Alkalic parental magmas for chassignites?

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Abstract-Detailed analysis of cumulate and melt inclusion assemblages in the chassignites provide important constraints on the nature of the melt trapped as inclusions in cumulus olivine (and, by extension, parental magma compositions), the pressures of crystallization, and magmatic volatile contents. These mineral assemblages show strong similarities to the experimental fractionation assemblages that produce the sodic silica-saturated alkalic lavas on Earth (e.g., Ascension Island, Azores, the Nandewar volcano of Australia). The experimental assemblages were produced from silica-saturated hawaiite at pressures above 4.3 kbar with dissolved water contents above 0.5 wt%. Such pressures are consistent with Ti:Al ratios of the melt-inclusion pyroxenes in the Chassigny meteorite. Pyroxene compositions suggest early high crystallization temperatures and thus relatively low initial water and F contents. Feldspars indicate that melt evolution proceeded to rhyolite compositions both within the interstices of the cumulate olivine and within the melt inclusions, even though rhyolitic glass is only found within olivine-hosted polyphase melt inclusions. The observed rhyolite glass is compositionally similar to the alkali-rich rhyolite of Ascension Island which is produced experimentally by crystallization of hawaiite. It is proposed that the melt trapped in cumulus olivine of the Chassigny dunite was similar to a terrestrial silica-saturated hawaiite, while that trapped in olivine of the Northwest Africa (NWA) 2727 dunite was less evolved, perhaps mildly alkalic basalt. Melts similar to terrestrial intra-plate tholeiite could be parental to the cumulus minerals and evolve upon crystallization at pressures above 4.3 kbar and water contents above ~0.4 wt% to mildly alkalic basalt, silica-saturated hawaiite, and alkali-rich rhyolite. The melt inclusion assemblages are inconsistent with either crystallization of a low-Al, high-Fe basalt, or lowpressure crystallization of a terrestrial-like tholeiite.

INTRODUCTION

Magmatism has played a major role in shaping the surficial environment of Mars, from the chemistry of its crust and atmosphere, to its surface morphology. The Martian shergottite, nakhlite, and chassignite (SNC) meteorites (e.g., McSween and Treiman 1998) are invaluable sources of information about Martian magmatism. However, this information has proven singularly difficult to extract because of the partly cumulate nature of many of the meteorites. Efforts to determine the compositional characteristics of the parental magmas of the basaltic shergottites Shergotty and Zagami (Stolper and McSween 1979; McCoy et al. 1992; Hale et al. 1999; Dann et al. 2001) have focused on melting experiments and mass balance computations of interstitial and cumulate rim material. For the cumulates, specifically Chassigny and the nakhlites, workers have developed

approximations of bulk melt inclusion chemistry (e.g., Johnson et al. 1991; Harvey and McSween 1992; Treiman 1993; Varela et al. 2000; Treiman and Goodrich 2001; Imae et al. 2005; Stockstill et al. 2005). All of these studies have led to the conclusion that the magmas that produced the SNC meteorites share low-Al, high-Fe "Martian" characteristics, but no experimental work on proposed liquids has demonstrated their viability by successfully producing the assemblages found in the meteorites.

This work focuses on constraining the nature of melt trapped in olivine in the Martian dunites Chassigny and NWA 2727 by identifying liquids that could give rise to observed crystalline assemblages within polyphase melt inclusions. This melt may not be parental to the meteorite as a whole, but understanding its nature can aid in constraining the nature of the actual parental liquid. The focus on the mineral assemblage rather than analytical reconstruction of the liquid

composition avoids the possibility that plating of olivine or orthopyroxene in the walls of the inclusion has obscured the bulk melt inclusion composition. This approach can also take into account the likely possibility that Fe:Mg exchange occurred between the host olivine and the included melt. We focus specifically on the chassignites Chassigny and NWA 2737 because they may provide information on the early high-temperature stages of Martian magma crystallization.

In spite of extensive study of the Chassigny meteorite by many workers, the nature of the melts trapped as melt inclusions remains enigmatic. Experimental work on a proposed parent for the Chassigny (A* of Johnson et al. [1991]) with typical high-Fe, low-Al characteristics has not produced the chassignite cumulate or melt inclusion assemblages at either low pressure (Minitti and Rutherford 2000) or elevated pressure (Filiberto et al. 2005) under dry or hydrous conditions. For this assessment of the nature of the trapped melt inclusion liquid, we have expanded considerations of possible liquids to include terrestrial magmas. Consideration of terrestrial compositions is justified on the basis of several observations. MER Spirit data on Martian surficial rocks (e.g., Gusev basalts) show geochemical characteristics that are surprisingly terrestriallike (e.g., Gellert et al. 2004; McSween et al. 2004; Filiberto et al. 2006a). Furthermore, there are recent indications that even the SNC meteorites may have terrestrial analogs. Filiberto and Nekvasil (2005) and Filiberto et al. (2006a) showed that the cumulate SNC meteorites may have terrestrial analogs in entrained cumulate nodules of intraplate volcanic suites, and that their compositions reflect more the nature of the accumulating minerals than primary Martian mantle characteristics. Filiberto et al. (2006b) have shown that the Martian meteorites considered by some workers to contain no cumulate component and thus represent liquid compositions (e.g., Yamato-980459, Queen Alexandra Range [QUE] 94201) may have terrestrial analogs in the ferropicrites of the large igneous provinces on Earth (e.g., of the Pechenga complex of the Kola Peninsula, Russia, Hanski [1992]; of Etendecka, Namibia, Gibson et al. [2000]). Since the chassignites specifically share many important geochemical characteristics with intra-plate nodules on Earth (e.g., mineral phases, Filiberto et al. [2006a]; light rare earth element (LREE) enriched signatures, Wadhwa and Crozaz [1995]), their mineral assemblages will be compared with obtained experimentally from crystallization those experiments on terrestrial intra-plate magmas.

