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DIFFERENTIATION IN IMPACT MELT SHEETS AS A MECHANISM TO
PRODUCE EVOLVED MAGMAS ON MARS

BY

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THESIS

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ABSTRACT

Asteroid bombardment contributed to extensive melting and resurfacing of ancient (> 3 Ga) Mars, thereby influencing the early evolution of the Martian crust. However, information about how impact melting has altered Mars' crustal petrology is limited. Evidence from some of the largest impact structures on Earth, such as Sudbury and Manicouagan, suggests that some impact melt sheets experience chemical differentiation. If these processes occur on Mars, we expect to observe differentiated igneous materials in some exhumed rock samples. Some rocks observed in Gale crater are enriched in alkalis (up to 14 wt% $\text{Na}_2\text{O} + \text{K}_2\text{O}$) and silica (up to 67 wt% SiO_2) with low ($< 5\text{wt}\%$) MgO. This alkaline differentiation trend has previously been attributed to fractional crystallization of magmas resulting from low-degree mantle melting analogous to ocean island or rift settings on Earth. In this study, we investigate the hypothesis that differentiation of impact-generated melts provides a viable alternative explanation for the petrogenesis of some evolved rocks on Mars. We scaled melt volumes and melt sheet thicknesses for a range of large impact magnitudes and employed the MELTS algorithm to model mineral phase equilibria in those impact-generated melts. Model runs consider a range of possible oxidation states (IW to QFM), crystallization regimes (batch, fractional and liquid segregation), and volatile contents (initially water-saturated and nominally anhydrous). Moderate pressure and water are required to produce alkaline differentiation trends in mafic melts. Large impacts that melt a water-bearing early basaltic crust provide a mechanism to generate wetter magmas on Mars, consistent with some observed Martian differentiation trends. Low-degree partial melting and/or an alkali-enriched source are required to generate the most alkaline observed compositions, motivating future work to examine partial melting regimes during large impacts.

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TABLE OF CONTENTS

1. INTRODUCTION	1
2. BACKGROUND	3
3. IMPACT MELTING ON MARS	4
3.1 MELT SCALING	5
4. THE INITIAL COMPOSITION OF IMPACT MELTS	9
4.1 VOLATILES.....	9
4.2 OXYGEN FUGACITY	10
5. DOES MELTS WORK ON MARS?	11
5.1 MODES OF DIFFERENTIATION	12
6. RESULTS	13
6.1 MELT SCALING	13
6.2 WATER SATURATION.....	14
6.3 SENSITIVITY TO OXYGEN FUGACITY, PRESSURE, AND INITIAL COMPOSITION	14
6.4 GEOCHEMICAL TRENDS.....	16
7. DISCUSSION.....	17
7.1 FRACTIONAL CRYSTALLIZATION LIQUID EVOLUTION	17
7.2 CRATER SIZE VS. MELT COMPOSITION	18
7.3 UNCERTAINTIES IN MODELLING DIFFERENTIATION OF MARTIAN IMPACT MELT POOLS.....	20
7.4 DO IMPACT MELTS DIFFERENTIATE ON MARS?	21
7.5 THE ROLE OF PARTIAL MELTING DURING IMPACT CRATERING.....	24
8. CONCLUSION.....	25
REFERENCES	28
FIGURES	33

1. Introduction

The discovery of evolved silica and alkali-rich igneous rocks on Mars (up to 67 wt% SiO₂ and up to 14 wt% Na₂O + K₂O) attests to the diversity of igneous processes that have shaped the planet's crust (Ehlmann and Edwards, 2014; Filiberto, 2017; Sautter et al., 2015; Schmidt et al., 2014). These materials contrast with the basalts that comprise the bedrock and dust across most of Mars' surface, indicating a degree of magmatic differentiation not typically seen in Mars' effusive lavas, including those of the large Tharsis and Elysium volcanic provinces (Baratoux et al., 2014; Ehlmann and Edwards, 2014). As *in situ* rover measurements (Sautter et al., 2015), high resolution orbital spectra (Bandfield et al., 2004; Christensen et al., 2005) and analysis of Martian meteorites (Santos et al., 2015) expose greater abundances of felsic and silica and alkali-rich material on Mars, it is important that new models for Mars' crustal composition provide explanations for the origins of the observed heterogeneity.

Asteroid impacts are known to melt enormous volumes of rock and may generate the necessary conditions for magmatic differentiation. In this study we investigate the petrologic evolution of Martian impact melt bodies for large (> 100 km diameter) craters using the thermodynamic phase equilibria calculator MELTS. Large impacts are unique in that they can simultaneously generate substantial near-surface melt bodies derived from high-degree melting of the crust and mantle and may also produce pockets of partial melt scattered through the crust and mantle. We identify signatures of differentiation in impact melt sheets under a range of conditions and compare geochemical trends with measurements of Martian meteorites and evolved rocks from Gusev and Gale craters.

2. Background

Igneous differentiation refers to the changing chemical composition of a magma due to processes such as partial melting, fractional crystallization, assimilation, and liquid immiscibility (Wilson, 2007). On Earth, water is key to the differentiation that produces continental crust because it lowers melt viscosity and increases the solubility of near-solidus, high silica and alkali phases such as quartz and plagioclase (e.g., Sisson and Grove, 1993). Moderate pressures at depth also enhance these processes and encourage early crystallization of iron and magnesium-rich phases such as olivine and pyroxenes (Wilson, 2007).

In many of Mars' evolved igneous rock samples, such as those examined in Gale crater by the Curiosity rover, Al_2O_3 is also enriched (> 14 wt%), indicating that the crystallization of plagioclase, the primary aluminous phase, was suppressed in evolving melts (Rogers and Nekvasil, 2015; Stolper et al., 2013). It seems likely then, that the source magmas for these samples contained some dissolved H_2O (> 1 wt%) (Schmidt et al., 2014; Stolper et al., 2013; Udry et al., 2014), though the origins of the water in these magmas is uncertain and the subject of debate. Some measurements of minerals in Martian meteorites suggest that their parental melts contained dissolved H_2O in weight percent values (Balta and McSween, 2013a; Mcsween et al., 2001). Low-degree partial melting in a volatile bearing mantle could result in higher concentrations of water, alkalis, silica and alumina in initial melts (Humayun et al., 2013; Sautter et al., 2015; Schmidt et al., 2014). However, some estimates suggest the bulk mantle is water poor (Dreibus and Wanke, 1985; Filiberto et al., 2016; Usui et al., 2012), and the abundance and origins of water in Martian magmas remains uncertain.

