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Exploring fractionation models for Martian magmas

Arya Udry,¹ J. Brian Balta,¹ and Harry Y. McSween Jr.¹

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[1] Martian primary compositions, i.e., magmas that did not experience fractionation and/or contamination after extraction from the mantle, occur as a subset of Martian meteorites and a few lavas analyzed on the planet's surface by rovers. Eruptions of primary magmas are rare on Earth and presumably on Mars. Previous studies of fractional crystallization of Martian primary magmas have been conducted under isobaric conditions, simulating idealized crystallization in magma chambers. Polybaric fractionation, which occurs during magma ascent, has not been investigated in detail for Martian magmas. Using the MELTS algorithm and the pMELTS revision, we present comprehensive isobaric and polybaric thermodynamic calculations of the fractional crystallization of four primary or parental Martian magmas (Humphrey, Fastball, Y-980459 shergottite, and nakhlite parental melts) using various pressure-temperature paths, oxygen fugacities, and water contents to constrain how these magmas might evolve. We then examine whether known Martian alkaline rock compositions could have formed through fractional crystallization of these magmas under the simulated conditions. We find that isobaric and polybaric crystallization paths produce similar residual melt compositions, but given sufficient details, we may be able to distinguish between them. We calculate that Backstay (Gusev Crater) likely formed by fractionation of a primary magma under polybaric conditions, while Jake_M (Gale Crater) may have formed through melting of a metasomatized mantle, crustal assimilation, or fractional crystallization of an unknown primary magma. The best fits for the Backstay composition indicate that consideration of polybaric crystallization paths can help improve the quality of fit when simulating liquid lines of descent.

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1. Introduction

[2] The Martian crust is mainly composed of igneous rocks of mafic and ultramafic compositions [McSween *et al.*, 2009] and sediments derived from these rocks [e.g., Squyres *et al.*, 2004]. Chemical compositions of surface terrains measured by the gamma ray spectrometer (GRS) on Mars Odyssey [e.g., Gasnault *et al.*, 2010], volcanic rocks analyzed by alpha particle X-ray spectrometers (APXS) on rovers, and Martian meteorites analyzed in the laboratory are nearly all basalts or cumulates from basaltic magmas. Two schools of thought exist concerning the origin and evolution of these rocks: (1) they are mostly primary compositions, formed by partial melting of the mantle and largely unaffected by fractional crystallization; or (2) they are mostly evolved compositions derived by fractionation of primary melts. Schmidt and McCoy [2010] modeled the compositions of volcanic rocks

in Gusev Crater analyzed by the Spirit rover as primary magmas, although their partial melting models did not exclude later fractional crystallization. Baratoux *et al.* [2011, 2013] likewise interpreted varying compositions in Martian basaltic units analyzed by GRS as indicating variations in the mantle temperatures and pressures of primary melt formation. Conversely, McSween *et al.* [2006a] and Tuff *et al.* [2013] modeled Gusev rocks as arising from fractionation of a primary magma composition, and Stolper *et al.* [2013] modeled the Jake_M alkaline rock from Gale Crater as forming from the fractionation of basaltic magma. Numerous petrologic studies have demonstrated that fractionation has been the key in creating the compositions of many Martian meteorites, including the cumulate nakhlites, chassignites, and ALH 84001 [e.g., McSween and Treiman, 1998; Mittlefehldt, 1994; Mikouchi *et al.*, 2003; Treiman, 2005; Nekvasil *et al.*, 2007a], and some of the shergottites, such as the olivine-rich lherzolitic shergottites [Goodrich, 2002]. On Earth, primary magmas do not erupt on a global scale and are in fact uncommon, as most magmas undergo fractionation and/or assimilation en route to the surface [e.g., O'Hara, 1965; Stolper and Walker, 1980; Basaltic Volcanism Study Project, 1981]. Most volcanic rocks on the Moon and on asteroid 4 Vesta are also thought to represent fractionated magmas [e.g., Basaltic Volcanism Study Project, 1981; Shearer *et al.*, 2006a, 2006b; McSween *et al.*, 2011], despite differences in gravity, volatile contents, the compositions of mantle sources,

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and the crusts through which they ascended. It seems likely, then, that most Martian magmas would be fractionated, a hypothesis that can be tested by comparing fractional crystallization paths with the compositions of observed Martian igneous rocks.

[3] Prior studies have investigated fractionation of Martian primary magmas under static pressure conditions using experimental techniques and petrologic modeling tools [e.g., *McSween et al.*, 2006a; *Monders et al.*, 2007; *McCubbin et al.*, 2008; *Filiberto et al.*, 2008; *Symes et al.*, 2008; *Liu et al.*, 2013]. While fractional crystallization of magmas under near-isobaric conditions occurs in magma chambers, complete or almost complete crystallization at a single pressure is not geologically common and probably unlikely for lavas that reach the surface. To date, researchers have not explicitly tested the influence of polybaric crystallization paths on Martian magmas. Here we investigate Martian magmatic evolution using thermodynamic modeling of three primary and one parental magma compositions (Humphrey, Fastball, Yamato-980459, and nakhlite parental melts), which span much of the known range of Martian basalt compositions. We model isobaric as well as polybaric fractional crystallization to compare the resulting liquid lines of descent. We also evaluate whether fractionation of these tholeiitic primary magmas can give rise to some observed Martian alkaline rock compositions (Backstay, Jake_M, and nakhlite intercumulus glass). The various fractional crystallization models presented here provide a basis for further experiments to better constrain Martian magmatism.

2. Background and Compositions Used in Calculations

2.1. Previous Numerical Models and Experiments of Martian Magma Fractionation

[4] *McSween et al.* [2006a] performed a series of liquid line of descent calculations using the MELTS algorithm [*Ghiorso and Sack*, 1995], attempting to fit the measured compositions of Gusev alkaline rocks (Backstay, Irvine, and Wishstone) as products of isobaric crystallization of the Adirondack-class Humphrey composition at different depths. They inferred that the alkaline rocks could have formed by crystallization of a Humphrey-like magma at distinct pressures (0.1, 0.3, and 1.0 GPa, respectively), high oxygen fugacities (between FMQ—fayalite-magnetite-quartz—and FMQ-1), and modest water contents (0.5 wt% H₂O). *McCubbin et al.* [2008] performed isobaric fractional crystallization experiments using wet (1.67 wt% H₂O) and nearly dry (0.07 wt% H₂O) Humphrey-like compositions at a static pressure of 0.93 GPa, equivalent to the base of a thick Martian crust. Although they did not produce compositions similar to the measured Gusev alkaline basalts, they confirmed that the compositional evolution of a Humphrey-like parental magma depends strongly on whether the magma was wet or dry. Therefore, as is the case with magmas on Earth, fractionation of a limited set of primary magmas is able to generate substantial compositional diversity.

[5] Fractional crystallization has also been modeled using shergottite compositions. *Symes et al.* [2008] performed MELTS fractional crystallization calculations using the Y-980459 composition and concluded that shergottite compositional diversity is produced by a combination of

both fractional crystallization and compositionally distinct sources. *Liu et al.* [2013] reported pMELTS calculations on the EETA 79001A shergottite composition and suggested that its parental magma underwent polybaric fractionation, with crystallization occurring first beneath the Martian crust and continuing during ascent. In addition, based on petrogenetic studies and MELTS calculations, numerous authors have concluded that nakhlites formed from closed-system fractional crystallization of a single lava flow or shallow magma body [*Mikouchi et al.*, 2003; *Treiman*, 2005; *Stockstill et al.*, 2005; *Day et al.*, 2006; *Imae and Ikeda*, 2008; *Sautter et al.*, 2012; *Udry et al.*, 2012; *McCubbin et al.*, 2013]. Other fractional crystallization calculations using MELTS have been performed using the compositions of Shergotty [*Dann et al.*, 2001], LAR 06319 [*Peslier et al.*, 2010; *Basu Sarbadhikari et al.*, 2011; *Balta et al.*, 2013], and Dhofar 019 [*Taylor et al.*, 2002].

2.2. Alkaline Magma Formation

[6] On Earth, alkaline magmatism can be generated in oceanic hotspots, continental rift settings, flood basalt provinces, and during the late stages of island arc magmatism [e.g., *Basaltic Volcanism Study Project*, 1981]. Terrestrial alkaline rocks can be produced in a variety of ways, including high pressure melting (>1 GPa or 30 km depth, e.g., East African Rift) [*Hirose and Kushiro*, 1993], low degrees of partial melting (e.g., Maymecha River basin, Siberia) [*Arndt et al.*, 1998], partial melting of metasomatic veins (e.g., French Massif Central) [*Pilet et al.*, 2008] or metasomatic lithosphere (e.g., Nunivak Island, Alaska) [*Menzies and Murthy*, 1980], and fractional crystallization of wet, hotspot-derived magma at crustal pressures (e.g., Nandewar Volcano, Australia) [*Nekvasil et al.*, 2000, 2004]. This final process, fractionation of mantle-derived magma in the crust, is common on Earth and should be expected on Mars due to its thick, stagnant crust. The combination of crustal pressures and hydrous magmas produces alkaline magmas during crystallization by delaying plagioclase crystallization in favor of pyroxene and olivine. In addition, *Nekvasil et al.* [2000, 2004, 2007b] and *Whitaker et al.* [2005, 2007] showed that polybaric crystallization paths, which form pyroxene at high pressure and plagioclase at low pressure, can also contribute to alkaline magma formation. It was also shown that the role of CO₂ is critical for the formation of alkaline basalts [e.g., *Hirose*, 1997; *Dasgupta et al.*, 2007].

[7] *Dreibus and Wänke* [1985, 1987] were the first to propose alkali-rich basalts on Mars. Martian alkaline rocks have been analyzed in situ by rovers [*McSween et al.*, 2006a; *McSween et al.*, 2009; *Stolper et al.*, 2013] but have not been distinguished from orbit [*Dunn et al.*, 2007]. GRS (with a footprint of 300 km) measured Si and K but not Na [e.g., *Boynton et al.*, 2007] and likewise cannot clearly distinguish alkaline compositions. Consequently, alkaline rocks may be widespread on the Martian surface and simply not be recognizable by the available measurements. None of the primary magmas studied here are alkaline, raising the question of whether the processes that form alkaline rocks on Earth are analogous on Mars.