MINERAL ASSEMBLAGES OF THE CHASSIGNITES

The Chassigny meteorite is a dunite consisting primarily of accumulated unzoned Fo_{68} olivine and less abundant subhedral chromite (which is also present as crystalline inclusions in olivine). Augite, $En_{50}Wo_{34}Fs_{16}$ (mol%); pigeonite, $En_{63}Wo_{12}Fs_{25}$; and unexsolved orthopyroxene

En₆₈Wo₄Fs₂₈ (e.g., Floran et al. 1978; Wadhwa and Crozaz 1995) have been reported in the interstitial assemblage. The chassignite NWA 2737 is also an olivine-spinel cumulate, with a mean olivine composition of Fo₇₉ (Beck et al. 2006). Three pyroxenes (augite, pigeonite, and orthopyroxene), chromite, analbite glass, and apatite are found interstitial to the cumulate phases.

To obtain additional textural and analytical information needed to assess petrogenetic sequence, two thin sections of the Chassigny meteorite were studied petrographically and via electron microprobe analysis (EPMA). Electron microprobe analysis was performed using a Cameca Camebax electron microprobe with four wavelength dispersive spectrometers, one of which was equipped with an OV-60 detector crystal necessary for obtaining accurate fluorine analyses. An accelerating voltage of 15 kV and a nominal beam current of 10 nA were used during analysis. The following standards were used for element X-ray intensity standardization; microcline (Si, K), anorthite (Ca, Al), albite (Na), forsterite (Mg), ilmenite (Fe, Ti), rhodonite (Mn), chromite (Cr), apatite (P), and magnesium fluoride (F). For Na-bearing phases, the largest possible raster size was used to minimize Na volatilization that occurs during highly focused electron beam analysis on such matrices. Because some problems with Na loss during maskelynite analysis still persisted, these analyses were recast into the CIPW norm, and Na was added back computationally to form albite until either all normative quartz or all normative corundum was consumed.

Pyroxenes

Petrographic textural analysis of the cumulate and interstitial assemblages of the Chassigny meteorite revealed no unequivocal cumulus texture among the pyroxenes and suggests that they likely postdate accumulation of olivine and chromite. They appear to have crystallized in the sequence pigeonite, then subcalcic (high temperature) augite plus pigeonite, and finally, orthopyroxene and high-Ca augite. This is in keeping with the sequence suggested by Wadwha and Crozaz (1995) based on their petrographic study coupled with backscattered electron imaging. This sequence of pyroxene crystallization suggests high initial crystallization temperatures and preservation of a polythermal history. Figure 1a shows this sequence schematically with the expected changes in Wo component with dropping temperature.

Analytical examination indicates a range of pyroxene compositions (Fig. 1b). The composition of the high-temperature subcalcic augite was used to get a first-order estimate of its minimum stability temperature, that is, the temperature below which subcalcic augite would be replaced by calcic augite and orthopyroxene. QUILF calculations (Andersen et al. 1993) yielded minimum temperatures

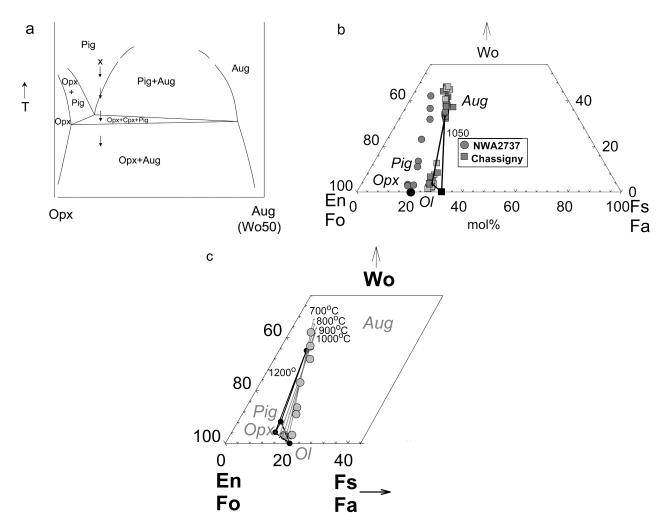


Fig. 1. a) Schematic change in pyroxene assemblage with dropping temperature. X marks a pigeonite composition that would give rise to the observed sequence of pyroxene phases. (Pig: pigeonite; Aug: augite; Opx: orthopyroxene). Section drawn from information in Lindsley (1983). b) Compositions of pyroxenes from NWA 2737 (dark gray circles; Beck et al. [2006]) and Chassigny (dark gray squares; this work) projected into the pyroxene quadrilateral using the QUILF methodology of Andersen et al. (1993). Plotted data from Beck et al. (2006) include their reported averaged compositions as well as individual pyroxenes with highest and lowest Ca contents. Light gray squares show specifically melt inclusion pyroxene compositions for the Chassigny (this work). Black symbols refer to olivine compositions. Black tie lines indicate the computed pyroxene/olivine equilibrium assemblage at 1050 °C and 10 kbar. c) Compositions of pyroxenes from NWA 2737 (light gray circles; Beck et al. [2006]) projected into the pyroxene quadrilateral using the QUILF methodology of Andersen et al. (1993). Black tie lines link calculated ferromagnesian phases in equilibrium at 1200 °C. Gray tie lines show changes in composition of equilibrium phases with dropping temperature if the olivine composition is held constant.

between 1177 °C and 1130 °C at 1 kbar, and 1228 °C and 1166 °C at 10 kbar for several pyroxene grains (exemplified by analyses 5 and 6 of Table 1). Continued growth during cooling can be seen in the zoning of augite from more Ca-poor interiors to Ca-enriched rims.

Pyroxenes are also found in large olivine-hosted polyphase "melt" inclusions in both chassignites. Within individual inclusions in the Chassigny meteorite, the pyroxenes are variable, consisting in some cases of orthopyroxene and pigeonite, in others of orthopyroxene alone, and in a third variety, of orthopyroxene and clinopyroxene (although it is recognized that the absence of phases is not definitive, and each could have contained all

three phases prior to sectioning). Interestingly, the minimum temperatures for subcalcic augite from melt inclusions is high (>1100 °C) and similar to values seen in the interstitial pyroxene, while that for orthopyroxene in the melt inclusion extends to lower temperatures <970 °C (reflected by the low-Ca orthopyroxene in the melt inclusions) (Fig. 1b). The melt inclusion and interstitial pyroxenes from NWA 2737 differ from those of Chassigny in their higher mg#. Additionally, the pyroxenes and olivine in the former share the same mg# (Fig. 1c).