One mechanism for incorporating both felsic and volatile-rich materials into Martian magmas would be through assimilation of a wetter crust (Beard and Lofgren, 1991; Rogers and Nekvasil, 2015; Udry et al., 2014). However, because subduction is not known to have occurred on Mars, if melts contained recycled crustal materials at depth, another mixing mechanism, such as fluid fluxing or crustal delamination, is required (Baratoux et al., 2014; Filiberto, 2017). Some crustal mass constraints contradict a delamination model though (Morschhauser et al., 2011). It has also been proposed that during overturn of an early magma ocean, volatile-rich crustal regions could have been mixed into the mantle (Elkins-Tanton et al., 2003; Filiberto, 2017; McCubbin et al., 2010), though this specific component of the magma ocean overturn model has not been explored in depth.

Another mechanism for generating melts that access crustal volatiles and mafic material from depth may be through melting and mixing during an asteroid or comet impact (Cintala and Grieve, 1998; Grieve and Pilkington, 1996; Melosh, 1989). Early observations of Mars' surface (Soderblom et al., 1974) demonstrated the ubiquity of ancient ($> 3\text{Ga}$) impact alterations to the surface, and it is thought that impacts played a key role in early crustal evolution after planet formation (Grieve et al., 2006; Reese and Solomatov, 2006). Observations of quartzo-feldspathic material in the rims and central peaks of Martian craters (Bandfield et al., 2004), as well as olivine enrichment in and around Isidis basin (Mustard et al., 2007), point to crystallization and differentiation in impact melt bodies on Mars.

Petrological studies of impact structures on Earth (O'Connell-Cooper and Spray, 2011; Theriault et al., 2002; Zieg and Marsh, 2005) and the Moon (Hurwitz and Kring, 2014; Kramer et al., 2013; Uemoto et al., 2017; Vaughan and Head, 2014; Vaughan et al., 2013) indicate that chemical differentiation is widespread in large impact melt sheets (Osinski et al., 2018). While,

detailed petrologic analysis of samples from melt sheets are possible on Earth, much of bases for studies of lunar impact melts come from satellite spectroscopy (Kramer et al., 2013). Mars faces the additional challenge of a global dust layer, which makes bedrock mineral detection with satellite spectroscopy even more difficult than on the Moon.

Igneous rocks sampled by the Curiosity rover in Gale crater, therefor, offer a rare glimpse into material within Mars' ancient crust (Farley et al., 2014; Sautter et al., 2016). All samples are either conglomerate clasts or float rocks (Cousin et al., 2017) and seem to come from strata eroded by one of the fluvial networks draining into Gale crater (Ehlmann and Buz, 2015; Mangold et al., 2017; Palucis et al., 2014). This suggests a Noachian crystallization age since these rocks must have predated the formation of Gale crater ~ 3.6 Ga, and they are likely much older given a K-Ar age of detrital rim material of 4.21 ± 0.35 Ga (Farley et al., 2014).

We use chemical data from Gale crater samples as a point of comparison for modeling of impact melt differentiation on Mars. However, because we employ a simplified impact and crystallization model, and because future missions may discover further diversity among igneous rocks on Mars, this study is more focused on estimating general petrologic and geochemical trends for impact melts on Mars than it is on reproducing specific compositions.

3. Impact Melting on Mars

During impacts, *in situ* melting of target rock occurs as material experiencing adiabatic decompression behind the impact's shockwave returns to a higher temperature state than prior to shock (Melosh, 1989). In impacts on Mars, these melts are less voluminous for a given final crater size than their terrestrial and lunar counterparts. This is because on Earth, stronger gravity

enhances crater collapse and leads to larger final crater structures. Also, Martian basalts require more energy to melt than lunar anorthosites or terrestrial granites, thereby producing less melt. Still, numerous large impact basins such as Isidis, Argyre, Hellas, Utopia, and potentially the Borealis basin prominently define topography at the surface and contained orders of magnitude larger melt volumes than any confirmed impact structure on Earth (Andrews-Hanna et al., 2008; Reese and Solomatov, 2006).

Here, melt volumes are scaled for a range of representative impact sizes defined by observed rim-to-rim diameters of well-known craters on Mars. This range includes: Gale (154 km), Schiaparelli (459 km), 700 km, Isidis (1500 km), Argyre (1800 km), Hellas (2300 km), and Utopia (3300 km) (see figure 1). Note that there are no named craters within the 700 km diameter range according to the Robbins and Hynek, 2012 database.

3.1 Melt Scaling

We use the universal scaling equations outlined in Abramov et al. (2012) to estimate volumes of impact melt produced by shock decompression melting and retained within the crater. Kinetic modelling of planetary scale impacts suggests that such scaling estimates are applicable in both small and large regimes, even for up to 8000 km diameter craters (Marinova et al., 2011; Reese et al., 2011). We scale our results in terms of final crater diameter D_f . First, we calculate the transient cavity diameter D_{tc} , which denotes the size of the crater after material is ejected, but before rim collapse. This depends on a characteristic simple to complex crater transition diameter $D_Q = 8$ km for Mars, the size in which craters trend to transition from more bowl-like, to exhibiting a central peak or peak rings (Abramov et al., 2012; Garvin and Frawley, 1998).

$$D_{tc} = (D_Q^{0.15 \pm 0.04} D_f^{0.85 \pm 0.04}) / 1.2$$

Then, using an estimated specific internal energy of melting for the Martian crust of $E_m = 9 \times 10^6 \frac{J}{kg}$ for basalt, a density ratio of the projectile to target as $\frac{\rho_p}{\rho_t} \approx 1$ for a stony meteorite, gravity $g = 3.72 \text{ m/s}^2$, and impact angle $\theta = 45^\circ$ (representing the average), melt volume is estimated as:

$$V_{melt} = 0.12 E_m^{-0.85} \left(\frac{\rho_p}{\rho_t}\right)^{-0.28} D_{tc}^{3.85} g^{0.85} \sin^{1.3} \theta$$

In order to calculate melting depth, we assume an initially spherical geometry to the melt due to the radial propagation of the shock front (see figure 2a) (Barr and Citron, 2011; Kring, 2005). We place the top of this sphere at Mars' surface. Following Cintala and Grieve (1998), we assume the melt is well-mixed and that material crystallizing within the melt sheet is representative of the stratigraphy sampled by the spherical melt region. This is a basic approach to approximating volumes of melt that does not include other forms of melt production such as frictional melting or heating and decompression of near solidus material beneath the crater.