2.3. Martian Primary and Parental Magmas

[8] On planetary bodies, a primary bulk composition should display high Mg# (molar Mg/[Mg + Fe] > 70) and

Table 1. Bulk Rock Composition of Martian Basalts Used in This Study

	Humphrey ^a	Fastball ^b	Y98 ^c	Nakhlite Parental Melts (NPM) Stockstill ^d	NPM Sautter ^e	Jake_M ^f	MR Nakhlite ^g
SiO ₂	45.9	45.3	49.66	47.2	49.1	51.8	60.2
TiO ₂	0.55	0.67	0.48	0.88	1.10	0.91	0.53
Al ₂ O ₃	10.7	7.85	6.03	5.90	6.20	16.0	17.7
Fe ₂ O ₃	3.55	9.26	0	0	0	0	0
Cr ₂ O ₃	0.6	0.49	0.71	0	0.04	0	0
FeO	15.6	8.54	15.88	26.9	22.6	11.66	6.82
MnO	0.41	0.47	0.43	0.71	0.55	0.17	0.09
MgO	10.4	12	18.2	4.60	5.30	3.61	0.15
CaO	7.84	5.8	7.24	10.1	12.1	6.76	4.63
Na ₂ O	2.54	2.35	0.80	2.30	1.80	6.39	6.11
K ₂ O	0.1	0.23	0.02	0.39	0.32	2.23	1.68
P ₂ O ₅	0.56	0.79	0.31	0.09	0.36	0.56	1.09
Total	98.8	93.8	99.8	99.1	99.5	100.0	98.9

^aMcSween *et al.* [2008].^bSquyres *et al.* [2007].^cMusselwhite *et al.* [2006].^dStockstill *et al.* [2005].^eSautter *et al.* [2012].^fStolper *et al.* [2013].^gAverage from Day *et al.* [2006] and Udry *et al.* [2012].

MgO content (>11 wt%), have no trace element or isotopic indicators of fractionation or assimilation, and be multiply saturated with the residual phases of the mantle (e.g., olivine and pyroxenes) at a particular combination of pressure and temperature [Basaltic Volcanism Study Project, 1981; Asimow and Longhi, 2004]. The multiple saturation point, taken to approximate the pressure and temperature at which the primary magma formed, can be found by experiments or calculated using an appropriately calibrated model [Balta and McSween, 2013a]. Investigations of Martian meteorites and rocks analyzed by rovers indicate that a few Martian basalts are candidates for primary magmas. For our calculations, we chose three possible Martian primary magmas and one parental magma that cover the presently recognized compositional range (Table 1).

2.3.1. Humphrey

[9] Humphrey is an Adirondack-class basalt from Gusev Crater analyzed by the Spirit rover [McSween *et al.*, 2004, 2006a, 2006b]. The rock is picritic [McSween *et al.*, 2008] as revealed by the Rock Abrasion Tool (RAT)-abraded rock analyzed by APXS and Mössbauer. Based on phase equilibrium experiments, Monders *et al.* [2007] inferred that Humphrey is a primary magma that formed by ~15–20% melting of an undepleted Martian mantle source. These authors measured a multiple saturation point with olivine + orthopyroxene + spinel at 1.0 GPa and 1320°C, corresponding to a depth of ~85 km, which they inferred to be the depth of the mantle source region. Alternatively, Filiberto *et al.* [2008] conducted dry experiments and suggested that Humphrey does not display a primary composition based on the fact that its composition is multiply saturated with the wrong pyroxene (pigeonite, rather than orthopyroxene as found in the Monders *et al.* [2007] experiments).

2.3.2. Fastball

[10] Fastball was analyzed by the Spirit rover at the Home Plate outcrop in the Columbia Hills of Gusev Crater and was interpreted as pyroclastic based on its texture. Its composition is depleted in Al₂O₃, FeO, and CaO compared to Humphrey (Table 1). Fastball was an unbrushed rock, and its measured composition might have greater uncertainties

than others compositions discussed in this paper; however, we adopt the composition as Filiberto *et al.* [2010] argued that Fastball represents a primary magma based on its multiple saturation point with olivine + orthopyroxene occurring at ~1.2 GPa and ~1430°C. Fastball and Humphrey are the only rover-analyzed compositions for which multiple saturation experiments suggest that they could represent primary compositions.

2.3.3. Yamato-980459

[11] The most primitive and magnesian (Mg# = 0.67) of the shergottites is the olivine-phyric shergottite Yamato-980459 (henceforth Y-98). It consists of olivine megacrysts set in a groundmass of Fe-rich olivine and pyroxene, basaltic glass, and skeletal Fe-Ti-Cr oxides [Greshake *et al.*, 2004; Ikeda, 2004; McKay *et al.*, 2004; Musselwhite *et al.*, 2006; Usui *et al.*, 2008]. Musselwhite *et al.* [2006] argued that Y-98 represents a primary composition with an experimentally produced multiple saturation point (olivine + low-Ca pyroxene) at 1.2 ± 0.5 GPa and $1540 \pm 10^\circ\text{C}$. Although a few other shergottites have been proposed as primary magmas (NWA 5789 and NWA 6234 [Gross *et al.*, 2011; Filiberto and Dasgupta, 2011; Gross *et al.*, 2013]), experiments have only been conducted on Y-98. Usui *et al.* [2012] measured low water contents in olivine-hosted melt inclusions in Y-98 and suggested they required a dry parental magma. However, Balta *et al.* [2013] argued that those inclusions could be susceptible to water loss after trapping while the crystals resided in the magmatic system, so in our calculations we also consider the possibility that Y-98 (or a similar magma) was more hydrous than argued by Usui *et al.* [2012]. In addition, Draper [2007] and Balta and McSween [2013b] hypothesized its composition could be consistent with the presence of some magmatic water.

2.3.4. Nakhlite Parental Melts

[12] The nakhlites are olivine-bearing clinopyroxenites thought to have crystallized in a cumulate pile from a single magma [Harvey and McSween, 1992; Mikouchi *et al.*, 2003]. They are mainly composed of augite, olivine, and glassy intercumulus phase [e.g., Treiman, 2005; Day *et al.*, 2006; Udry *et al.*, 2012]. Although the nakhlite parental melt

Table 2. MELTS and pMELTS Thermodynamic Calculations Performed in This Study

Water Contents	Oxygen Fugacities	Humphrey (pMELTS)	Fastball (pMELTS)	Y-98 (pMELTS)	Nakhlite Parental Melt (MELTS and pMELTS)
<i>P-T Path α: High Pressure Fractionation Followed by Subadiabatic Ascent</i>					
Dry (0.0/0.07 wt% H ₂ O)	FMQ-3.5-FMQ-2.5			X	
	FMQ-2.5-FMQ-2-FMQ-1	X	X		
	FMQ-1-FMQ				X
Wet (0.5/1.67 wt% H ₂ O)	FMQ-3.5-FMQ-2.5			X	
	FMQ-2.5-FMQ-2-FMQ-1	X	X		
	FMQ-1 - FMQ				X
<i>P-T Path β: Medium Pressure Fractionation Followed by Subadiabatic Ascent</i>					
Dry (0.0/0.07 wt% H ₂ O)	FMQ-3.5-FMQ-2.5			X	
	FMQ-2.5-FMQ-2-FMQ-1	X	X		
	FMQ-1-FMQ				X
Wet (0.5/1.67 wt% H ₂ O)	FMQ-3.5-FMQ-2.5			X	
	FMQ-2.5-FMQ-2-FMQ-1	X	X		
	FMQ-1-FMQ				X
<i>P-T Path γ: Subadiabatic Ascent Followed by Low Pressure Fractionation</i>					
Dry (0.0/0.07 wt% H ₂ O)	FMQ-3.5-FMQ-2.5			X	
	FMQ-2.5-FMQ-2-FMQ-1	X	X		
	FMQ-1-FMQ				X
Wet (0.5/1.67 wt% H ₂ O)	FMQ-3.5-FMQ-2.5			X	
	FMQ-2.5-FMQ-2-FMQ-1	X	X		
	FMQ-1-FMQ				X
<i>P-T Path σ: Isobaric Fractionation</i>					
Dry (0.0/0.07 wt% H ₂ O)	FMQ-3.5-FMQ-2.5			X	
	FMQ-2.5-FMQ-2-FMQ-1	X	X		
	FMQ-1-FMQ				X
Wet (0.5/1.67 wt% H ₂ O)	FMQ-3.5-FMQ-2.5				
	FMQ-2.5-FMQ-2-FMQ-1	X	X		
	FMQ-1-FMQ				

is not necessarily a primary magma [e.g., *Sautter et al.*, 2012; *McCubbin et al.*, 2013], it was included in this study in order to expand the range of available Martian compositions. Augite-liquid partition coefficients and augite- and olivine-hosted melt inclusions have been used to constrain the nakhlite parental melt composition [e.g., *Harvey and McSween*, 1992; *Treiman and Goodrich*, 2001; *Varela et al.*, 2001; *Stockstill et al.*, 2005; *Sautter et al.*, 2012]. *Stockstill et al.* [2005] argued that the nakhlite parental melt had a low water content, although recent measurements have identified some hydrous apatites and amphiboles that may contradict this conclusion [*McCubbin et al.*, 2009; *Hallis et al.*, 2012]. For the nakhlite parental melt compositions, we used the estimates of *Stockstill et al.* [2005] and *Sautter et al.* [2012], which

analyzed melt inclusions in Nakhla augites after fast-heating rehomogenization. These compositions are broadly similar to other proposed nakhlite parental melts [e.g., *Harvey and McSween*, 1992; *Treiman*, 1993; *Treiman and Goodrich*, 2001] but differ slightly from each other: The composition of Sautter (NPM05) is moderately depleted in CaO, MgO, P₂O₅, and alkalis and enriched in FeO relative to that of Stockstill (NA03) (Table 1). The NK01 parental melt composition calculated by *Treiman and Goodrich* [2001] was not used in this study because *Stockstill et al.* [2005] showed that their NA03 models better matched the major element compositions measured in nakhlites, despite the fact that NK01 and NA03 major element compositions are very similar.

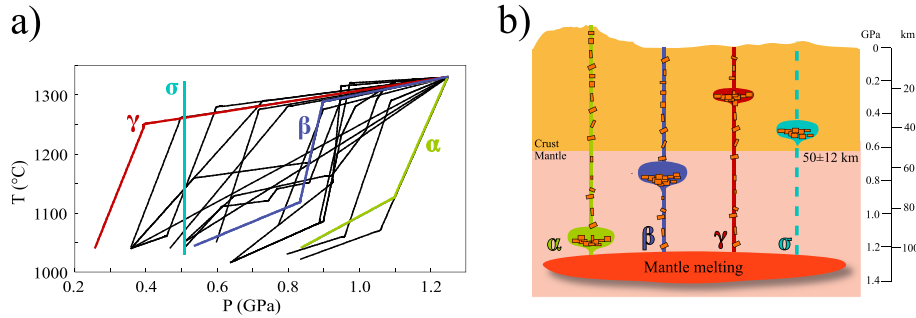


Figure 1. (a) Various P-T paths used in this study with highlighted endmembers P-T paths. (b) Schematic representing fractional crystallization of a primary tholeiitic magma in the Martian interior following different endmembers P-T paths: Path α (green): fractionation at high pressure followed by subadiabatic ascent. Path β (blue): fractionation at medium pressure followed by subadiabatic ascent. Path γ (red): subadiabatic ascent of primary magma followed by stagnation at shallow level. Path σ (turquoise): isobaric fractionation at static pressure (~ 0.5 GPa). Crustal thickness from *Wieczorek and Zuber* [2004].

