus Aestuum may also reflect oxidation to a degree.

The major spectral features of the pyroclastic spinel at Sinus Aestuum (doublet ~1000 nm bands and 2000 nm band, Fig. 3) can be explained by Fe alone (cf. Fig 1. & Fig. 3). Cr does not appear required [e.g. 8].
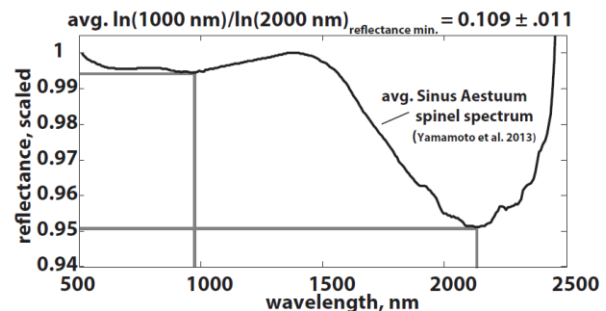
Figure 3: Average reflectance spectra of pyroclastic spinel at Sinus Aestuum (scaled, continuum-corrected) plotted with line indicating reflectance minima at ~1000 and ~2000 nm. Average includes A7, B14, C2, and F4 spectra from [8].

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