It has been shown that partial melts produced by shock decompression melting are comprised of the local bulk rock composition because this form of melting affects all silicate minerals equally and does not occur at grain boundaries (Hurwitz and Kring, 2014 and references therein). However, melts produced by heating or isostatic decompression beneath the crater may represent only compositions of phases with the lowest melting points (Bertka and Holloway, 1994). These melt compositions may be another starting point for crystallization of isolated melt lenses and are heavily dependent on the degree of partial melting. While these alternative forms of melting are not treated explicitly as components of the melts scaled in this study, their contribution in large impacts may be significant (Edwards et al., 2014; Elkins-Tanton and Hager, 2005), and they will be discussed later on.

For estimating amounts of crust and mantle in the melt sheet, we use an average crust-mantle boundary depth of 50 km, constrained by topography and gravity fields, along with density requirements for estimated crust and mantle compositions (Andrews-Hanna et al., 2008; Zuber, 2001). We allow the material above 50 km to be a homogenous crust, and the material below 50 km to be a homogenous mantle. Mass contributions from the crust and mantle are then calculated from the volumes of spherical caps of a 2900 kg/m^3 crust and 3500 kg/m^3 mantle (Andrews-Hanna et al., 2008; Zuber, 2001). From this mixture, a melt composition is calculated for each crater size.

Though impact melts may involve material originating from significant depth, isostatic rebound and uplift lead to the formation of melt sheets that are only a fraction as thick as the maximum depths from which they are sampled (Cintala and Grieve, 1998). In order to calculate the final thickness of the melt sheet, and thus the maximum pressures at the melt sheet's base, we estimate that the entire melt sheet is emplaced within the base of the final crater, and that it takes a paraboloidal shape (see figure 2b) (Edwards et al., 2014; Grieve and Pilkington, 1996). This is a simplification, however, because melt volume scales exponentially with crater size, and impacts of different sizes may result in dramatically different melt and crater floor geometries. Smaller impact melts take up only a minute fraction of the volume of the transient cavity and crystallize quickly as a thin veneer before forming a cohesive pool in the base of the crater (Cintala and Grieve, 1998). If large enough, craters may take on shapes that are no longer bowl-like, as ejecta and melt compromise a discrete rim structure and rebound inverts the crater floor (Grieve and Cintala, 1992). Melt sheets in these large craters may be more disc-like (Hurwitz and Kring, 2014; Marinova et al., 2011). In planetary-scale impacts beyond what is included in this study, the curvature of the planet also affects the melt volume to cavity size relationship and

may lead to more complex geometries or crater overflow (Marinova et al., 2011; Reese et al., 2011; Reese and Solomatov, 2006). Despite these caveats, assuming a paraboloid geometry allows us to take a standardized approach using topographic data for craters on Mars to approximate melt sheet diameter and thickness.

Crater diameter-to-depth ratios were calculated for melt-bearing complex craters on Mars in Tornabene et al. (2018) from Mars Orbiter Laser Altimeter observational data: $d_f = (0.323 \pm 0.017)D_f^{0.538 \pm 0.016}$ where d_f is the rim-to-floor height. If we assume the apparent depth of a crater is roughly representative of the distance to the top of the melt sheet, then we can use the integral equation for the volume of a paraboloid to solve for the thickness of the melt sheet, d_m :

$$V_{paraboloid} = \pi \int_0^{h_a} \frac{r^2 z}{h_0} dz, \quad r = \frac{D_f}{2}, h_0 = d_f + d_m, h_a = d_m$$

$$V_{melt} = \pi \int_0^{d_m} \frac{D_f^2 z}{4(d_f + d_m)} dz$$

$$0 = \frac{\pi D_f^2}{8V_{melt}} d_m^2 - d_m - d_f$$

$$d_m = 1 \pm \sqrt{\frac{1 + \frac{\pi D_f^2 d_f}{2V_{melt}}}{\frac{\pi D_f^2}{4V_{melt}}}}$$

Once d_m is known, the pressure at the melt sheet's base is determined using a density that is drawn from the masses of crust and mantle in the mixed melt sheet.

4. The Initial Composition of Impact Melts

The initial composition of impact melts determines subsequent petrogenetic evolution and depends on the composition of the mantle and crust as well as the melting conditions (see table 1). For the primitive mantle composition, we refer to the Dreibus and Wänke (1985) estimate of the parent body for Shergottite-Nakhlite-Chassignite (SNC) class meteorites. For the crust composition, we choose Taylor and McLennan (2009)'s average crust, which is derived from globally averaged soil and dust compositions. While other compositional estimates for the crust and mantle of Mars exist, these two sources have been widely used and thus offer an opportunity to compare results from the methods shown in this work to other melt-crystallization models for Mars.

4.1 Volatiles

A major control on phase stabilities in magmas is volatile element contents. Water in particular is a key ingredient in terrestrial magmas and was at least briefly abundant on Mars' surface, where it incised channel networks, deposited lacustrine sediments, generated clay minerals and even remains in the groundmass of some Northern terranes today (McSween et al., 2006). Figure 3 presents a literature review of estimates of water contents in Mars' crust and mantle based largely on analysis of phase assemblages and included volatiles in SNC meteorites. The relevance of water in impact settings was highlighted by the discovery of pitted materials, interpreted to be degassing features, found within impact craters across the planet (Tornabene et al.,

2012). Additionally, in some smaller craters, fluidized ejecta indicates crustal water contents of as much as 20 wt % (Barlow, 2004).

In this study, we explore two extremes for possible water contents. “Dry” models are run with an anhydrous crust and 35 ppm H₂O mantle (Dreibus and Wänke, 1985). In the alternative, we adopt a “wet” crust concept from Ivanov and Pierazzo (2011), and assume a wet, hydrothermally altered Martian crust with 5.2 H₂O wt%, which is based on upper measurements for water contents in altered terrestrial oceanic basalt (Staudigel et al., 1996). This could represent structurally bound water in hydrothermal minerals and pore fluids in the upper crust. Because the distribution and form of water in this scenario is uncertain, we neglect geophysical effects of water on rock strength, porosity, density and liquidus, which can either be positive or negative (Barlow, 2004). We also avoid some of the complications introduced by water to melt scaling because we consider variations in final crater diameter, which is directly correlated to melt volume, rather than impact energy.