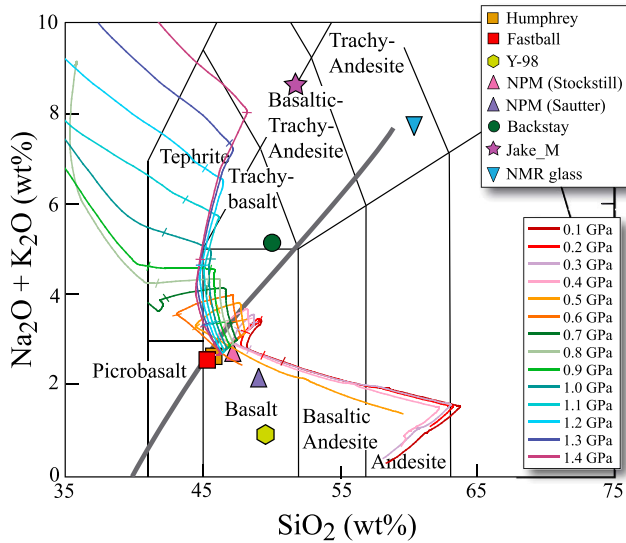


Figure 2. Total alkali-silica diagram for classifying volcanic rocks [Le Bas *et al.*, 1986], showing the compositions of Humphrey, Fastball, Y-98, nakhlite parental melts (NPM), Backstay, Jake_M, and nakhlite Miller Range intercumulus glass average compositions (references as in Table 1). Gray line is the boundary between alkaline and subalkaline compositions [Irvine and Baragar, 1971]. Different colored lines represent calculated liquid lines of descent for fractional crystallization of a Humphrey-like magma, under dry, isobaric conditions from 0.1 to 1.4 GPa at FMQ-1. Tick marks delineate 25% fractionation increments.

2.4. Alkaline Martian Magmas

[13] Our fractional crystallization modeling produced a wide variety of plausible Martian igneous compositions. We selected several Martian alkaline rock compositions measured by rovers and in meteorites (Table 1) and attempted to use our database to better understand magma formation conditions.

2.4.1. Backstay

[14] Backstay was one of the first alkaline basaltic rocks encountered by Spirit in the Columbia Hills in Gusev Crater [McSween *et al.*, 2006a]. Backstay is a trachybasalt (also called hawaiiite) [McSween *et al.*, 2006a] and is the least altered rock found on the Columbia Hills [Ming *et al.*, 2006]. It is silica-saturated and hypersthene-normative, as are various terrestrial continental and oceanic island alkaline basalts (e.g., Nandewar Volcano, Ascension Island) [Nekvasil *et al.*, 2000, 2004; Harris, 1983]. McSween *et al.* [2006a] argued that in these alkaline rocks, the plagioclase is richer in sodium, the olivine is richer in iron, and the pyroxene: olivine ratio is higher than in Adirondack-class rocks (e.g., Humphrey).

2.4.2. Jake_M

[15] Near the beginning of its traverse in Gale Crater, the Curiosity rover analyzed a volcanic rock named Jake_M [Grotzinger *et al.*, 2013]. Based on the norm calculated from APXS analyses, it contains >15% nepheline, as well as albite and orthoclase, and has a composition similar to a terrestrial mugearite (also called trachy-andesite) [Stolper *et al.*, 2013]. Using isobaric MELTS calculations and a terrestrial starting composition, Stolper *et al.* [2013] argued that Jake_M formed

by suppression of plagioclase during fractionation of a parental magma, which they estimated could occur at ~0.4 GPa in the presence of water (~1 wt%).

2.4.3. Nakhlite Intercumulus Glass

[16] Based on rare earth element abundance patterns, nakhlites are interpreted to have fractionally crystallized in a closed system [e.g., Wadhwa and Crozaz, 1995; Day *et al.*, 2006; Udry *et al.*, 2012] in which augite crystallized prior to olivine. The intercumulus glass in Miller Range (MR) nakhlites displays alkaline compositions, plotting in or around the trachy-andesite and trachyte fields in the TAS diagram [Day *et al.*, 2006; Udry *et al.*, 2012].

3. Modeling Techniques

[17] In total, we conducted more than 600 polybaric and isobaric fractional crystallization calculations using different P-T paths, variable oxygen fugacities (between FMQ-3.5 and FMQ), and water contents that ranged from dry to ~1.67 wt% H₂O using the AlphaMELTS front end of the MELTS algorithm [Smith and Asimow, 2005]. The calculations are summarized in Table 2. AlphaMELTS runs the routines of MELTS, pMELTS, and pHMELTS [Ghiorso and Sack, 1995; Ghiorso *et al.*, 2001; Asimow *et al.*, 2004]. MELTS is a thermodynamic-based algorithm calibrated using petrologic experiments on both terrestrial and planetary compositions [Balta and McSween, 2013a] and is commonly used in calculating mineral assemblages along crystallization paths. pMELTS is an updated calibration to the initial version which allows for application of the algorithm at elevated pressures up to 3 GPa. Balta and McSween [2013a] argued that calculations using the MELTS algorithm can be expected to reproduce Martian compositions close to the liquidus to within uncertainties better than 1 wt% for most major oxides if the conditions of crystallization are fully explored. In this study, we used both MELTS and pMELTS, depending on the conditions. pMELTS has been found to be more accurate in determining pyroxene and olivine stabilities [Balta and McSween, 2013a]; consequently, the pMELTS calibration was principally used for determining the pressure and temperature of multiple saturation points involving these minerals. However, the pMELTS calibration poorly simulates the composition of phases that crystallize outside its calibrated range and thus calculations using the MELTS calibration were required at low pressures. It was shown that the effect of water modeled by pMELTS yields similar results to experiments, whereas MELTS does not reproduce the effect of water on olivine liquidus temperatures [Medard and Grove, 2008]. Spinel stability is also overestimated in both calibrations [Balta and McSween, 2013a], so we avoid drawing conclusions based on its crystallization. Apart from water, other volatiles such as F, Cl, and SO₃ have been hypothesized as contributors to Martian magmas, particularly Cl in nakhlites [Filiberto and Treiman, 2009; McCubbin *et al.*, 2013] and CO₂ in alkaline magmas [e.g., Hirose, 1997; Dasgupta *et al.*, 2007], but the software is not well constrained for these components, and thus, we are unable to consider them explicitly. Instead, we focus on whether crystallization involving the available components can reproduce the trends discussed.

[18] We calculated the results of magmatic crystallization along a large series of P-T paths (Figure 1). These P-T paths

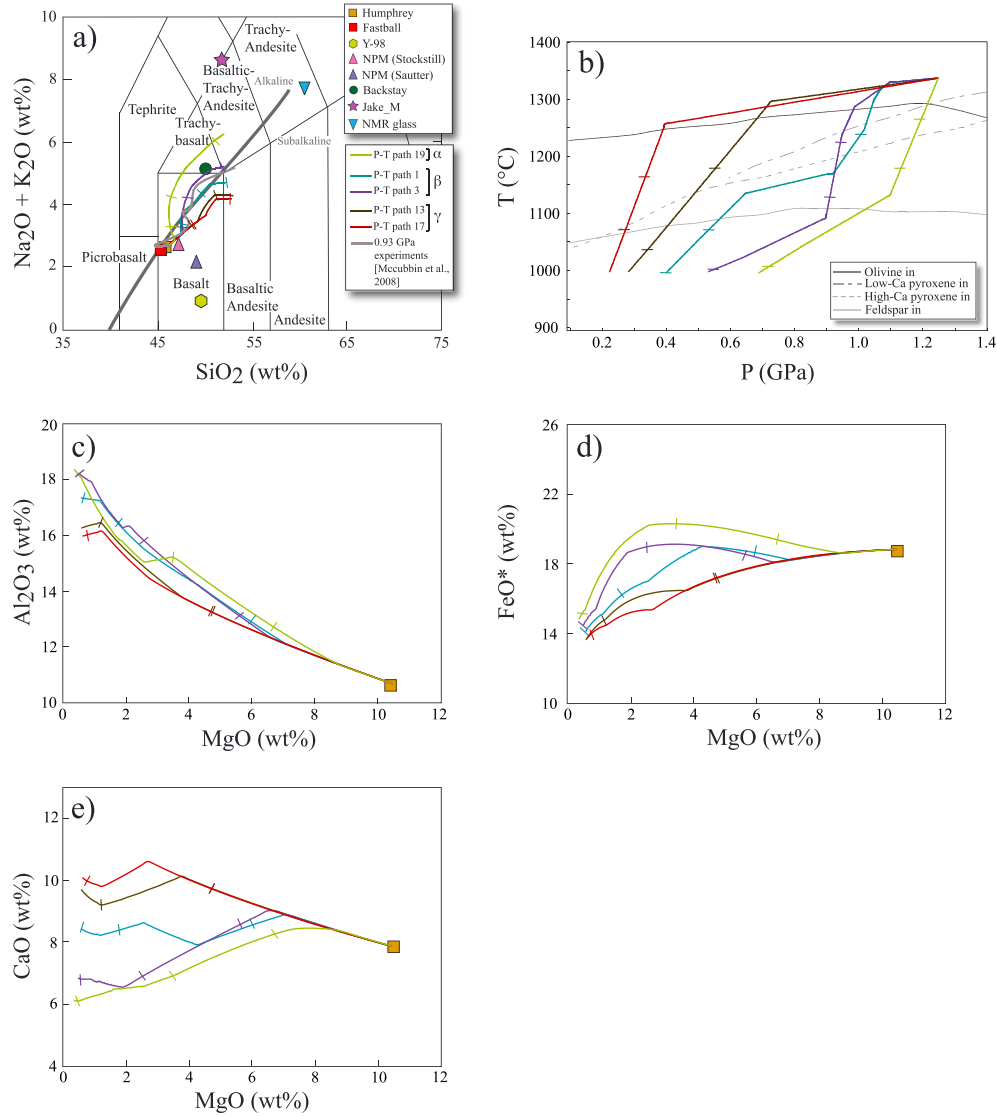


Figure 3. (a) Total alkali-silica diagram showing liquid lines of descent calculated with pMELTS for fractional crystallization of the Humphrey composition with 1.67 wt% H₂O at FMQ-2 and P-T paths. The liquid line of descent under wet conditions from *McCubbin et al.* [2008] is indicated in grey. (b) P-T paths used to calculate liquid lines of descent in Figures 3a and 3c–3e. Olivine, low-Ca pyroxene, high-Ca pyroxene, and feldspar liquid lines are shown as black and gray solid and dashed lines, respectively. Plots of Al₂O₃, FeO*, and CaO versus MgO for liquid lines of descent in Figures 3c–3e, respectively. Tick marks delineate 20% fractionation increments.

can be generally described by four endmembers: (1) high-pressure fractionation followed by subadiabatic ascent (requiring minor heat loss) and decompression (Path α), (2) medium-pressure fractionation followed by subadiabatic ascent (Path β), (3) subadiabatic ascent followed by low-pressure fractionation (Path γ), and (4) isobaric fractionation (Path σ), calculated for comparison with polybaric paths. Path σ in Figure 1 shows simple fractionation at static pressure within a magma chamber. The three polybaric P-T paths α, β, and γ do not involve true adiabatic ascent because that would cause remelting of previously formed phases, effectively resetting the calculation until it again becomes subadiabatic [Liu et al., 2013]. We began calculations ~10°C above the liquidus temperatures, which depend on the starting compositions and water contents. For isobaric

calculations, fractional crystallization was modeled in 5°C steps, whereas for polybaric calculations, the temperature steps varied from ~1°C to 10°C and pressure steps varied from 5 to 200 bars. The calculations were halted when they became unstable, stopping the calculated crystallization sequence, or at ~900°C, as lower temperatures are outside of the MELTS-calibrated range.

