

**WEATHERING AND IMPACT MELTING DETERMINED THE MINERALOGY OF THE EARLY MARTIAN CRUST PRESERVED IN NORTHWEST AFRICA 7533.** M. Humayun<sup>1</sup>, R. H. Hewins<sup>2,3</sup>, J.-P. Lorand<sup>4</sup> and B. Zanda<sup>2</sup>, <sup>1</sup>Florida State University, Tallahassee, FL 32310, USA ([humayun@magnet.fsu.edu](mailto:humayun@magnet.fsu.edu)), <sup>2</sup>LMCM, MNHN, 75005 Paris, France, <sup>3</sup>Rutgers University, Piscataway, NJ 08854, USA, <sup>4</sup>LPG Université, 44322 Nantes, France.

**Introduction:** The ubiquitous presence of olivine from a variety of Martian highlands settings has been spectrally determined from orbit [Bandfield 2002; Bibring 2006; Rogers 2008] and by the MER rovers [Yen; Goetz 2005]. Olivine is inferred to rapidly undergo weathering in the Martian environment and so its presence is an important constraint on the Martian weathering environment [e.g., Hurowitz; stopar]. The discovery of the first Martian regolith breccia (NWA 7034/7533/7475) in the meteorite collection [8-9] allows us to study the potential impact of weathering of silicate minerals preserved in this meteorite.

NWA 7533 preserves clasts and matrix as ancient as 4.4 Ga [8]. This breccia contains several important clast types including noritic impact melt rocks, fine-grained clast laden impact melt rocks (CLIMR), felsic clasts of monzonitic composition, and numerous coarse (>100  $\mu\text{m}$ ) crystal clasts. The overall chemical composition of the meteorite, and of the CLIMR and intraclast crystalline matrix (ICM) are alkali basalt. There is a notable dearth of olivine (for a rock containing 12 wt % MgO) in the clasts. Dendritic olivine ( $\text{Fo}_{74-65}$ ) has been reported within some impact melt spherules [9-10]. The abundance of norite clasts in NWA 7533 deserves explanation since norites are known in terrestrial igneous contexts where excess silica is available (e.g. island arcs, Sudbury). Prominently absent for an ancient highlands breccia are clays, carbonates and other weathering products, that are reported in situ on Mars [3-4]. Given that NWA 7533 contains a wide variety of clast types, possible wind-blown dust, etc., accumulated between 4.4-1.7 Ga [8-9] this paucity of secondary phases also deserves an explanation.

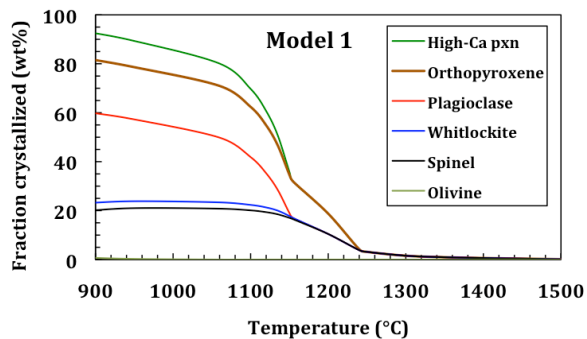
The hypothesis we explore here is that olivine in the source region(s) of NWA 7533 weathered to form Fe-oxides, free silica, and clays or serpentine, and that these secondary minerals were destroyed by subsequent impact melting of the regolith. The oxidation reaction of fayalite to form Fe-oxides and free silica is irreversible on heating in the absence of a reducing agent (e.g., organic matter). In this study, we explore the effects of weathering of olivine to form secondary minerals, particularly magnetite or maghemite, followed by impact melting that destroyed hydrated silicates and allowed free silica to combine with the forsterite component to form orthopyroxene. This reaction is a potent means of creating Ni-rich secondary pyrox-

enes [11] by the reworking of the impactor debris into new minerals. The silica made available by this process contributes to the differentiation trend that formed the monzonite clasts, all of which were found to have high siderophile element contents consistent with an origin from differentiated impact melts [8].

**Modeling:** We assumed that the bulk chemical composition of fine-grained CLIMR is representative of the mean composition of the melts that formed the Martian highlands crust [8], except that oxygen was added during weathering. When 5% of total Fe is assumed to be ferric, the CIPW normative mineralogy of CLIMR is olivine normative (~35 wt %,  $\text{Fo}_{58}$ ) with  $\text{cpx} > \text{opx}$ . The MELTS program [12-13] was used to calculate the mineralogy for impact melts of CLIMR composition. At low pressures (<0.2 GPa), olivine ( $\text{Fo}_{82-55}$ ) + Cr-spinel crystallize from this melt over a temperature range >150°C before plagioclase and low-Ca pyroxene enter the crystallization sequence. Orthopyroxene does not crystallize from the CLIMR composition at  $P < 0.2$  GPa, but replaces olivine as the dominant phase at higher pressures. The final equilibrium olivine composition ( $\text{Fo}_{55}$ ) was weathered to yield serpentine, maghemite and silica, to varying degrees of weathering, and then the ferric/ferrous ratio was recalculated to form a new composition that was entered into MELTS. The crystallization sequence of an impact melt initially above its liquidus temperature was calculated by the MELTS program for this composition. The amount of olivine weathered was varied to investigate the effect of variable weathering efficiency. The MELTS program does not partition MnO into pyroxenes, the principal host of MnO, so MnO was included with FeO for modeling.