4.2 Oxygen Fugacity

In addition to volatiles, redox conditions affect liquid lines of descent (LLDs) in crystallizing magmas. Measurements of mineral assemblages, trace element partitioning, and oxide compositions in Martian meteorites constrain oxygen fugacity (fO_2) in parental melts from very reducing conditions (near the Iron-Wüstite buffer) to somewhat oxidizing conditions (above the Fayalite-Magnetite-Quartz buffer) (Righter et al., 2008). Generally, more oxidizing values are thought to represent Mars’ crust, while the isolated mantle is thought to be much more reducing,

and intermediate values may indicate mixing of the two reservoirs or fluid exchange (Wadhwa, 2001).

5. Does MELTS Work on Mars?

The chemical compositions and masses of phases within cooling melt sheets were calculated using the thermodynamic calculator MELTS with the alpha-MELTS 1.8 front end (Ghiorso and Sack, 1995; Smith and Asimow, 2005). MELTS uses experimentally determined partition coefficients to calculate phase affinities over a range of thermodynamic conditions. Of the different calibrations (MELTS, rhyolite-MELTS, and pMELTS), MELTS was selected because it is calibrated within temperatures from about 500-2000 °C and pressures of about 0-1 GPa, which represents the range for impact melts below liquidus temperatures in this study.

In Martian compositions, MELTS performs within an uncertainty of 1 wt% or better for most major oxides according to results from experimental studies of Martian meteorite compositions (Balta and McSween, 2013b). It appears that much of the uncertainty stems from a failure of MELTS to correctly estimate the olivine-pyroxene multiple saturation temperature, and from an overestimate of chromium-spinel liquidus in Martian magmas by about 50° C (Udry et al., 2014). This affects how MELTS determines which phases appear first in Martian melts at crustal depths. Balta and Mcsween (2013a) found that either using the pMELTS calibration or adjusting pressure by multiplying it by a factor of 4 will more accurately estimate the olivine-pyroxene multiple saturation point. But these corrections do not work well enough for predicting other phase affinities to justify their use. Thus, in this study, we elect not to make any changes to the normal MELTS procedure for modeling magmas below 10 kbar. In order to assess possible

sources of error however, we do conduct a series of sensitivity tests in which we alter water contents, oxygen fugacity, pressure, and composition one at a time (see figure 5 and section 6.3).

Despite its issues, MELTS has been widely used to model crystallization in studies of Martian igneous processes (Stolper et al., 2013; Udry et al., 2014) and it provides our best estimates of some of the mineral and chemical trends we might expect to see in Martian magmas, given our limited ability to collect laboratory samples. In this study, MELTS runs are conducted from liquidus to complete, or near-complete, crystallization in steps of 1° C at isobaric conditions.

5.1 Modes of Differentiation

MELTS simulations are run at two crystallization settings, batch and fractional crystallization. In fractional crystallization (figure 2e), which may represent crystal settling, crystals are isolated from the melt continuously and never experience chemical exchange with the main melt chamber. This is idealized here as chemicals organized into solid phases are instantaneously removed at each temperature step, though in reality fractionation is neither instantaneous nor complete (Bachmann and Bergantz, 2008).

In batch crystallization (figure 2c), solid phases are in constant chemical equilibrium with the melt, and thus the liquid and solid systems evolve in tandem. If this process behaves ideally, the solidified melt sheet composition will reflect the bulk composition of the liquidus magma, and no differentiation will have occurred. However, compositions along a batch crystallization LLD may represent melt from that point in the crystallization process that has become chemically isolated, or alternatively, they may represent the compositions of partial melts.

One mechanism by which liquid may separate from crystals, that does not involve crystal fractionation, is through compaction-driven segregation (figure 2d), wherein buoyant siliceous melt permeates through the pore spaces between denser Mg and Fe-rich crystals (Bachmann and Bergantz, 2008). In this case

Calculating the relative likelihoods for the occurrences of the variety of mechanisms by which melts might differentiate in Martian impact melts is a topic for future study. Whether differentiation occurs by either crystal settling, porous flow or at all is dependent on the timescales of those processes whether they are shorter than the time it takes a melt sheet to solidify beyond a critical crystal fraction. Prior work that provides some insight on the factors that dictate these timescales is discussed in Section 7.4.

6. Results

6.1 Melt Scaling

We have estimated melt volumes, liquidus compositions and melt sheet thicknesses for completely molten regions produced in impact craters from 154 km to 3300 km diameter. The top panel of figure 4 displays scaling results for a continuous range of impact sizes from 0-2000 km. Melt volume increases exponentially, while depth of melting and melt sheet thickness increase linearly with crater size. Mantle material is incorporated into melt sheets of craters around 450 km diameter and larger and reaches half the mass of the melt sheet at about 750 km diameter. The mantle composition reaches 90% of the melt sheet at around 1800 km. At 2000 km diameter, a crater's melt sheet is approximately 15 km thick after uplift, while the deepest regions incorporated into the melt may be approximately 133 km below the initial surface. This is rough-

ly consistent with an estimated stratigraphic central uplift of 215 km (Caudill et al., 2012; Grieve and Pilkington, 1996).

6.2 Water saturation

Though initial water content in the “wet” crust model is above 5 wt %, saturation in initial melt sheets is reached below 2 wt % for all crater sizes in this study (see figure 4 bottom) consistent with upper estimates for SNC parental magmas (see figure 3). Water solubility increases with depth (pressure), however the fraction of melt that is sourced from wet crust also decreases with depth. At about 1000 km diameter, melts incorporate enough anhydrous mantle material (69% of the total) to bring water contents below solubility. As crystallization proceeds however, solubility of water in residual liquid increases, and low degree melts contain as much as 4.5 wt% water. Thus, at 10% residual liquid, the maximum water is found in craters of around 1500 km in diameter, or an 86% mantle melt.