A more detailed look at the compositional changes in pyroxenes of both chassignites during cooling shows that the change in augite within both meteorites to high Ca values and

Table 1. Representative analyses of minerals from the Chassigny meteorite.

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Analysis no.	1a	2ª	3b	4 _b	5	9	7c	s8c	6	10
	Melt	Melt	Melt	Melt					Melt	Melt
Assemblage	inclusion	inclusion	inclusion	inclusion	Interstitial	Interstitial	Cumulate	Cumulate	inclusion	inclusion
Phase	Aug	Opx	Aug	Opx	Cpx	Cpx	Spinel core	Spinel rim	Spinel	Kaersutite
SiO_2 (wt%)	51.34	51.71	50.28	52.21	52.21	52.46	0.03	60.0	0.11	40.97
TiO_2	0.72	0.65	1.47	0.43	0.25	0.24	1.54	3.09	0.7	6.46
AI_2O_3	3.51	3.42	4.57	2.48	1.02	6.0	98.9	10.81	38.53	12.07
Cr_2O_3	0.49	0.01	1.13	0.45	0.83	0.7	55.46	44.61	21.25	98.0
${ m FeO_T}$	7.64	17.29	6.61	15.94	9.79	10.63	31.96	34.23	27.04	9.3
MnO	0.27	0.53	0.25	0.54	0.31	0.42	0.47	0.56	0	0.17
MgO	15.03	24.01	13.71	23.8	16.9	17.05	80.0	0.12	0.33	12.04
CaO	18.4	1.74	20.68	2.38	15.96	15.13	3.57	3.29	7.63	11.41
Na_2O	0.67	0.03	0.74	0.07	0.3	0.24	0	0	0.15	3.11
K_2O	0.02	0.0	0.04	0.02	0	0	0	0.03	0	0.33
H	0	0	0	0	0	0	0.01	0	0.04	0.34
CI	0.02	0.01	0.02	0	0	0	0.03	0.05	0	0.12
Total	98.11	99.40	99.5	98.32	97.57	77.77	100.01	88.96	95.78	97.18
3.1 1.3.5										

a1 and 2 from same grain.
b3 and 4 from same melt inclusion.
c7 and 8 from same grain.

orthopyroxene to low Ca values (in Chassigny) occurs with little change in Fe content (Fig. 1b). Such compositional changes in pyroxene differ from the changes normally seen during crystallization, where the Fe:Mg ratio of the pyroxenes increases as the melt changes composition during cooling. They suggest Fe:Mg exchange equilibrium with the surrounding cumulate olivine rather than with the main magma body. Near invariance of Fe:Mg ratio in olivine during cooling is a predictable result of volumetrically dominant olivine in a cumulate which cannot change composition as the magma cools because of the small amount of interstitial melt.

Figure 1c shows the results of a computational investigation using the QUILF calculation methodology of Andersen et al. (1993) in which the effect of decreasing temperature on pyroxene compositions is shown for the case when olivine retains a constant Fe:Mg ratio. With decreasing temperature, the mg# of orthopyroxene shifts towards that of olivine, and the augite compositions increase in Ca content. The observational result would be pyroxene compositions that appear co-linear with olivine. This can be seen most readily for NWA 2737 (Fig. 1c) (Beck et al. 2006).

The Chassigny pyroxene compositions appear to have been less affected by re-equilibration with cumulus olivine upon cooling than those of NWA 2737, and they seem to preserve at least one possible equilibration temperature along the cooling path. This temperature is calculated by QUILF to be 1050 °C based on the compositions of olivine and pyroxenes of Wadhwa and Crozaz (1995). According to the QUILF results, pigeonite is no longer stable at this temperature.

Feldspars

Maskelynite and K-feldspar glass are found both interstitially and in melt inclusions (e.g., Floran et al. 1978; Beck et al. 2006) in both chassignites. Figure 2 shows published glass data from Chassigny and NWA 2737 as well as new analyses based on the two slides of the Chassigny meteorite studied here. Both sets of data for Chassigny show a range in feldspar glass compositions from andesine, through oligoclase, possible high-temperature anorthoclase/sanidine pairs, to final low-calcium anorthoclase, and occasional albite. (The scatter of the early data of Floran et al. [1978] may have been caused by Na loss during microprobe analysis). The variation in feldspar glass composition is not the same in the Chassigny interstitial regions as in the melt inclusions (Fig. 2), with the former showing a typical elevated temperature crystallization sequence of plagioclase crystallizing first and decreasing in anorthite content with dropping temperature, intersection of the feldspar solvus while the compositions are still significantly ternary in character, and further increases in albite component with continued cooling. Feldspar glasses of the olivine-hosted melt

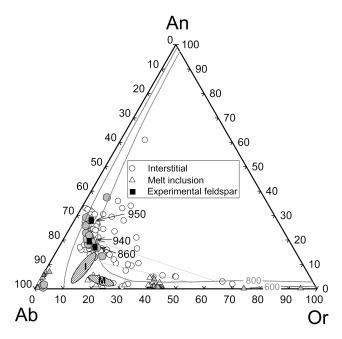


Fig. 2. Analysis of interstitial feldspar glass from Floran et al. (1978) (open circles) and this work (gray circles) and melt inclusion feldspar glass (Floran et al. [1978], open triangles; this work, gray triangles) plotted into the feldspar ternary system. Feldspar glass data from NWA 2737 (Beck et al. 2006) are shown from both interstitial regions (field labeled I) and melt inclusions (field labeled M). Also shown are two isothermal solvus sections computed at 5 kbar and 800 and 600 °C using the thermodynamic model of Lindsley and Nekvasil (1989) and the methodology of Wen and Nekvasil (1994). Tie lines show co-existing feldspar pairs along the solvus at 800 °C. Black squares show experimental feldspar compositions from Nekvasil et al. (2004).

inclusions seem to preserve evidence of lower temperature stages of feldspar growth.