[19] We also investigated the effect of water on fractional crystallization. Previously, it has been demonstrated that some Martian magmas were wet based on several lines of evidence, including (1) hydrated minerals in trapped melt inclusions (0.2 wt% H₂O in the original magma) [Treiman, 1985], (2) soluble light lithophile element zoning patterns in pyroxenes (1.8 wt% H₂O in parent magma) [Lentz et al., 2001; McSween et al., 2001], (3) pyroxene crystallization

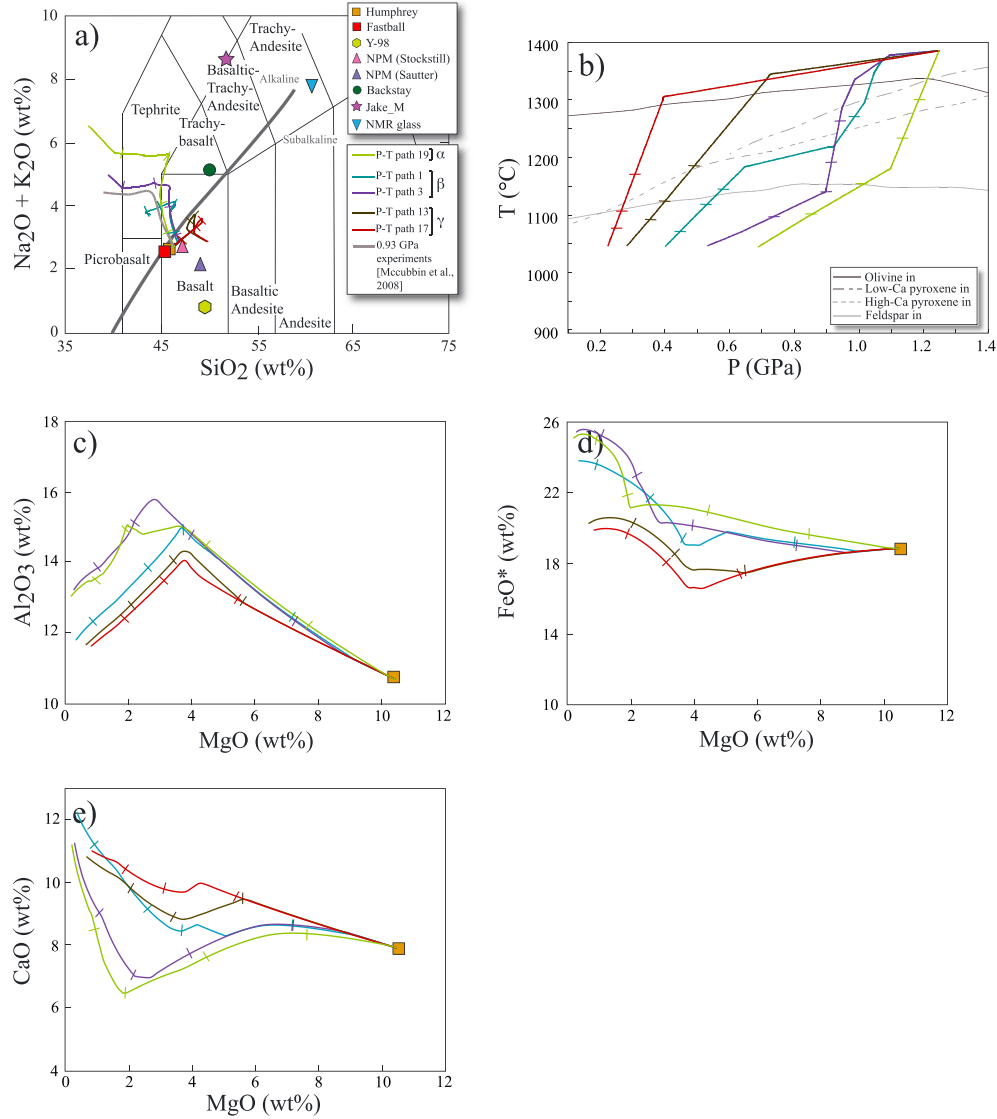


Figure 4. (a) Total alkali-silica diagram showing liquid lines of descent calculated with pMELTS for the fractional crystallization of the Humphrey composition with 0.07 wt% H₂O at FMQ-2 and P-T paths. The liquid line of descent under dry conditions from McCubbin *et al.* [2008] is indicated in grey. (b) P-T paths used to calculate liquid lines of descent in Figures 4a and 4c–4e. Olivine, low-Ca pyroxene, high-Ca pyroxene, and feldspar liquidus are shown as black and gray solid and dashed lines, respectively. Plots of Al₂O₃, FeO*, and CaO versus MgO for liquid lines of descent in Figures 4c–4e, respectively. Tick marks delineate 20% fractionation increments.

systematics (1.8 wt% H₂O in the parent magma) [Dann *et al.*, 2001], (4) H and O isotopic compositions (75–116 ppm H₂O in the parent magma) [Usui *et al.*, 2012], and (5) water analyses in apatite (at least 0.07–0.29 wt% H₂O in the parent magma) [McCubbin *et al.*, 2012] and in amphiboles (0.15–0.25 wt% H₂O in the parental magma) [Watson *et al.*, 1994; McCubbin *et al.*, 2010]. We selected 0.5 wt% H₂O as a reasonable approximation for wet primary magmas [e.g., Watson *et al.*, 1994; McSween *et al.*, 2001; Usui *et al.*, 2012; McCubbin *et al.*, 2012] and also calculated crystallization of the Humphrey composition with 1.67 wt% H₂O in order to compare with the experiments of McCubbin *et al.* [2008].

[20] To examine the influence of oxygen fugacity on the fractionation of Martian primary magmas, we varied oxygen

fugacities for each composition within the ranges estimated for those samples (Table 2). The oxygen fugacity of Humphrey was estimated between FMQ-3.1 and FMQ-1.7 [Schmidt *et al.*, 2011], whereas no clear oxygen fugacity has been determined for Fastball. Martian meteorites show oxygen fugacities between FMQ-3.5 (equal to the iron-wüstite buffer) and FMQ-0.5 [Richter *et al.*, 2008]. The depleted Martian mantle is thought to be reduced (~FMQ-3.5) [Herd *et al.*, 2002], and the source of oxidation in some meteorites is debated. The oxidized character may be due to metasomatism, ferric iron-rich material, or the presence of water, and its source may be located within the crust or within a heterogeneous mantle [Herd *et al.*, 2002; Herd, 2003; Wadhwa, 2008]. Thus, we used FMQ-2.5 and

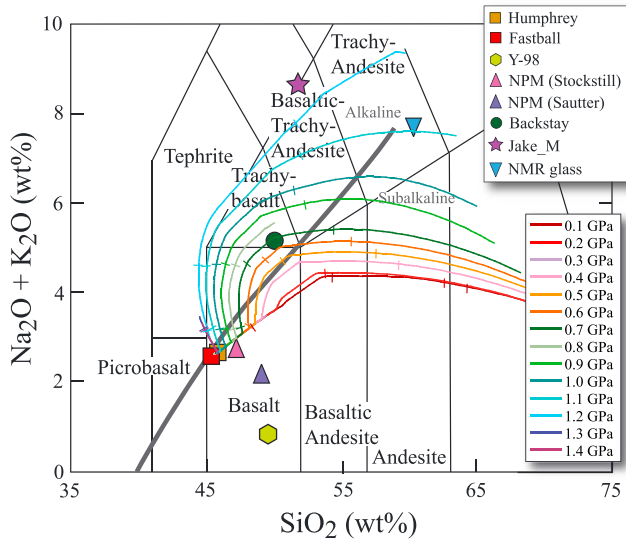


Figure 5. Total alkali-silica diagram showing liquid lines of descent of melts formed by fractional crystallization of Fastball composition, calculated with pMELTS under wet (0.5 wt% H₂O), isobaric conditions from 0.1 to 1.4 GPa at FMQ-1. Tick marks delineate 25% fractionation increments.

FMQ-1 in Humphrey and Fastball calculations, which reasonably encompass the range of Martian meteorite oxygen fugacities and those calculated by *Schmidt et al.* [2011], as well as FMQ-2, in order to compare our results to the *McCubbin et al.* [2008] experiments. Oxygen fugacities applied to Y-98 and nakhlite parental melt calculations are the same as those assessed for their magma sources: FMQ-3.5 and FMQ-2.5 for Y-98 [Shearer et al., 2006a] and FMQ and FMQ-1 for nakhlites [Wadhwa et al., 2004; Righter et al., 2008; McCubbin et al., 2013].

[21] To explore how known Martian alkaline compositions (Backstay, Jake_M, and nakhlite intercumulus glass) may have formed on Mars, we used major element compositions to constrain the plausible conditions of formation (e.g., isobaric and polybaric P-T paths, water contents, and oxygen fugacities) from the investigated starting compositions. To obtain major element composition best fits, we applied a least squares fit calculated from deviations between the calculated and measured compositions. We cross-checked the least squares method manually with the individual important oxide values to estimate the accuracy of the fits.

4. Isobaric and Polybaric Fractional Crystallization of Martian Magmas

4.1. Humphrey

[22] Isobaric fractional crystallization calculations (starting at 1.25 GPa and 1400°C) for a dry magma showed that unsurprisingly, the liquid lines of descent vary due to changes in mineral stability associated with the pressures and the volatile contents. Under dry conditions, at relatively low pressures (<0.6 GPa), the liquid evolves toward the subalkaline field in the total alkalis versus silica (TAS) diagram (Figure 2) due to plagioclase fractionation with a decrease in FeO* due to olivine crystallization, whereas at higher

pressure (>0.7 GPa), the liquid decreases in SiO₂ (extending to the tephrite field), increases in FeO*, and moves toward the alkaline field due to increasing pyroxene stability at higher pressures. Under wet conditions, the residual liquid shows increasing SiO₂ and decreasing FeO* at every pressure and forms alkaline magma at pressures >0.8 GPa under isobaric conditions. The evolution of these liquid lines of descent is similar to those of terrestrial silica-saturated alkaline rocks [Nekvasil et al., 2004].