6.3 Sensitivity to water contents, pressure, oxygen fugacity, and initial composition

We ran a series of MELTS simulations varying water contents, pressure, oxygen fugacity, and initial composition independently in order to gauge sensitivity within parameter ranges explored in this study (figure 5). For these sensitivity tests, we assume constant initial compositions as calculated for a 700 km diameter crater (approximately 42% mantle, 58% crust without water), constant fO_2 at FMQ, and constant pressure of 1 kbar, except when each of these parameters is varied. Results are plotted with Mars igneous rock data from Martian meteorites, Meridi-

ani Planum, Gusev crater and Gale crater, which is categorized into five groups based on textural classifications from Cousin et al. (2017) (Filiberto, 2017).

In figure 5a, we change starting water contents from anhydrous to above saturation levels and find that chemical changes are minimal for concentrations below 0.01 wt% H₂O or above 1.5 wt% H₂O, and that most sensitivity lies continuously between these two values. Key changes represent a shift in timing of clinopyroxene, orthopyroxene, and plagioclase feldspar crystallization, as they appear later at lower temperatures with more water, up to the saturation point. Additionally, hydrous phases such as apatite and biotite appear in small amounts in some hydrous melts.

Similarly, when fO_2 conditions are changed from more oxidizing (FMQ+1 log unit) to reducing (FMQ-4 log units) (figure 5b), pyroxenes and feldspar again crystallize later. Under the most oxidizing conditions, orthopyroxene crystallization also has the effect of temporarily lowering the silica concentration in the melt, while in more reducing environments silica melt concentrations rise continuously from liquidus to solidus.

Still, within the range of estimates for Martian crust and mantle redox states (fO_2 ~FMQ-3 to FMQ) enrichment trends are only slightly offset and parallel, with more oxidizing conditions leading to slightly more alkali enrichment, but not by more than 1 wt%. Some recent work suggests that the discrepancy between phase equilibria in melts at different fugacities widens at higher pressures found at depths beyond the reach of melt sheets studied here (Udry et al., 2014).

We also varied pressure in isobaric melts from 0.1 to 8 kbar (figure 5c). As pressure increases, more silica is removed from the melt by pyroxenes, which also seem to crystallize before olivine above 5 kbar. However, as noted previously, MELTS does a poor job of estimating this transition point from pyroxene to olivine crystallization so this transition point is not reli-

ble. Higher pressures also suppress feldspar crystallization until very low degree melts. In sum, increasing pressure has the effect of lowering silica enrichment, widening the range of calcium concentrations seen in the liquid, and raising the enrichment of alkalis and alumina.

Finally, we also tested for the effects of composition (figure 5d), ranging from more Martian crust-like to more Martian mantle-like. Crustal melts begin at higher silica, alkali and alumina contents, but because plagioclase and orthopyroxene crystallization occur early, before olivine, greater alkalis are removed from the melt relative to silica, with the effect of less alkali enrichment and more silica enrichment in low degree crustal melts. Interestingly, the greatest alkali enrichment occurs not in the mantle, but in mixed crust-mantle melts where initial alkali contents are still higher than the mantle, but the crystallization sequence is similar to the mantle's and involves prolonged crystallization of olivine and spinel with pyroxenes and plagioclase appearing later.

6.4 Geochemical trends

Our impact melt crystallization results are discussed in terms of major oxide weight percentages in liquids as they change with each temperature step. This provides continuous LLDs from the starting primitive primary melts to evolved low degree residual liquids. LLDs are again juxtaposed against geochemical data from igneous Martian materials from Gale Crater, Gusev Crater, Meridiani Planum and from Martian meteorites. Each set of initial conditions was run under batch equilibrium crystallization (figure 6) and fractional crystallization regimes (figure 7).

As crystallization progresses, MgO is steadily removed from the melt. This means melt evolution, cooling and crystallization drive residual liquid compositions toward lower MgO con-

tents (figures 6, 7 and 8). SiO_2 , Na_2O and K_2O melt concentrations generally increase exponentially as olivine removes MgO from the melt. Similarly, Al_2O_3 and CaO display an upward trend before dipping back down when plagioclase and clinopyroxene begin to crystallize respectively. For Cr_2O_3 and FeO there is a decreasing trend due to spinel and olivine crystallization. In large mafic melts, pyroxene crystallization begins early, and there is some FeO enrichment before depletion. In the same cases, orthopyroxene crystallization initially lowers the SiO_2 concentration before it rises again.

7. Discussion

7.1 Fractional crystallization liquid evolution

Under the fractional crystallization regime, particularly in model runs for larger craters, FeO is enriched in the melt well above amounts found in felsic materials on Mars. This results from less olivine crystallization (Balta and McSween, 2013b). CaO is also high, and Al_2O_3 is lower by at least 5 wt % than most of Mars' evolved igneous samples, indicating simple fractional crystallization in impact melts cannot explain those compositions. Fractional crystallization runs do show some enrichment of SiO_2 and Na_2O in melt and could perhaps replicate trends seen in some higher Mg samples such as SNC meteorites and group 1 in Gale crater, which are aphanitic, extrusive, mafic, lacking cumulates, and possibly glassy.

Cousin et al. (2017)'s group 4 rocks align with the melt evolutions in both fractional and batch runs for large and small craters. These are intrusive and coarse-grained and contain near equal mixes of mafic and felsic minerals, similar to a norite.

7.2 Crater size vs. melt composition

Crater size strongly influences both initial melt composition and differentiation. If Mars' early crust was water-rich, we expect the initial water contents of impact melts to decrease for larger craters due to increasing dominance of mantle-derived melts. By the same logic, larger craters will also generate more mafic initial melt compositions, leading to early crystallization of mafic phases and higher Na and Al contents in the residual melt (see figure 9). Because phase equilibria are sensitive to pressure, melt sheet thickness also exerts an important control on crystallization sequence. Greater pressure allows more water to dissolve in the melt, and water increases the solubility of plagioclase and pyroxenes.

During equilibrium crystallization in water-rich melt pools formed by large, basin-forming impacts, olivine, clinopyroxene, and apatite crystallization, and plagioclase suppression, lead to progressively higher Al_2O_3 , higher Na_2O and lower CaO concentrations. This trend appears to align with some rocks classified in group 2 of Cousin et al. (2017)'s scheme for igneous rocks in Gale crater, which includes rocks that are extrusive and porphyritic, with relatively low silica compositions (<58 wt% SiO_2) and mid-level alkalis (5-10 wt% $\text{Na}_2\text{O} + \text{K}_2\text{O}$) (see figure 6). Some rocks in group 2 have been labeled as trachyandesites (Sautter et al., 2015).