The differential behavior of the feldspars within these two regions can be explained in many ways, one of which is that the melt inclusions retained a fluid phase into the subsolidus thermal regime, while open-system fluid loss prevailed in the interstitial regions. Importantly, this difference does not necessitate a difference in composition between the liquid trapped in the melt inclusions and that trapped in olivine.

Additional Phases

In addition to pyroxenes and feldspar glass, the large polyphase melt inclusions in both chassignites contain kaersutite, fluorapatite, and Cr-rich spinel, and, in the Chassigny melt inclusions, some rhyolitic glass (Johnson et al. 1991; Meyer 1998; McCubbin et al. 2006a). Johnson et al. (1991) reported Ti-biotite as an additional, albeit rare, phase in the Chassigny. Table 1 gives a representative analysis of Chassigny kaersutite. Importantly, the Chassigny kaersutite shows nearly the same mg# as the host olivine in spite of the

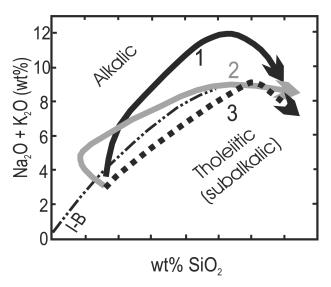


Fig. 3. Variation of total alkalis versus silica in lavas and fine-grained plutonic rocks of the silica-saturated magmatic suites from intraplate regimes on Earth (1) the sodic silica-saturated alkalic suites, (2) the potassic silica-saturated alkalic suites, (3) the ocean island tholeiitic suites (adapted from Nekvasil et al. [2004]). Arrows indicate direction of decreasing mg#. The curve indicated by I-B is the alkalic/subalkalic boundary of Irvine and Baragar (1971).

likelihood that it formed at lower temperature. Therefore, just as was suggested for the pyroxenes, kaersutite appears to have been affected by Fe:Mg exchange and does not record the effect of increasing Fe content of the residual melt within the melt inclusion.

MINERALOGIC COMPARISON OF CHASSIGNITE PHASE ASSEMBLAGES WITH THOSE OF TERRESTRIAL INTRA-PLATE MAGMAS

Intra-plate igneous environments on Earth are characterized by extreme compositional diversity of associated rocks. Viewed globally, intra-plate magmatic suites (defined by spatially and temporally associated rock units) follow three major silica-saturated trends (Fig. 3) and additional silica-undersaturated trends defined by the liquid lines-of-descent. The former are characterized by the presence of late-stage rhyolite, the latter by late-stage phonolite. Because of the presence of rhyolitic residuum in the large polyphase inclusions of the Chassigny, the silica-undersaturated suites are not considered further here.

Experimental investigations of the role of fractionation in producing these trends have yielded the fractionation pressures and mineral assemblages required for each liquid trend (Spulber and Rutherford 1983; Litvin et al. 2001; Rossier et al. 2001; Nekvasil et al. 2002; DiFrancesco et al. 2003; Nekvasil et al. 2004; Whitaker et al. 2005). Experimental determination of the effect of pressure on mineral assemblages and comparison with mineral assemblages in natural rocks have indicated that rocks from

Table 2. Typical mafic silica-saturated hawaiite along Trend 1 and that used as starting material for the experiments of Nekvasil et al. (2004).

SiO ₂ (wt%)	46.99	
TiO_2	2.65	
Al_2O_2	14.55	
FeO_T	10.49	
MnO	0.13	
MgO	8.18	
CaO	8.97	
Na ₂ O	2.8	
K_2O	1.43	
P_2O_5	0.47	
Total	96.66	

intra-plate suites generally preserve evidence for the highpressure stage of fractionation only in accidental cognate inclusions and the bulk composition of the lavas. The natural mineral assemblages reflect primarily the final low-pressure ponding stage before eruption. If this is also the case on Mars, comparison with terrestrial intra-plate magmas necessitates comparison with experimental data that elucidate both the high- and low-pressure mineral assemblages.

Comparisons of the chassignite melt inclusion and cumulate assemblage with the experimental mineral assemblages of the three trends in Fig. 3 show significant similarities with the assemblages that experimentally produced the typical sodic silica-saturated alkalic trend from a natural mafic hawaiite from the Nandewar volcano of New South Wales, Australia (Table 2). Table 3 shows the assemblages crystallizing from this hawaiite at 9.3 kbar with an initial bulk water content of 2 wt%. Most of this data was presented along with details of experimental and analytical techniques in Nekvasil et al. (2004). The additional experiments conducted and presented in Table 3 (at temperatures of 1055 and 1050 °C \pm 13 °C) used the same experimental and analytical techniques presented previously (Nekvasil et al. 2004). All experiments were conducted in piston-cylinder apparatus using graphite furnaces and extradense barium carbonate cells. The starting material for each experiment was powdered natural lava from the Nandewar volcano, NSW, Australia dried at 175 °C. For each crystallization experiment, the sample was heated to 1250 °C for 12 h to ensure complete melting and then dropped to the final crystallization temperature at which it was held for 3 days before quenching.

Clinopyroxene and olivine are the earliest appearing minerals of the hawaiite and are followed by kaersutite and orthopyroxene (Table 3). Once orthopyroxene appears, olivine abundance decreases, and apatite and, finally, plagioclase and ilmenite join the assemblage. Table 3 also shows the cumulate, interstitial, and melt-inclusion minerals of the two chassignites. Each phase in each chassignite that has an analog with a phase along the crystallization path is

Table 3. Experimental mineral compositions and abundances along the fractionation path of a mildly alkalic hawaiite from the Nandewar (Trend 1) suite and mineral phases of the chassignites NWA 2737 and Chassigny.