[23] Polybaric P-T paths for Humphrey began at 1.25 GPa and 1350–1390°C (Figure 3b). Our calculations show that the liquid evolution paths are not significantly impacted by oxygen fugacity. However, the addition of water stabilizes olivine relative to pyroxene and plagioclase, such that residual melts increase in SiO₂ and decrease in FeO* under wet conditions (0.5% H₂O). Humphrey-like magma that ponds at shallow depth (path γ) remains subalkaline, whereas alkaline magma forms during fractionation at depth (>0.8 GPa: path α). Alkaline magma formation is favored when crystallization takes place at elevated pressures with water present as those conditions reduce the crystallization of plagioclase, causing retention of alkali elements (such as Na) in the magma. Under anhydrous conditions, liquids decrease in SiO₂ but can still form alkaline compositions if the parental magma is fractionated at high or medium pressure (>0.8 GPa, corresponding to paths α and β). Silica enrichment and subalkaline compositions are found for magma that undergoes lower pressure, subadiabatic ascent (path γ).

[24] We also calculated conditions to match the experiments of *McCubbin et al.* [2008] (0.07 and 1.67 wt% H₂O and f_{O_2} = FMQ-2) and to compare isobaric and polybaric fractionation and the effects of water. Polybaric calculations and isobaric experiments [McCubbin et al., 2008] reveal that residual melts from fractionation of a wet Humphrey magma (1.67 wt% H₂O: Figures 3, Figure S1 in the supporting information) increase in SiO₂ and decrease in FeO* (α , β , and γ), whereas relatively dry residual magma (0.07 wt% H₂O, Figure 4, Figure S1) broadly decreases in SiO₂ and increases in FeO*. One exception occurs when dry magma undergoes subadiabatic ascent (path γ), which first increases in SiO₂ and decreases in FeO* but then increases in FeO* during late-stage crystallization. Both dry and wet magmas show decreases in Al₂O₃ due to plagioclase crystallization after 40% solidification (Figures 3c and 4c) and decreases in CaO after augite and plagioclase crystallization begins (20% fractionation, Figures 3e and 4e; orders of mineral appearance for Humphrey and other compositions are shown in the supporting information).

4.2. Fastball

[25] pMELTS crystallization models started at 1.25 GPa and 1350–1390°C. As with Humphrey, the oxygen fugacities did not significantly influence the liquid paths. Isobaric calculations performed using a Fastball composition result in liquid lines of descent similar to Humphrey. Figure 5 shows liquid lines of descent for FMQ-1 with 0.5 wt% H₂O for isobaric fractionation: As with Humphrey, at high pressure (>0.9 GPa: path α), the melt evolves toward an alkaline composition with decreasing SiO₂ and increasing FeO*, whereas low-pressure isobaric crystallization results in subalkaline magmas, increasing SiO₂, and decreasing FeO*.

[26] Polybaric calculations for 0.5 wt% H₂O reveal that if the magma is held at depth followed by subadiabatic ascent

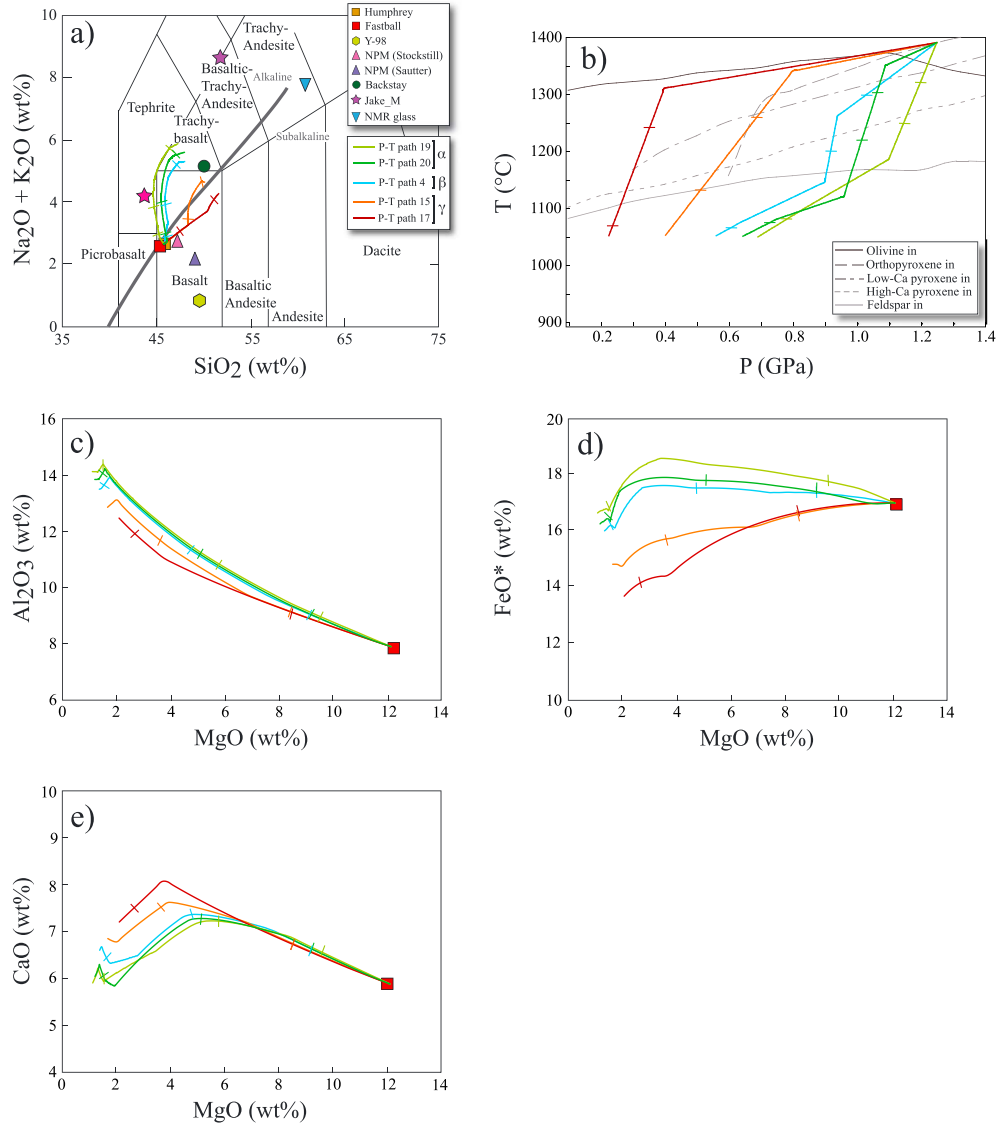


Figure 6. (a) Total alkali-silica diagram showing liquid lines of descent calculated with pMELTS for the fractional crystallization of the Fastball composition with 0.5 wt% H₂O at FMQ-1 and P-T paths. (b) P-T paths used to calculate liquid lines of descent in Figures 6a and 6c–6e. Olivine, orthopyroxene, low-Ca pyroxene, high-Ca pyroxene, and feldspar liquids are shown as black and gray solid and dashed lines, respectively. Plots of Al₂O₃, FeO*, and CaO versus MgO for liquid lines of descent in Figures 6c–6e, respectively. Tick marks delineate 20% fractionation increments.

(≥ 0.8 GPa; paths α and β), the residual melt has an alkaline composition regardless of oxygen fugacity. Conversely, the residual melt compositions from magma that underwent lower-pressure, subadiabatic ascent remain subalkaline (Figure 6, path γ). If the primary magma is dry, the liquid paths are similar to those of Humphrey and decrease in SiO₂ and increase in FeO* when the magma is held at high or medium pressures (≥ 0.8 GPa; paths α and β) and increase in SiO₂ and decrease in FeO* when it is held at low pressures (path γ). Decreasing Al₂O₃ is again observed when plagioclase crystallizes (after 40% fractionation) and decreasing CaO when augite and plagioclase crystallize. Calculations of Fastball crystallization show that the residual melts are similar to those produced from Humphrey magma under similar conditions, which is predictable, as their bulk

compositions are very similar and they may be derived from the same mantle source, consistent with the occurrence of both rocks in Gusev Crater.

4.3. Y-98 Shergottite

[27] Calculations for the Y-98 composition start at 1.25 GPa and 1480°C. As with the previous calculations, varying oxygen fugacities did not significantly change the liquid evolution paths. Isobaric crystallization calculations performed under both dry and wet (0.5 wt% H₂O) conditions show that the liquid lines of descent remain mostly within the subalkaline field and show increases in FeO*. Only under very high-pressure conditions (1.3 and 1.4 GPa) do liquids reach into the alkaline field (not shown). The liquid shows decreasing SiO₂ at high pressures (> 0.7 GPa) due to increasing