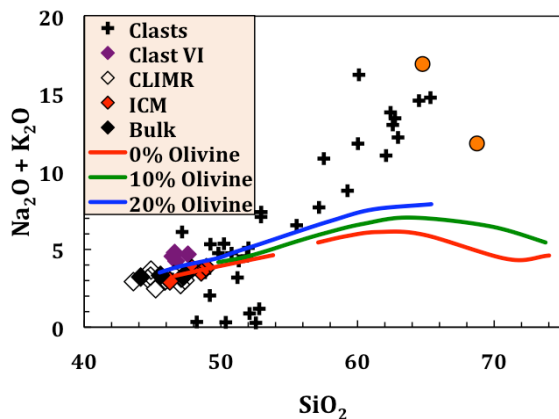
**Results:** Fig. 1 shows the crystallization sequence for a model composition where all the olivine was weathered to ferric oxides+silica. On impact melting above the liquidus, this melt yielded Cr-spinel as the sole mineral to crystallize over a 300-degree temperature range before it was joined by orthopyroxene. The composition of the spinel phase became increasingly enriched in magnetite component, as its abundance increased to ~20% at the end of the crystallization sequence. This amount is close to the normative abundance of magnetite (~20-25%). Orthopyroxene ( $\text{En}_{89}$ ,  $_{92}\text{Wo}_{2-3}$ ) was the first silicate phase to crystallize followed by plagioclase ( $\text{An}_{59-44}$ ) and high-Ca pyroxene

(En<sub>51</sub>Wo<sub>44</sub>), and a silica-rich liquid (SiO<sub>2</sub> = 60 wt%) remained after 70% crystallization. The MELTS program does not handle granitic liquids properly, and the details of the crystallization of this liquid depend on the volatile contents of the melts, which are not well constrained.



**Figure 1:** Crystallization sequence of a highly oxidized CLIMR composition calculated from MELTS containing 0% residual olivine.

These calculations show that monzonitic and noritic liquids are directly related in impact melting. Monzonitic melts are late stage fractional crystallization products of impact melts of an oxidized basaltic regolith, while the norites are the impact melts. One artifact of the MELTS program is the high Fe<sup>+3</sup>/ΣFe atomic ratios for both low-Ca (~0.3) and high-Ca (~0.5) pyroxenes, which decreases the magnetite content (maghemite is not produced MELTS).



**Figure 2:** Total alkalis vs. silica plot for individual LA-ICP-MS spot analyses for clasts from NWA 7533, compared with MELTS models for models with 0%, 10% and 20% residual olivine in the bulk rock. Positions of pure Ab and Or are depicted as orange circles.

Calculations were also performed assuming that only a fraction of the olivine was weathered. At 50% of olivine weathered, the MELTS program yielded Fo<sub>85-89</sub> olivine as the first phase to crystallize before orthopyroxene joined the crystallization sequence, but

the total amount of olivine remained <5%. At lower olivine weathering fractions, the amount of opx diminished and the amount of olivine increased, becoming progressively less forsteritic (Fo<sub>70</sub>) falling within the range of shergottites (Fo<sub>76-60</sub>, [14]). In the most ferric iron-rich melts (e.g., Fig. 1), the large range of Cr-spinel crystallization implies that it is likely to be a relict mineral phase in impact melts.

**Discussion:** Weathering of olivine under acidic conditions leads to Fe- and Mg-sulfates, so the pH conditions are estimated to be nearly neutral in the source regions of NWA 7533. Recently, sediments at the bottom of Gale Crater were inferred to have formed by the weathering action of similar low salinity, neutral pH waters [15]. The requirement that water was involved in the NWA 7533 source region is also consistent with the lack of Cl, S and Zn enrichments in NWA 7533 [8]. These constraints imply that the source region of NWA 7533 formed in the Phyllosian period of [3], and the zircon ages on monzonitic clasts imply that the Phyllosian conditions extended from >4.4 Ga.

The model developed here successfully explains the absence of olivine, while accounting for the high abundance of Fe-oxides observed in NWA 7533. The observation that Late Noachian highlands terrains are devoid of olivine [17] could be linked to similar processing. Our model also successfully explains the predominance of orthopyroxene over high-Ca pyroxene (norites) without requiring high silica-regions in the Martian interior. The crystallization of noritic melts yields evolved siliceous melts which may form monzonites. However, a plot of Na<sub>2</sub>O+K<sub>2</sub>O vs. SiO<sub>2</sub> (Fig. 2) reveals that these liquids are too silica-rich compared with clast compositions.

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