Experimental assemblage at 9.3 kbar; 2 wt% H ₂ O	NWA 2737 assemblages	Chassigny assemblage
1200 °C: Olivine (<1) ^a (Fo ₈₂)		
1130 °C: Olivine (2) (Fo ₈₀) Clinopyroxene (3) (En ₅₇ Wo ₃₃ Fs ₁₀)	Olivine (Fo ₇₉) Augite (En ₅₆ Wo ₃₂ Fs ₁₂) [Pigeonite]	
1080 °C: Olivine (6) (Fo ₇₂) Clinopyroxene (21) (En ₅₄ Wo ₃₂ Fs ₁₄)		
1060 °C: Olivine (2.5) (Fo ₆₆) Clinopyroxene (18) (En ₅₁ Wo ₃₀ Fs ₁₉) Kaersutite (22)	Kaersutite (MI)	Olivine (Fo ₆₈) Clinopyroxene (En ₅₀ Wo ₃₄ Fs ₁₆)
1055 °C: Olivine (1) (Fo ₆₅) Clinopyroxene (12) (En ₄₉ Wo ₃₂ Fs ₁₉) Orthopyroxene (5) (En ₆₈ Wo ₄ Fs ₂₈) Kaersutite (24)	Orthopyroxene (En ₈₂ Wo ₃ Fs ₁₅)	$\begin{array}{l} Orthopyroxene \\ (En_{68}Wo_4Fs_{28}) \\ [Pigeonite] \\ Kaersutite (MI) \end{array}$
1050 °C: Olivine (<1) (Fo ₆₃) Clinopyroxene (19) (En ₄₉ Wo ₃₀ Fs ₂₁) Orthopyroxene (3) (En ₆₇ Wo ₅ Fs ₂₈) Kaersutite (25)		
1040 °C: Clinopyroxene (16) (En ₄₈ Wo ₂₈ Fs ₂₄) Orthopyroxene (1) (En ₆₂ Wo ₅ Fs ₃₃) Kaersutite (41) Apatite (<1)	Apatite	Apatite
1020 °C: Orthopyroxene (5) (En ₆₁ Wo ₄ Fs ₃₅) Kaersutite (31) Apatite (2)		
950 °C: Kaersutite (50) Apatite (3) Ilmenite (6) Plagioclase (4) (An ₂₄ Ab ₆₅ Or ₇)	Oxides maskelynite/feldspar glass	Oxides maskelynite/feldspar glass

shown on the same row. However, since the exact paragenetic sequence is not known for all of the minerals in the meteorites, caution must be exercised when using matches to imply crystallization temperatures.

Comparison of the compositions of the experimental minerals with those of the meteorite assemblages allows for further assessment of the possibility that an alkalic liquid was parental to the melt inclusion assemblage. All ferromagnesian minerals obtained experimentally from the Nandewar hawaiite show continuous compositional changes over the crystallization temperature range. The compositional changes in olivine along this path encompass the compositions of the NWA 2737 and Chassigny cumulus olivines. The compositions of pyroxenes of the Chassigny meteorite also lie

within the compositional range of the experimentally produced pyroxenes.

The compositional similarities between the hawaiite assemblages and those of the chassignites extend to the feldspars. Figure 2 shows that the experimental feldspars crystallized from the hawaiite lie directly along the higher-temperature portion of the feldspar evolution trend exhibited by interstitial feldspar glass of the Chassigny meteorite.

Three phases in the Chassigny mineral assemblages, however, are not seen along the experimental path of Table 3 and deserve mention: Ti-biotite, pigeonite, and chromite. Titanium-rich biotite is common in a variety of alkalic rocks on Earth (e.g., Bachinski and Simpson 1984) and appears to be stable at higher temperatures than low-Ti biotite (e.g.,

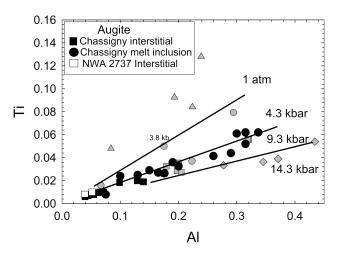


Fig. 4. Ti versus Al cationic abundances of Chassigny interstitial augite (black squares; Floran et al. [1978]; Wadhwa and Crozaz [2005]) and augite from melt inclusions (black circles; Johnson et al. [1991]; Varela et al. [2000]) assemblages compared with approximate pressure fields (heavy lines) determined by experiments on rocks from the Nandewar volcano with 2 wt% water as a function of pressure (gray symbols: triangles, 1 atm; circles, 4.3 kbar; squares, 9.3 kbar; diamonds, 14.3 kbar; from Nekvasil et al. [2004]). White squares are interstitial (?) augites from NWA 2737 (Beck et al. 2006).

Zhou 1994). Titanium-biotite appears before kaersutite along the experimental fractionation path of the Nandewar hawaiite at bulk water contents lower than those for the path of Table 3. For example, the data of Nekvasil et al. (2004) at 960 °C and 4 wt% bulk water content indicate that the mineral assemblage of a trachytic starting composition along Trend 1 is the assemblage kaersutite + plagioclase + apatite + ilmenite. The same trachyte at 970 °C with 1.4 wt% bulk water content has Ti-biotite in the crystallizing assemblage, and at 950 °C Ti-biotite + kaersutite. At low water contents (specifically 0.4 wt% H₂O), there appears to be no field of biotite stability. The higher temperatures would also permit the stability of high-temperature pigeonite.

The absence of kaersutite in the cumulus assemblage of the Chassigny may indicate that bulk water contents for the Chassigny parental magma was lower than the 2 wt% of the experiments. On the other hand, this absence may simply reflect the fact that dynamic magmatic processes produce individual layers that typically do not include all mineral phases crystallizing at any one stage. Finally, it may relate to fluid loss from the interstitial melt pockets (e.g., McCubbin et al. 2006a).

Chromite commonly appears very early in terrestrial alkalic rocks, changing toward magnetite with increasing fractionation. Zoning toward Ti-magnetite and decreases in Cr content is also seen in the Chassigny spinel (Table 1); however, a significant amount of Cr persists in the spinel of the melt inclusions. Persistence of Cr-rich spinel throughout the crystallization interval for Chassigny but not in the experiments may simply be the result of Cr₂O₃ values in the

hawaiite that are lower than those of the Chassigny melt inclusion liquid due to early fractionation of chromite. Alternatively, its persistence in the Chassigny melt inclusion assemblage may indicate higher Martian magmatic Cr values. However, the presence of cumulus chromite and chromite inclusions in olivine may have induced (through re-equilibration) high Cr in the trapped melts. In this case, high Cr contents in pyroxene and kaersutite (Table 1) need not be a reflection of generally high Martian magma Cr contents.