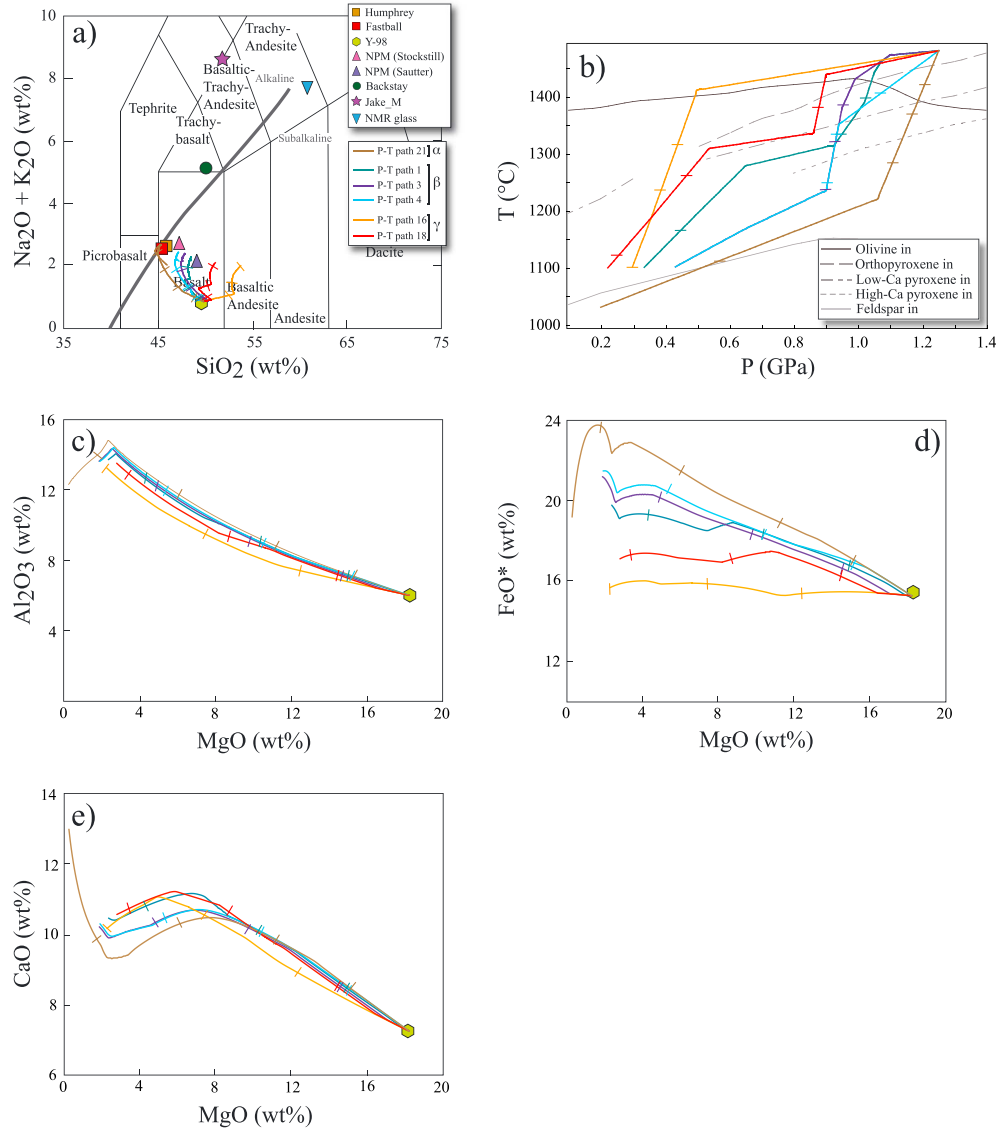


Figure 7. (a) Total alkali-silica diagram showing liquid lines of descent of melts formed from fractional crystallization of the Y-98 shergottite composition, calculated with pMELTS under dry, polybaric conditions at FMQ-2.5. (b) P-T paths used to calculate liquid lines of descent in Figures 7a and 7c–7e. Olivine, orthopyroxene, low-Ca pyroxene, high-Ca pyroxene, and feldspar liquid lines are shown as black and gray solid and dashed lines, respectively. Plots of Al₂O₃, FeO*, and CaO versus MgO for liquid lines of descent in Figures 7c–7e, respectively. Tick marks delineate 20% fractionation increments.

pyroxene stability with higher pressure and increasing SiO₂ at lower pressures (<0.7 GPa).

[28] For the polybaric paths (α, β, and γ) in dry or wet systems at FMQ-3.5 and FMQ-2.5, the liquid lines of descent also remain subalkaline (Figure 7). The fact that mostly subalkaline magma is produced is due to the fact that Y-98 bulk composition is depleted in alkali elements relative to the other compositions studied. However, overall decreases in SiO₂ are observed for P-T paths α and β, whereas those representing path γ increase in SiO₂. Again, both Al₂O₃ and CaO decrease when plagioclase and augite begin to crystallize.

4.4. Nakhilite Parental Melt

[29] Both *Stockstill et al.* [2005] and *Sautter et al.* [2012] used MELTS (at FMQ and FMQ-1) to assess crystallization

of the nakhilite parental magmas believed to have occurred at a shallow level (low pressure) [Day *et al.*, 2006]. As the MELTS routine is calibrated for low-pressure processes and to compare results from both routines, we used MELTS in addition to pMELTS for nakhilite parental melt calculations. Starting conditions were 1.25 GPa and 1330–1380°C. We performed calculations for both nakhilite parental melt compositions, Stockstill (NA03) and Sautter (NPM05), under dry conditions. The liquid lines of descent evolve differently for the two parental melts. Residual melts from NPM05 remain within the subalkaline field at all pressures (not shown), whereas residual melt from NA03 extends into the trachy-andesite field on the TAS diagram (Figure 8). This difference is likely due to the fact that NA03 is enriched in alkalis compared to NPM05. However, both compositions

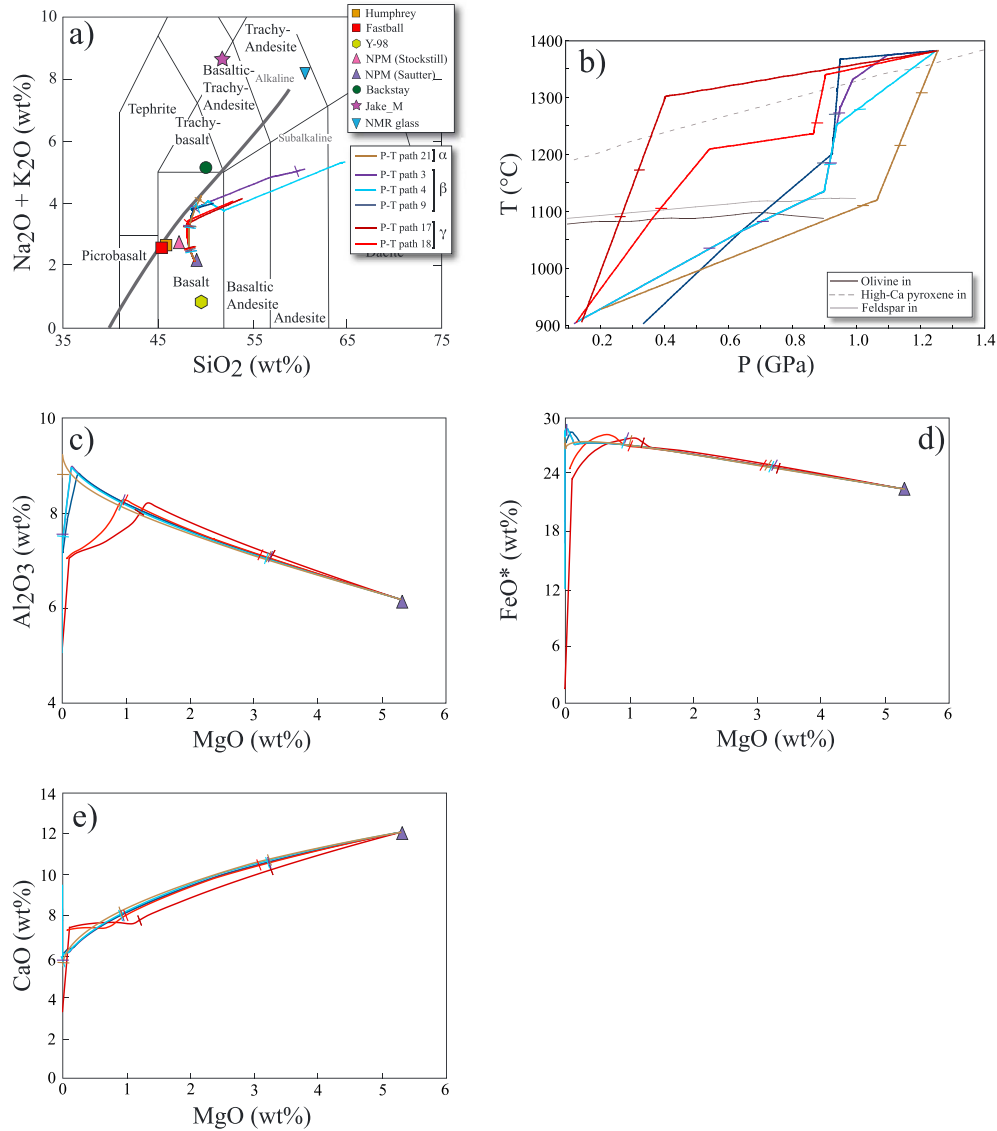


Figure 8. (a) Total alkali-silica diagram showing liquid lines of descent of melts formed by fractional crystallization of the nakhlite parental melt composition from *Sautter et al.* [2012], calculated with MELTS under dry, polybaric conditions at FMQ-1. (b) P-T paths used to calculate liquid lines of descent in Figures 8a and 8c–8e. Olivine, high-Ca pyroxene, and feldspar liquids are shown as black and gray solid and dashed lines, respectively. Plots of Al_2O_3 , FeO^* , and CaO versus MgO for liquid lines of descent in Figures 8c–8e, respectively. Tick marks delineate 20% fractionation increments.

show initial increases in SiO_2 and FeO^* , followed by decreases in FeO^* , due to olivine fractionation, at high and low pressures.

[30] For both NA03 and NPM05 compositions, pMELTS polybaric calculations at FMQ and FMQ-1 for the dry and wet (0.5 wt% H_2O) systems remain in the subalkaline field for all P-T paths (α , β , and γ), although wet melts more closely approach the alkalic field than dry melts. MELTS calibration calculations for NPM05 under dry and wet conditions also remain subalkaline (Figure 8). Finally, MELTS calculations using NA03 (for a dry magma with FMQ-1) evolve into the alkaline field and toward trachyte compositions for all P-T paths, similar to isobaric calculations. FeO^* variation in the magma is due to crystallization of augite and olivine. Feldspar crystallization is responsible

for decreasing Al_2O_3 (which begins after 30% fractionation). The only pyroxene to crystallize is augite, so the residual liquid shows continuously decreasing CaO .

4.5. Alkaline Magma Generation

4.5.1. Backstay

[31] Based on our calculations, we conclude that despite some differences, Backstay could have formed from a primary magma similar to Humphrey or Fastball if the fractionation of the primary magma occurred under appropriate conditions.

[32] Figure 9 shows liquid lines of descent for paths β , γ , and σ , all of which lead to major elemental compositions close to Backstay. The P-T path which gives the best fit for Backstay from an Adirondack basalt parent involves medium-pressure fractionation followed by subadiabatic ascent