Our simulations indicate that large mantle-rich impact melts that are dry can also suppress plagioclase under the pressure of the melt sheet without the presence of water (see figures 8 and 9). These produce melts that are high in alkalis with only moderate SiO_2 and are somewhat less evolved (higher MgO wt %), similar to the Jake_M sample, a rock that is aphanitic and vesicular.

Shallow, crust-rich melts crystallizing in batch conditions appear more conducive to the highest SiO_2 , K_2O and FeO trends at low MgO amounts, where silica and alkalis are richer in the crust and more plagioclase is crystallized than olivine (see figures 6 and 9). This effect is enhanced by the presence of water, which initiates apatite crystallization. The analogue here may be some rocks in Cousin et al. (2017)'s group 5 which are intrusive coarse-grained granodiorite or quartz diorite-like rocks, high in silica but lower in alkalis.

These two crystallization regimes, one that enriches melt in sodium and aluminum and depletes calcium and the other which enriches melt in silica, act in opposition to each other. Yet, both must be accomplished in order to achieve the geochemical signatures of rocks in Cousin et al. (2017)'s groups 3, which are intrusive fine-grained trachytes containing potassium-feldspar crystals, silica glasses and light-toned aphanitic vesicular rocks, as well as the rocks in group 5 which are enriched in alumina.

Thus, a middle ground is perhaps the most conducive to the combined enrichment regimes (see figures 8 and 9). At 700km diameter, an impact incorporates enough crust (~50%) to experience SiO_2 enrichment, enough mantle to mostly crystallize mafic phases early on, while also creating a melt that is thick enough to generate pressures that allow for more dissolved H_2O , leading to plagioclase and Ca-rich clinopyroxene suppression. Still, a substantially stronger response appears when we raise input pressures by as little as 400 bar, from 0.6 to 1 kbar in the 700 km diameter impact composition. Given the simplified nature of our melt sheet thickness estimates, such a pressure difference may be within reason. Amongst our results, this scenario, a mixed wet-crust-mantle crystallizing in equilibrium at 1 kbar is the best fit to the largest enrichments in SiO_2 , Na_2O , K_2O and Al_2O (see figure 8).

7.3 Uncertainties in modelling differentiation of Martian impact melt pools

Inputs to our impact melting and crystallization model are derived from estimates that, along with the issues discussed for MELTS, introduce inherent and compounding uncertainty to our results. Additionally, information on the composition of the buried Martian crust is limited to data from only a few locations. We do not yet know whether observations of felsic and evolved materials represent structures that are rare or commonplace, and there is the possibility that post-emplacement alteration affected the chemical compositions of the igneous targets in Gale crater (Siebach et al., 2017).

Other potential discrepancies from the compositional inputs used in this study include a crust and/or mantle that is rich in volatile elements other than water, such as sulfur, CO₂, fluorine and chlorine (Filiberto and Treiman, 2009). Some experiments on Martian meteorites indicate that CO₂ and Cl could lead to decreased solubilities of felsic phases, generating rocks lower in Al₂O₃ and higher in FeO (Balta and McSween, 2013b). Further examination of materials on Mars for evidence of volatiles, such as melt inclusions, will place constraints on volatile contents.

Additionally, no petrologic models using current estimates of Martian primary melts, including this study, have been able to explain the extreme potassium enrichment in some of Gale's igneous samples (group 3) (Stolper et al., 2013). If asteroid impact melts did contribute to the formation of high K₂O (> 4 wt%) rocks, they also require supplemental potassium in the primary melt. This might include a potassium-rich region of a heterogeneous mantle that has yet to be observed, or mantle metasomatism (Schmidt et al., 2014).

It is also possible that an ancient Martian crust may have been hotter and thinner than it is at present, and than our models take into account (Edwards et al., 2014; Zuber, 2001). One consequence of this is that the target region would be more conducive to melting beneath the crater due to by heating and isostatic decompression, thereby generating more melt. Also, these deep melts would more easily propagate through a thin, fractured crust to the surface.

Finally, the fate of water during impacts into a water rich crust may also hold important implications for not only melt mineralogy, but also for questions of Mars' climate, fluvial networks and habitability by water-based life. Impacts melt or vaporize water-ice contained within target rock, and some work shows this can lead to hydrothermal circulation through cracks and fissures (Ivanov and Pierazzo, 2011; Osinski et al., 2013). Further work should constrain the vigor of these processes as they relate to known impacts on Mars.

7.4 Do impact melts differentiate on Mars?

In this study, we consider differentiation after equilibrium and fractional crystallization in impact melt sheets on Mars. There is evidence for fractional crystallization in the impact melts of terrestrial craters Manicouagan (O'Connell-Cooper and Spray, 2011) and Sudbury (Therriault et al., 2002; Warren et al., 1996), as well as for impact melts on the Moon (Hurwitz and Kring, 2014; Kramer et al., 2013; Uemoto et al., 2017; Vaughan and Head, 2014; Vaughan et al., 2013). However, it is thought that rapid cooling and/or dynamic convection prevents fractional crystallization in the majority of observed impact melts on the Earth and Moon (Osinski et al., 2018).

The likelihood and vigor of crystal settling within an impact melt pool is dependent on the particle Reynolds number, which dictates laminar or turbulent flow. This critical parameter is

defined by the viscosity and density of the fluid, the densities and shapes of the crystals, and gravitational force. Assuming laminar flow, Cassanelli and Head (2016) used Stoke's Law to determine crystal settling timescales and found that convective mixing would prevent settling of crystals smaller than about 1.5 mm prior to complete solidification in large lunar impact melts. Because lunar impact melt samples, and in particular cumulates, are limited, whether crystals grew large enough to settle is unknown. This crystal size threshold is likely to be lower on Mars where gravity is higher, although the viscosity of Martian impact melts may vary considerably from those on the Moon.

Liquid immiscibility has also been proposed as a mechanism of differentiation within impact melts (Zieg and Marsh, 2005) and basaltic magmas (Charlier et al., 2013), but large-scale stratification stemming from this process has yet to be confirmed in impact melts. Immiscible textures have been observed on the grain scale in impact melts that incorporate both silicates and carbonates (Osinski et al., 2018), however carbonates are not known to exist on Mars. If immiscibility driven segregation were to occur on Mars, it is more likely that it would resemble differentiation patterns seen in basaltic intrusions such as the Skaergaard intrusion, where iron-rich liquids separated from silica-rich liquids (Jakobsen et al., 2005). This process would be enhanced by anhydrous fractional crystallization at low pressure that produces iron-rich, alumina-poor liquids (Charlier et al., 2013).