Constraints on the Pressure of Crystallization

If magmas exist on Mars that are similar to those on Earth that produce the sodic silica-saturated alkalic trend, the marked change in mineral assemblage with pressure permits pressure constraints to be placed on the crystallization history. The experimental assemblage produced at 4.3 kbar lacks orthopyroxene and shows early precipitation of plagioclase (Nekvasil et al. 2004). Furthermore, the clinopyroxene crystallized contains much lower alumina than that found in the Chassigny melt inclusions. Thus, this pressure (and crystallization depths of <~30 km on Mars) does not produce mineral assemblages comparable to those of the Chassigny. At pressures of 12.3 kbar (Filiberto and Nekvasil 2003), residual liquids are nepheline-normative, thereby deviating strongly from the rhyolite seen in the melt inclusion glass. Thus, crystallization depths greater than 95 km are likewise precluded.

The change in assemblage with pressure, the almost ubiquitous presence of augite at all pressures, and the sensitivity of Ti:Al ratio of augite to pressure, provide additional means for checking the consistency of the Chassigny assemblages with elevated pressure. Figure 4 shows the pressure dependence of Al versus Ti cationic abundances of clinopyroxene from experiments on rocks along the sodic silica-saturated trend (from Nekvasil et al. [2004]) These data indicate that Al content can vary at constant pressure in titanaugites and that the ratio of Ti:Al may be a more reliable indicator of pressure. This ratio will be affected by the crystallization of feldspar and its use here is restricted to the stage of pyroxene crystallization prior to feldspar crystallization. It is also recognized that nucleation delay of plagioclase can cause large increases in Al content of pyroxene which can also obscure the pressure relationship.

Melt inclusion augites from Chassigny (Wadhwa and Crozaz 1995; this study) indicate a pressure fully consistent with the pressure range indicated by the phase assemblage, that is, pressures of crystallization above about 4.3 kbar (Fig. 4). Interstitial pyroxene from the Chassigny and NWA 2737 (Beck et al. 2006) lie in the low-Al, low-Ti region of this compositional space. Although the effect of pressure in this region is difficult to discern, their Ti:Al ratios are not inconsistent with the elevated pressure of the melt inclusion

pyroxene. Nonetheless, it is worth considering if the low Al contents of the intercumulus pyroxene could have arisen from a low-Al parental liquid. This would require that the intercumulus pyroxene crystallized from a less-evolved melt than that trapped in the melt inclusion (since the Al content of evolving liquid should rise during crystallization of Al-poor ferromagnesian minerals). This is inconsistent with our textural study which indicates that the pyroxene is intercumulus and hence postdates entrapment of melt inclusions in olivine. Locally, however, low-Al environments could develop interstitially as chromite continues to grow and becomes increasingly Al-rich (Table 1).

The presence of kaersutite may also indicate elevated pressure of crystallization of melt inclusions. McCubbin et al. (2006b) have shown that the presence of kaersutite alone is not a pressure indicator since they were able to stabilize kaersutite at 1 atm. However, the kaersutite stabilized is a fluor-kaersutite with F contents much higher than observed in the kaersutite of Chassigny. Even if significant oxycomponent is taken into account, the F contents of the natural kaersutites are significantly lower than that of kaersutite stable at low pressure. The OH content of kaersutite is likely a better indicator of pressure rather than simply the presence of kaersutite since the dissolution of water in silicate melts is so pressure-dependent (e.g., Burnham 1994). However, available data on the OH content of Chassigny kaersutite are inconclusive. Watson et al. (1994) characterized this kaersutite as OH-poor based on their ion microprobe analysis of kaersutite. However, the Fe micro-XANES analysis of Monkawa et al. (2006) indicates little to no Fe³⁺. This would be consistent with an OH-poor kaersutite only if the kaersutite had unusually high amounts of oxy-component.

Constraints on Liquid Compositions

The possibility of a terrestrial-like alkalic liquid parental to the Chassigny was considered by Prinz et al. (1974) and Floran et al. (1978) based on their observation that the Chassigny cumulate and melt inclusion assemblages are found on Earth as phenocrysts in lavas of sodic alkalic continental intra-plate suites. Support for the possibility that the melt trapped as inclusions in olivine was alkalic was seen in the alkalic nature of compositions obtained by broad-beam bulk analyses of Chassigny melt inclusions (Floran et al. 1978), those computed to be in equilibrium with kaersutite (composition B of Johnson et al. 1991), and those obtained by analysis of holohyaline melt inclusions (Varela et al. 2000; Monkawa et al. 2003). The results of the comparative study presented here support such previous observations and suggest further that the melts trapped in olivine of both NWA 2737 and Chassigny were alkalic and silica-saturated. Coupling this study with the experimental results of Nekvasil et al. (2004) provides more details on the nature of these trapped liquids.

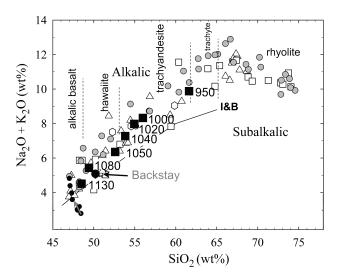


Fig. 5. Variation in total alkalis versus silica in experimental liquids (black squares) derived by crystallization of hawaiite. Temperatures (°C) indicated correspond to those of Table 3. Natural lavas from three sodic silica-saturated alkalic suites from Trend 1 (of Fig. 3) (Nandewar volcano, Australia, gray circles, Stolz [1985]; Azores, open triangles, White et al. [1979]; Ascension Island, open squares, Harris [1983]) are shown for comparison with experimental liquids. The composition of the Martian rock "Backstay" (McSween et al. 2006) is indicated by the large black circle. Small black circles show the compositional evolution of liquids residual to crystallization of continental olivine tholeiite at 9.3 kbar and 0.35 wt% water (from Whitaker et al. [2005]) into the alkalic regime.