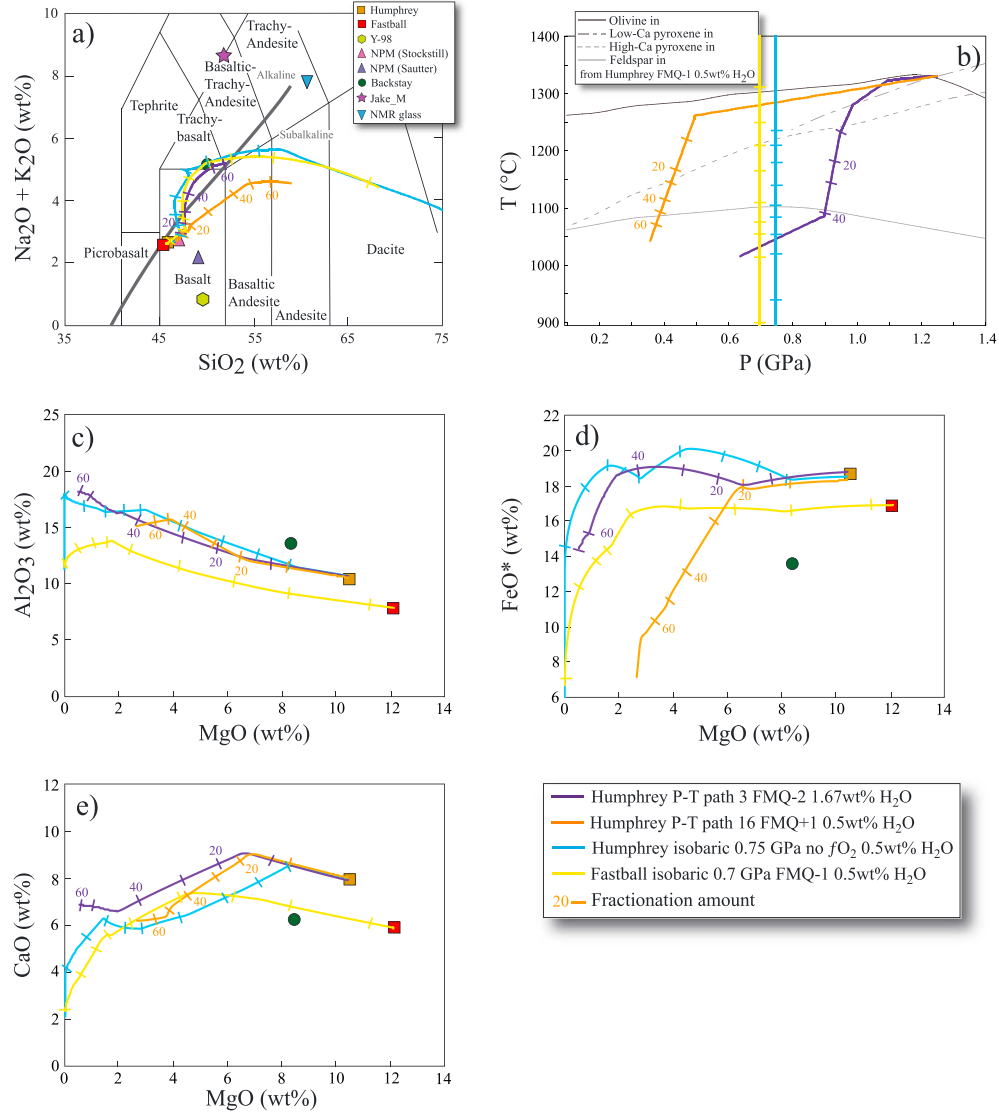


Figure 9. (a) Total alkali-silica diagram showing liquid lines of descent of melts formed by fractional crystallization of Humphrey and Fastball compositions under conditions selected because the melts best matched the Backstay major element composition. (b) P-T paths used to calculate liquid lines of descent in Figures 9a and 9c–9e. Plots of Al₂O₃ in Figure 9c, FeO* in Figure 9d, and CaO in Figure 9e versus MgO for the same liquid lines of descent in as in Figure 9a. The tick marks and numbers on the liquid lines of descent correspond to the amount of fractionation during the ascent of the primary magma (from 10% until 60% fractionation with 10% increments).

(path β). Based on our least squared comparison, using a polybaric path improves the quality of the fit compare to an isobaric path. Calculations show that water (~ 0.5 wt% H₂O) must have been present in the initial magma to produce this composition, and it requires 10–30% fractionation of olivine and pyroxene. Although f_{O_2} only slightly impacts the final composition, the fit is slightly better at FMQ-1.

4.5.2. Jake_M

[33] We performed best fit calculations on Jake_M; however, we considered a wider range of conditions than *Stolper et al.* [2013] (isobaric and polybaric conditions, f_{O_2} values, water contents, and Martian starting primary compositions) for our calculations and used pMELTS. It has been shown that MELTS underestimates the pressure of multiple saturation for Martian liquids while pMELTS more

accurately reproduces them [Balta and McSween, 2013a]. Using their correction, isobaric MELTS calculations between 1 bar and 0.6 GPa conducted by *Stolper et al.* [2013] would correspond roughly from 1 bar to 2.4 GPa [Balta and McSween, 2013a]. Our pMELTS calculations show that the Jake_M composition can be obtained from crystallization of a Humphrey starting composition with 0.5 wt% H₂O and an oxygen fugacity of FMQ-1 if the fractionation occurs at high pressures (1.0–1.25 GPa) followed by subadiabatic ascent (Figure 10b, path α). The calculated residual liquid composition has a very low MgO content compared to the actual Jake_M composition (0.3 versus 3.6 wt%: Figure 10). This low MgO content is a consequence of the best fit composition occurring after 90% fractionation of olivine, garnet, feldspar, and pyroxene, whereas *Stolper et al.* [2013] argued that the

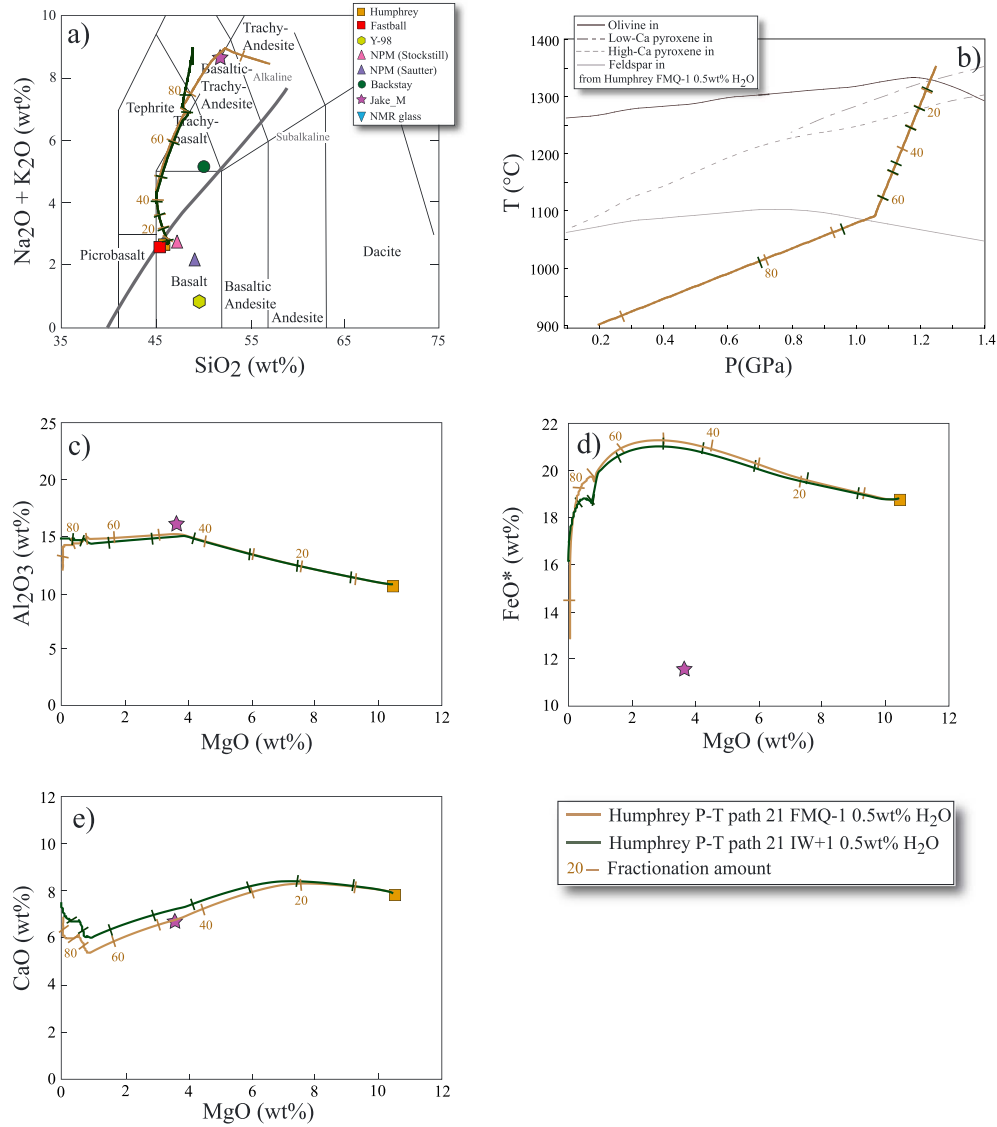


Figure 10. (a) Total alkali-silica diagram showing liquid lines of descent of melts formed by fractional crystallization of Humphrey composition under conditions selected because the melts best matched the Jake_M major element composition. (b) P-T paths used to calculate liquid lines of descent in Figures 10a and 10c–10e. Plots of Al_2O_3 in Figure 10c, FeO^* in Figure 10d, and CaO in Figure 10e versus MgO for the same liquid lines of descent as in Figure 10a. The tick marks and numbers on the liquid lines of descent correspond to the amount of fractionation during the ascent of the primary magma (from 10% until 90% fractionation with 10% increments).

rock formed by 57% fractionation of olivine and pyroxene. The percentage of fractionation calculated in our polybaric model seems too high to be realistic. Thus, we cannot conclude that Jake_M formed from a primary Humphrey-like magma but instead requires an unknown primary magma produced by melting of an alkali rich, possibly metasomatized mantle source or by crustal assimilation.

4.5.3. Nakhlite Intercumulus Glass

[34] We obtained residual liquids similar in composition to the Miller Range intercumulus glass using MELTS fractional crystallization calculations from the NA03 parental melt composition [Stockstill *et al.*, 2005]. According to our models, the best fit crystallization path occurs when the initial NA03 magma follows polybaric path β while dry and close to

FMQ-1 (Figure 11), consistent with previous nakhlite studies [Wadhwa *et al.*, 2004; Richter *et al.*, 2008]. The requirement that the magma is dry is consistent with the melt inclusion measurements of Stockstill *et al.* [2005] (but contrary to hydrous apatite measurements of Hallis *et al.* [2012]). Fractionation of approximately 70% augite and 10% olivine is required to fit the groundmass composition, similar to the abundances observed in the Miller Range nakhrites [Udry *et al.*, 2012] (Figure 11). However, despite these calculations, nakhlite formation by polybaric fractionation appears impossible according to the petrological observations of Day *et al.* [2006], who argued that nakhrites formed in two steps: (1) isobaric crystallization of olivine and pyroxene in a magma chamber, and (2) eruption at the Martian surface with