Segregation of interstitial liquids from a crystalline matrix during compaction or melt migration remains to be considered. This process is physically constrained by many of the same melt dynamics as fractional crystallization, where a system that is convecting too vigorously to allow for crystal settling may develop an intact crystalline matrix with evolved melt in the pore spaces between grains. Whether this melt experiences porous flow depends on the magnitude of

the solid-liquid density contrast, along with the melt viscosity, solid matrix porosity and viscosity, crystal grain size and gravitational acceleration acting on the melt (McKenzie, 1984; Philpotts et al., 1996; Spiegelman, 1993; Tegner et al., 2009). Because viscosity decreases with the addition of water, and because rising gas bubbles can also filter-press interstitial liquids, water-rich melts may be more susceptible to segregation (Keller et al., 2017).

Completely assessing of the likelihood of compaction in the solidifying melt sheet is difficult for Mars, however, because we have a very limited knowledge of the physical characteristics of Martian melts. We do know that in order for segregation to take place, the timescale of melt extraction must be quicker than the time it takes for the melt sheet to solidify (Bachmann and Bergantz, 2004). In a batholith-scale mush body on Earth, which is analogous in volume to some basin-scale impact melt pools, Bachmann and Bergantz (2004) calculated the timescale of melt extraction needed to produce a rhyolitic cap to be on the order of 10^4 - 10^6 yr. Cooling time for a planetary scale impact basin on Mars to reach a 2% melt fraction was calculated to be on the order of 10^8 yr (Ivanov, 2006; Reese et al., 2011; Reese and Solomatov, 2006). These estimates suggest that some Martian impact melts likely remained partially molten for long enough for compaction to generate some stratification within the melt sheet.

Ultimately, large impact melts on the moon and Earth do show signs of some form of chemical separation, and it seems likely this would occur in melts on Mars as well. However, the dominant differentiation mechanisms will depend on melt sheet geometry, emplacement depth, cooling rate, and viscosity.

7.5 *The role of partial melting during impact cratering*

We have shown that the LLDs in equilibrium crystallization scenarios provide superior fits to almost the entirety of evolved igneous rocks on Mars. In this model, simple as it is, equilibrium crystallization may approximate an array of processes including partial fractional crystallization, mechanical separation driven by volatile degassing or liquid immiscibility, or partial melt accumulation through compaction-driven segregation (Warren et al., 1996). The accumulation of partial melts could mean two things: 1) segregation of some of the liquid from the solidified matrix part way through melt sheet crystallization, or 2) pooling of liquids in regions that were only partially melted by the impact. Given that prior work has estimated that partial melts could make up a significant component of the total melt volume produced in an impact (Barr and Citron, 2011; Ivanov et al., 2010; Ivanov and Pierazzo, 2011), and that segregation after partial crystallization is possible on Mars (Bachmann and Bergantz, 2008; Reese and Solomatov, 2006), these scenarios are worth consideration.

If porous flow occurred in impact-generated melt pools on Mars, segregation sheets would be enriched in alkalis and silica relative to the solid matrix as described by the equilibrium crystallization LLDs (figure 6) for the point where segregation occurred, mirroring compositions of partial melts. This would be consistent with the conclusion reached by Sautter et al. (2016) that low pressure partial melting of a mafic mantle source is responsible for the elevated silica, alkalis and alumina observed in rocks in Gale crater and some Martian meteorite clasts. Experimental melting of primitive Martian mantle compositions support the low degree melting or late residual melt model for alkaline enrichment (Collinet et al., 2015).

In studies of offset dikes surrounding the main mass of the Sudbury Igneous Complex (e.g. Wood and Spray, 1998), there is some suggestion that these melt structures may be injected differentiated melts, though the assimilation of locally heterogeneous country rock makes geochemical confirmation of this difficult (Hecht et al., 2008). If the low degree partial melting scenario is a major source of rock enrichment on Mars, we might expect to see such materials in dike-like structures around the edges of a crater's central melt sheet, where partial melts congregated after transport. Or, in the case of compaction of the central melt pool, we might expect planar stratification within the main melt sheet (Tegner et al., 2009).

8. Conclusions

The origin of felsic rocks on Mars remains a question. Impact cratering and impact melting are, however, key geologic mechanisms of alteration to terrestrial planets that can lead to chemical heterogeneity in surface rocks. While no single set of model runs can perfectly capture the diversity of rock compositions on Mars, our petrologic results indicate that it is possible for melts of the depth and scale produced by asteroid impacts on Mars to exhibit evolved compositions similar to what has been observed in Gale Crater and in Martian meteorites. More definitively perhaps, this project highlights important controls on enrichment in impact and non-impact related magmas on Mars:

- 1) Craters approximately larger than Schiaparelli (458.52 km diameter) on Mars access the mantle and contain larger melt sheets than known differentiated melt sheets on Earth.

- 2) In Martian impact melts, the mechanisms that enrich fluids in silica compete with those that enrich in alkalis. In order to achieve both, melts must be under pressures of a thick melt sheet, must be water-rich, and must contain a mixed crust-mantle composition.
- 3) Unless the initial melt is potassium rich, impact melt differentiation cannot explain the potassium enrichment found in some materials in Gale Crater.
- 4) Fractional crystallization cannot explain alkali and Al_2O_3 enrichment in residual liquids at impact melt sheet depths. Liquid evolution during equilibrium crystallization provides a better fit to enrichment trends and may represent partial melting or compaction-segregated melts produced by impacts.
- 5) The enrichment of SiO_2 , Na_2O , K_2O , and Al_2O_3 found in samples depleted in MgO (< 5 wt%) is achieved through the extended crystallization of olivine that occurs when feldspar and the pyroxenes are destabilized. In low degree melts, water raises the solubilities of feldspars and pyroxenes, thereby suppressing crystallization of those minerals. Asteroid impacts can mix water rich surface material with mafic mantle material, thereby providing conditions for this style of enrichment.