Liquids in equilibrium with the assemblages of Table 3 are shown in Fig. 5. They evolve from mildly alkalic basalt through trachybasalt (specifically, hawaiite), trachyandesite, trachyte, and finally alkali-rich rhyolite. This sequence may give insights into the nature of the earlier, higher-temperature liquids (that is, those that may be closer to parental to the chassignites than the hawaiitic liquid trapped as melt inclusions in olivine of Chassigny) as well as into the nature of the late-stage liquids.

The composition of the cumulus olivine and interstitial (?) augite in NWA 2737 was reproduced experimentally at 1130 °C (Table 3) along the crystallization path of the mafic hawaiite of Table 2. Table 4 and Figs. 5 and 6 show the composition of the melt at this stage. The more evolved cumulus olivine of Chassigny and its melt inclusion assemblage requires liquids that lie further along the differentiation trend of such a mafic hawaiite (Figs. 5 and 6). At 1050 °C, at which point the composition of the cumulus olivine and the augite and orthopyroxene of the melt inclusion could have been at equilibrium, this melt is still hawaiitic, but more evolved than that which can produce the olivine of NWA 2737 (Table 4; Fig. 5). Further evolution of this hawaiitic melt by crystallization of the lower temperature mineral assemblages of Table 3 leads to alkali-rich rhyolite (Figs. 5 and 6). Natural alkali-rich rhyolites from terrestrial sodic silica-saturated alkalic (Trend 1) suites (Figs. 5 and 6)

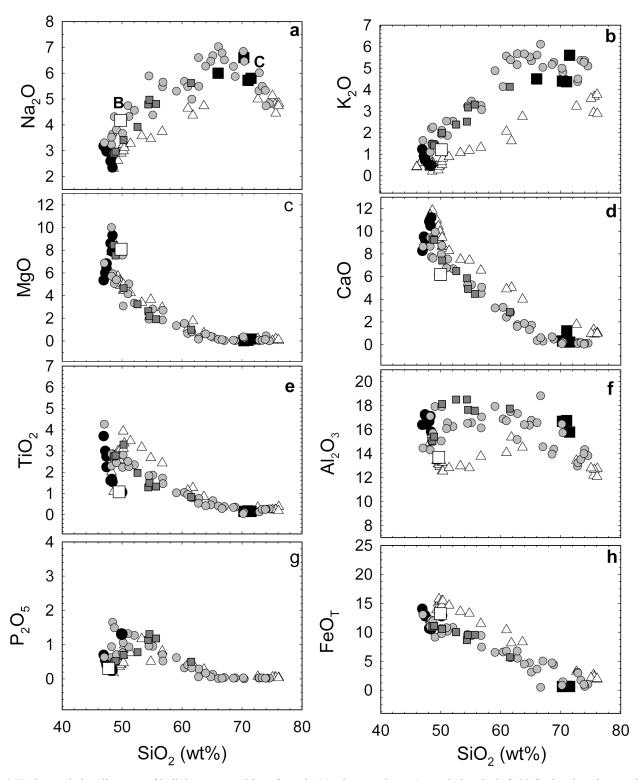


Fig. 6. Harker variation diagrams of bulk lava compositions from the Nandewar volcano (gray circles; Stolz [1985]) showing characteristic Trend 1 liquid evolution. Black squares indicate rhyolitic glass compositions from Chassigny melt inclusions (Johnson et al. 1991). The composition of the Martian rock "Backstay" (McSween et al. 2006) is shown by the large black circle. Experimental liquids are shown by small dark gray squares and correspond to those of Fig. 5. Small black circles show the compositional evolution of liquids residual to crystallization of continental olivine tholeite at 9.3 kbar and 0.35 wt% water (from Whitaker et al. [2005]). Shown for comparison are bulk lava compositions from Thingmuli, Iceland (open triangles; Carmichael [1964]) which show the typical low-pressure tholeitic liquid line-of-descent.

Table 4. Compositions of selected residual liquids along the crystallization path of the mafic hawaiite of Table 1 at 9.3 kbar and 2 wt% bulk H₂O (modified from Nekvasil et al. 2004).

1120	1050	
1130	1030	
47.2	50.37	
2.69	1.89	
14.88	17.7	
10.69	9.6	
0.14	0.12	
7.27	3.10	
8.91	6.21	
2.86	3.75	
1.36	2.28	
0.5	0.75	
96.5	95.8	
	2.69 14.88 10.69 0.14 7.27 8.91 2.86 1.36 0.5	47.2 50.37 2.69 1.89 14.88 17.7 10.69 9.6 0.14 0.12 7.27 3.10 8.91 6.21 2.86 3.75 1.36 2.28 0.5 0.75

are remarkably similar to the rhyolite glass within Chassigny polyphase melt inclusions (Fig. 6).

The presence of alkalic magmas on Mars is supported by the compositions of the Gusev rocks Wishstone, Irvine, and Backstay, whose compositions (McSween et al. 2006) were analyzed by the MER Spirit. Of these, the composition of Backstay is consistent with Trend 1 alkalic compositions (Figs. 5 and 6). Of particular note is Martian "hawaiite" Backstay, which differs from terrestrial silica-saturated hawaiite primarily in its lower Ti and slightly lower Al content, as shown in Fig. 6. These differences are retained upon comparison of terrestrial tholeite and the Gusev picrobasalts (Nekvasil, unpublished data) and may indicate the nature of innate differences between Martian and terrestrial hawaiites and basalts.

Alkalic magma is likely not restricted to the Columbia Hills of Gusev crater. Deconvolution of TES data of the Martian surface using an expanded database that includes data from minerals in alkalic rocks from the Nandewar volcano suggests the possible presence of scattered alkalic magmatism in Martian Surface Type I (Wyatt et al. 2003) regions (Dunn and McSween 2006).