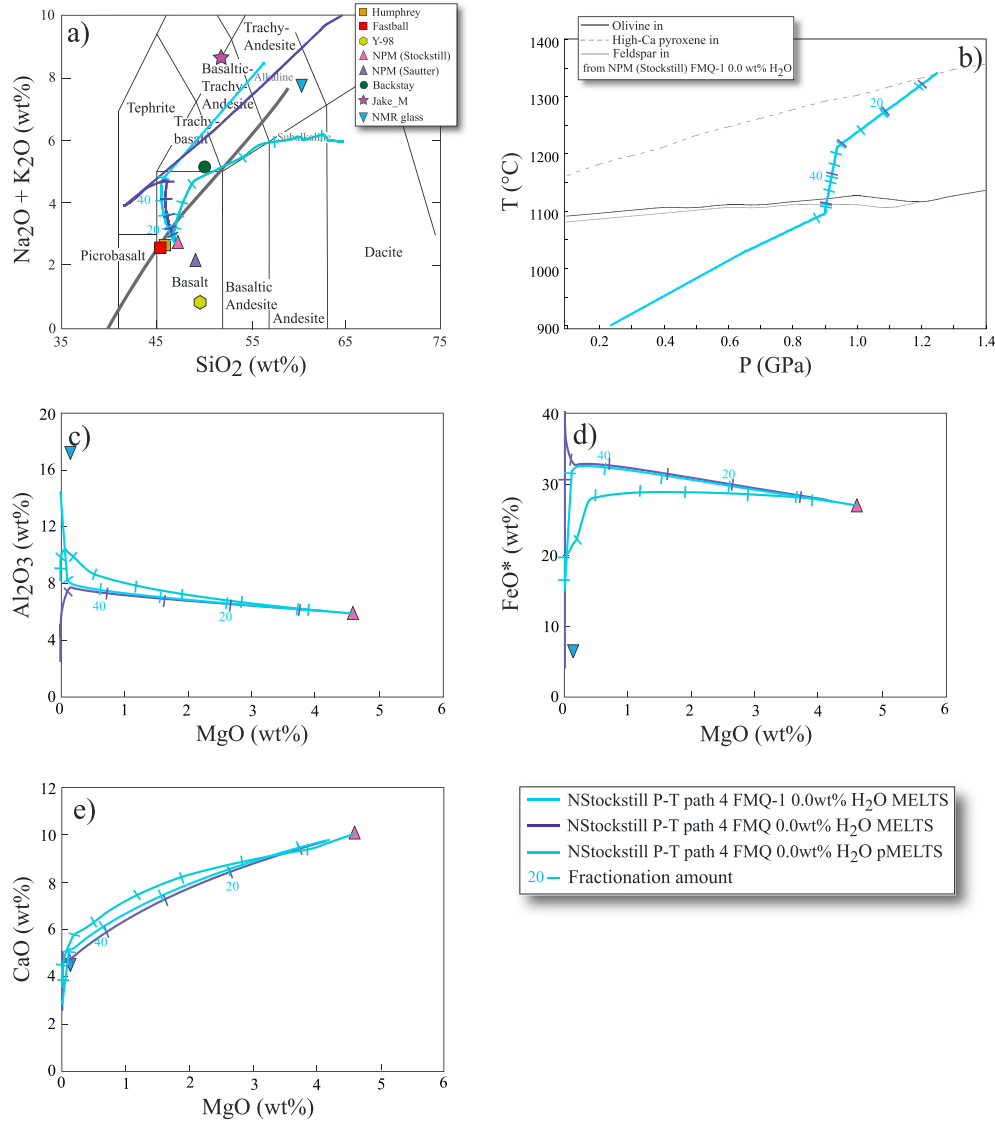


Figure 11. (a) Total alkali-silica diagram showing liquid lines of descent of melts formed by fractional crystallization of Humphrey composition under conditions selected because the melts best matched the Miller Range nakhlite intercumulus glass major element composition. (b) P-T paths used to calculate liquid lines of descent in Figures 11a and c–11e. Plots of Al₂O₃ in Figure 11c, FeO* in Figure 11d, and CaO in Figure 11e versus MgO for the same liquid lines of descent as in Figure 11a. The tick marks and numbers on the liquid lines of descent correspond to the amount of fractionation during the ascent of the primary magma (from 10% until 50% fractionation with 10% increments).

subsequent crystallization of the intercumulus phase. Notably, no continuous fractionation occurred during magma ascent and we present several possible explanations to explain this behavior. First, the MELTS and pMELTS calibrations may simply not be precise enough to produce an accurate pressure estimate in these high-augite content magmas [Balta and McSweeney, 2013a]. Alternatively, as we show below, continuous crystallization on a polybaric path can approximate isobaric crystallization or crystallization at several pressures; thus, our polybaric path could be describing the case where the melt formed most of its crystals at some pressure in a magma chamber and then upwelled to the surface where final crystallization took place, similar to the sequence hypothesized by Day *et al.* [2006]. Finally, McCubbin *et al.* [2013] hypothesized assimilation of a Cl-rich brine during

crystallization of the nakhlites. The algorithms do not include Cl as a component, and although there has been initial characterization of its impact on phase equilibria [e.g., Filiberto and Treiman, 2009], estimating its effect on compositions would require experiments detailing its impact on the full liquid line of descent (including compositions far from the liquidus). The assimilation of Cl could possibly produce a liquid line of descent for the Miller range groundmass that mimics those simulated in our Cl-free polybaric crystallization paths.

5. Discussion

5.1. Primary and Parental Martian Magma Evolution

[35] Both Fastball and Humphrey compositions show similar magmatic evolution paths under both isobaric and

polybaric conditions. High- and medium-pressure fractionation followed by subadiabatic ascent (paths α and β) causes evolution of both magmas to alkaline compositions, although the exact P-T paths which produce alkaline compositions depend on water content. The residual magmas that underwent low-pressure crystallization following subadiabatic ascent (path γ) remain subalkaline. Thus, Humphrey and Fastball melts can produce alkaline magmas under appropriate conditions. We note again that other mechanisms for generating alkaline compositions, such as direct melting of metasomatized mantle or low-degree melting, cannot be ruled out on Mars; however, they are not required by the Backstay composition.

[36] The evolution of nakhlite parental melts is distinct from that of the Humphrey and Fastball compositions. The NPM05 composition only yields subalkaline compositions even if the primary magma is held at high pressures; however, the dry NA03 magma produces alkaline compositions under both isobaric and polybaric conditions. These results show that water is not always necessary to form alkaline magmas by fractional crystallization of primary and parental magmas on Mars, analogous to Earth [e.g., *Whitaker et al.*, 2007].

[37] The evolution of the Y-98 shergottite magma differs from that of other Martian primary magmas in that only very high pressure conditions yield alkaline magma. Shergottites may not be abundant at the Martian surface [*Balta and McSween*, 2013b], even if we assume that shergottites are derived from primary magmas with similar composition to Y-98.

[38] The main conclusion we can draw from these thermodynamic models is that isobaric and polybaric fractional crystallization of the known primary and parental Martian magmas can lead to a large range of residual liquid compositions. Our calculations suggest that Martian igneous rocks could easily be more diverse than suggested by the limited Martian meteorites and mission data sets. Specifically, we hypothesize that alkaline rocks may be more common at that surface than has been recognized to date. This claim may be supported by the observation of clasts with alkaline composition in the Martian meteorite breccia NWA 7034 [*Santos et al.*, 2013], which is thought to be a sample of the Martian regolith.

[39] In addition, liquid lines of descent for each primary magma do not show significant differences between most isobaric and polybaric paths. The liquid lines of descent for each primary magma, determined using major-element trends under high-pressure isobaric conditions, are similar to the polybaric fractionation paths α and β . Likewise, trends under low-pressure, isobaric conditions are similar to path γ under polybaric conditions. These results imply that isobaric experiments conducted at different static pressures can likely reproduce realistic magmatic processes regardless of modest changes in pressure as the magmas migrate through the crust. In general, oxygen fugacity does not significantly alter Martian liquid evolution paths if the changes remain within the measured Martian magma range. However, water contents significantly influence the compositions of residual magmas, as shown in experiments [e.g., *McCubbin et al.*, 2008; *Nekvasil et al.*, 2009].

5.2. Implications for Mars Magmatic Evolution Over Time

[40] Our calculations imply that alkaline magma formation on Mars is analogous to Earth in that subalkaline magmas like Humphrey and Fastball are predicted to stagnate at

elevated pressures. Furthermore, high-pressure fractionation might be more common for younger rocks as Martian crustal thickness has increased over time [*Baratoux et al.*, 2011]. Consequently, formation of alkaline magmas on Mars should be more common in recent Martian history. *McCubbin et al.* [2008] hypothesized that crustal thickening with time could lead to magmas underplating the crust and forming cumulates; generation of residual alkaline magmas would be a byproduct of that process. Alkaline magmas in Gusev Crater have been dated as early Hesperian [*Greeley et al.*, 2005], suggesting that significant crustal thickening might have occurred by this time.

[41] The presence of water in Martian magma has been long debated [e.g., *Watson et al.*, 1994; *McSween et al.*, 2001; *Usui et al.*, 2012; *McCubbin et al.*, 2012]. This study provides indirect support for some wet Martian magmas due to the fact that Backstay requires water in order to be formed from a tholeiitic primary magma.

6. Summary

[42] More than 600 pMELTS and MELTS fractional crystallization calculations were conducted under isobaric and polybaric conditions using three Martian primary and one parental magma compositions. The results provide a better understanding of the evolution of primary Martian magmas and the formation of alkaline rocks.

[43] 1. Fractional crystallization of the different investigated magmas explains much of the observed diversity of Martian rock compositions. Residual liquids resulting from fractional crystallization of Humphrey and Fastball evolve similarly under the same conditions. The Y-98 shergottite and the nakhlite magma composition of *Sautter et al.* [2012] do not form alkaline magmas, whereas the *Stockstill et al.* [2005] dry nakhlite parental melt evolves toward a trachy-andesite composition similar to nakhlite intercumulus glass compositions.

[44] 2. MELTS and pMELTS calculations demonstrate that the liquid lines of descent determined from major element trends under high-pressure isobaric conditions are similar to the polybaric paths α and β , which remain at elevated pressures for the early portions of their crystallization paths. In addition, our calculations show that liquid lines of descent representing low-pressure isobaric conditions are similar to polybaric fractionation path γ . These results demonstrate that isobaric and polybaric calculations yield residual liquids with similar compositions, suggesting that isobaric experiments on Martian primary magmas can produce realistic results, even in cases where polybaric crystallization may have occurred.

[45] 3. Backstay may have formed from fractionation of a wet primary magma having a Humphrey- or Fastball-like composition, under either isobaric or polybaric conditions with 10–30% fractionation. Backstay calculations suggest that Martian magmatic water was present during the early Hesperian. The best fits for Backstay suggest that considering a polybaric crystallization path may improve the quality of the fit when simulating liquid lines of descent.

[46] 4. Jake_M was not formed by fractionation of any of the primary magma compositions evaluated here but more likely formed from a magma affected by melting of a metasomatized mantle source, crustal assimilation, or by fractional crystallization of a yet unrecognized primary melt.

[47] 5. Despite the fact that our models allow the nakhlite intercumulus glass to have formed by polybaric fractional crystallization of a nakhlite parental melt under dry conditions with 80% fractionation, our model seems to differ from petrological observations, arguing that nakhlites formed mostly under isobaric conditions, requiring an alternative explanation for the fit.

[48] 6. Because alkaline magmas are easily formed if crystallization occurs at high pressure, progressive thickening of the Martian crust may imply that alkaline magmas have become more widespread during recent Martian time.

[49] As shown in this study, MELTS and pMELTS are very useful in calculating isobaric and polybaric fractionation models with different variables. Experimental results to confirm these results are desirable, and further crystallization experiments under varying conditions can be guided by the results of these calculations.

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