Hypervelocity impacts were an important geologic process on early Mars. Because the resulting melts can differ from endogenic Martian magmas in their melting and solidification conditions, they can produce a range of distinctive igneous compositions. Such melts can introduce water from the crust to primitive mantle magmas. Impact melt sheets also provide a mechanism for generating partial melts of the Martian mantle at low pressure, and near-enough to the surface to be exhumed by erosion.

Exhumed Gale crater rocks sample ancient crust and the alkaline differentiation trend in Gale has been interpreted as potential evidence for igneous processes that operated primarily in the Noachian (Sautter et al., 2015), when impact processes were more numerous. Even if impacts were not responsible for the alkaline differentiation trends in Gale crater, impact melting and differentiation may have played an underappreciated role in shaping the petrology of the earliest Martian crust.

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FIGURES

Figure 1 Map of Mars with craters of the sizes examined in this study labelled. (USGS/ASU)

Figure 2. Conceptual depiction of (a) impact melting and (b) melt sheet formation, demonstrating properties used to determine melt sheet thickness. D_{tr} = transient cavity diameter, V_{melt} = melt volume produced by shock decompression, D_R = final rim-to-rim crater diameter, d_a = apparent rim-to-floor crater depth, d_m = melt sheet thickness. Dike structures beneath the melt sheet represent the irregularity of melt accumulation beneath the crater, and possible propagation of melt through fractured country rock. Possible crystallization scenarios explored for impact melt sheets include (c) batch crystallization in the melt sheet and in partial melts surrounding, (d) compaction of a porous crystalline matrix during crystallization, leading to expulsion of melt in segregation sheets (following red arrows), and (e) crystal settling, leading to fractional crystallization.

Source	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO ^t	MgO	MnO	CaO	K ₂ O	Na ₂ O	P ₂ O ₅	H ₂ O
Crust ^a	49.3	0.98	10.5	0.38	18.2	9.06	0.36	6.92	0.45	2.97	0.9	*
Mantle ^b	44.4	0.14	3.02	0.76	17.9	30.2	0.46	2.45	0.04	0.50	0.16	0.0035

Table 1. Major oxide values in weight percent of model input compositions. *5.2 for “wet” crust scenario, 0 for “dry”. ^ttotal iron = FeO + Fe₂O₃. ^aTaylor and McLennan (2009) ^bDreibus and Wänke (1985)

Figure 3. Literature estimates of Martian petrologic water contents. Estimates for parental magmas are in blue in the top panel and the mantle source regions are in red on the bottom. Boxes define range of estimate, arrows indicate undefined limits. *includes estimates from sources within.

Figure 4. Upper panel: Melt volume (black, solid) increases exponentially, and final melt sheet thickness (red, dashed) increases linearly with impact magnitude for stony asteroids travelling at 9.6km/s and 45° impact angle. Melt-volume $\propto$ final-crater-diameter^{3.2725} (Abramov et al., 2012; Johnson et al., 2016). Lower panel: H_2O content at the base of a mixed melt sheet ($f\text{O}_2 = \text{FMQ}$), assuming complete melting, for an impact into a “wet” crust (5.2 wt% H_2O), showing mass proportion of water in melted material (dashed blue), initial water content (solid blue), and mass proportion of water in liquid of a 90% crystalline melt sheet (solid red). The latter two values are dictated by the solubility and availability of H_2O .

Figure 5. Total alkali versus silica diagram (Le Maître, 2002) showing liquid lines of descent for sensitivity tests. Except for the panels for which single inputs are changed, conditions are held constant at an anhydrous 700 km diameter crater composition (~42% mantle, 58% crust) at 1 kbar and f_{O_2} = FMQ. A) only H₂O contents are varied. B) only pressure is varied. C) only f_{O_2} state is varied (along a log unit scale relative to the Quartz-Fayalite-Magnetite buffer). D) only composition is varied. Data points and shading represent measurements of known igneous Martian materials (Filiberto, 2017). Arrows point to the appearances of key phases controlling oxide concentrations (see figure 9 for information on abbreviations). *Average crust from Taylor and McLennan (2009).

Figure 6. Oxide vs MgO plot showing liquid lines of descent for a range of crater sizes, defined by rim-to-rim diameter. Each result shown here was computed under batch crystallization at $fO_2 = \text{FMQ}$ with 5.2 wt% H₂O in the crust and pressure equal to that at the base of the final melt sheet. Data points and shading represent measurements of known igneous Martian materials (Filiberto, 2017). Black tick marks indicate point at which 90% of the melt has crystallized. Arrows point to the appearances of key phases controlling oxide concentrations (see figure 9 for information on abbreviations). *Average crust from Taylor and McLennan (2009).

Figure 7. Oxide vs MgO plot showing liquid lines of descent during fractional crystallization for three representative crater sizes. Each result shown here was computed at $fO_2 = IW$ with 5.2 wt% H_2O in the crust and with pressure equal to that at the base of the final melt sheet. Data points and shading represent measurements of known igneous Martian materials (Filiberto, 2017). Black tick marks indicate point at which 90% of the melt has crystallized. Arrows point to the appearances of key phases controlling oxide concentrations (see figure 9 for information on abbreviations). *Average crust from Taylor and McLennan (2009).

Figure 8. Oxide vs MgO plot showing liquid lines of descent for two representative melt scenarios. Each result shown here was computed under batch crystallization at $fO_2 = \text{FMQ}$. Data points and shading represent measurements of known igneous Martian materials (Filiberto, 2017). Black tick marks indicate point at which 90% of the melt has crystallized. *Average crust from Taylor and McLennan (2009).

Figure 9. Pie diagrams representing relative proportions by mass of phases near solidus in magmas derived from mixtures of Mars' estimated crust and mantle, crystallizing in equilibrium. The order in which phases appear during crystallization begins at 12 O'clock and moves clockwise. Some phases, which are consumed before reaching bulk solidus, are not shown. Model runs are for crater diameters of 154 km (100% crust), 700 km (~50% crust-mantle), and 1800km (~90% mantle) with pressure equal to that at the base of the final melt sheet, $fO_2 = FMQ$ with H_2O contents varying on y-axis. The red background region indicates conditions conducive to the highest SiO_2 , K_2O and FeO trends at low MgO values. The blue background region indicates conditions conducive to the highest Al_2O_3 and Na_2O and lowest CaO trends at low MgO values. Alkali rich samples containing higher MgO are found in the green background region.