Tholeiitic versus Alkalic Parental Liquids

If the melt trapped in olivine were alkalic (ranging from mildly alkalic basalt for NWA 2737 to hawaiitic for Chassigny), does this require that the melt parental to the chassignites is alkalic? Whitaker et al. (2005) determined experimentally that tholeiitic basalt from the Snake River Plain can give rise to hawaiitic magma if crystallized above 4.3 kbars and with magmatic water contents above 0.4 wt% (Fig. 6). At the crystallization stage that can produce the chassignite assemblages, the tholeiitic character of the coexisting liquid is replaced by silica-saturated alkalic character (induced by crystallization of a pyroxene-rich assemblage). In this way, tholeiitic magma could be parental to the

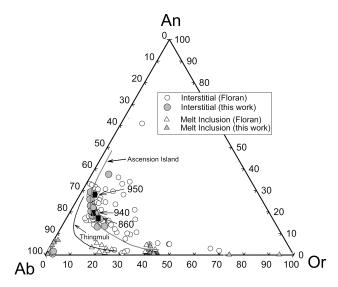


Fig. 7. Compositions of feldspar glasses from the Chassigny meteorite and from crystallization experiments on the Nandewar hawaiite (symbols and references as in Fig. 2). Natural feldspars from Ascension Island (a Trend 1 suite) lie along the dark gray curve (based on data from Harris [1983]). Those from Thingmuli lavas (a low-pressure intra-plate tholeiitic suite) lie along the black curve (from Carmichael 1964).

chassignites, while the more evolved liquid trapped in growing olivine is alkalic.

The transition from tholeiitic to alkalic character has only been noted experimentally at elevated pressure. Tholeiitic liquids crystallizing at low pressure retain their tholeiitic character throughout the crystallization stages (e.g., Juster et al. 1989). The residual liquids produced during lowpressure differentiation are quite different than those produced at elevated pressure (as shown in Fig. 6) and do not lead to the alkali-rich rhyolite seen in the melt inclusions of the Chassigny meteorite. Furthermore, the crystallizing assemblages along this low-pressure liquid trend consist of combinations of olivine, plagioclase, low-Al clinopyroxene, magnetite, and ilmenite, until silicic liquid compositions are reached (e.g., Spulber and Rutherford 1983; DiFrancesco et al. 2003). These assemblages are inconsistent with the olivine-high-Al clinopyroxene-orthopyroxene-kaersutite-(Tibiotite)-apatite-ilmenite assemblages of the Chassigny polyphase melt inclusions that lead to the sodic silicasaturated alkalic liquids along Trend 1 of Fig. 3. In addition, as shown in Fig. 7, the feldspars crystallizing along the tholeiitic path deviate significantly from the feldspar glass seen in the Chassigny meteorite. This contrasts with the excellent agreement between the high-pressure feldspars of terrestrial silica-saturated alkalic suites and the maskelynite compositions of the Chassigny meteorite (Fig. 7).

Relatively unevolved tholeiitic rocks have been found on the Martian surface and are represented by the Gusev picrobasalts Adirondack, Humphrey, and Mazatzal (Gellert et al. 2004). An intriguing question that remains is whether

such picrobasalts reflect, at least in part, liquids that could be parental to the chassignites, and whether they evolve to Backstay-like liquids (McSween et al. 2006). Coupled with this is the question whether the hawaiite Backstay could give rise to the chassignite melt inclusion assemblage.

Constraints on Ascent History

The cumulus and melt inclusion assemblages of the Chassigny suggest a significant crystallization interval at depths below 30 km. But how did this cumulate material make its way to the near-surface environment where it was available for meteorite bombardment? On Earth, sodic silicasaturated alkalic magmas show multiple evidence for a polybaric history, with a highest pressure stage that involves the earliest fractionation history from a primitive melt to the more evolved mildly alkalic basalt, followed by a highpressure stage (above 4.3 kbar) where Chassigny-like cumulate assemblages form, and finally a low-pressure, perhaps subvolcanic, stage of crystallization. Evidence for this second stage of crystallization is commonly preserved in megacrystic high-Al pyroxenes and amphibole pseudomorphs. It is further preserved in the bulk compositions of the associated lavas of the suites. Finally, the intermediate- and low-pressure stages are recorded by the compositions of the phenocrysts and microlites (Nekvasil et al. 2004). Importantly, the presence of moderate- and lowpressure minerals, yet preservation of the high-pressure path in the bulk compositions, implies that crystallization at the lower pressures was not accompanied by significant fractionation. This absence of a shallow-level fractionation stage (where crystals are left behind) may explain the common presence of high pressure nodules in mafic alkalic lavas on Earth.

The chassignites may have also seen a polybaric history because of the elevated crystallization pressure of the melt inclusion phases. However, at some stage the dunite was transported close enough to the surface to be excavated during a meteorite impact. The melt inclusion phases suggest crystallization at elevated pressure to at least intermediate compositions (e.g., trachyandesite). If thermal equilibrium was maintained between the cumulus olivine and host melt, the hosting magma must have also cooled and evolved in part at a depth of >30 km. Mobilization and ascent of this evolving magma may have resulted in accidental entrainment of some of the fractionated material as cognate dunite nodules. Alternatively, it is possible that a later batch of magma incorporated some of the fractionated material. This new batch of magma could not be hotter than the evolved trachyandesitic liquid in equilibrium with the kaersutitebearing melt inclusion assemblage. If it were, heating of the incorporated fractionated material would have melted the lower temperature kaersutite-bearing assemblage in the melt inclusions, and, after ascent of this magma toward the surface, only a low-pressure assemblage would form in the melt inclusions.

SUMMARY

Terrestrial silica-saturated hawaiite produces many of the mineral characteristics of the cumulus and melt inclusion assemblages observed in the chassignites as well as the alkalirich residual rhyolite of the polyphase melt inclusions. The melt inclusion assemblage requires some extent of fractionation of such hawaiite at depths of at least 30 km within the Martian crust. The rock Backstay analyzed by the MER Spirit may exemplify a Martian version of such hawaiite. On Earth, silica-saturated hawaiite can be produced by crystallization of tholeiite at pressures above 4.3 kbar and water contents above 0.4 wt%. This suggests the possibility that a terrestrial-like tholeiitic liquid could be parental to the chassignites. Such parental liquids may be exemplified by the Gusev picrobasalts, Humphrey, Adirondack, and Mazatzal. Neither low-pressure crystallization of tholeiite nor crystallization of silica-undersaturated alkalic liquids can produce the melt inclusion assemblages.

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