

The chlorine isotopic composition of Martian meteorites 1: Chlorine isotope composition of Martian mantle and crustal reservoirs and their interactions

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Abstract—The Martian meteorites record a wide diversity of environments, processes, and ages. Much work has been done to decipher potential mantle sources for Martian magmas and their interactions with crustal and surface environments. Chlorine isotopes provide a unique opportunity to assess interactions between Martian mantle-derived magmas and the crust. We have measured the Cl-isotopic composition of 17 samples that span the range of known ages, Martian environments, and mantle reservoirs. The ³⁷Cl of the Martian mantle, as represented by the olivine-phyric shergottites, NWA 2737 (chassignite), and Shergotty (basaltic shergottite), has a low value of approximately -3.8‰ . This value is lower than that of all other planetary bodies measured thus far. The Martian crust, as represented by regolith breccia NWA 7034, is variably enriched in the heavy isotope of Cl. This enrichment is reflective of preferential loss of ³⁵Cl to space. Most basaltic shergottites (less Shergotty), nakhlites, Chassigny, and Allan Hills 84001 lie on a continuum between the Martian mantle and crust. This intermediate range is explained by mechanical mixing through impact, fluid interaction, and assimilation-fractional crystallization.

INTRODUCTION

Chlorine has many unique chemical characteristics. Chlorine is a moderately volatile element and is strongly hydrophilic. It does not exhibit appreciable isotopic fractionation at high temperatures, but may fractionate significantly at low temperatures (Kaufmann et al. 1984; Sharp et al. 2007, 2013). Nearly half of Earth's Cl resides in the oceans and evaporites (Sharp and Draper 2013), and most reservoirs have minimal isotopic variability (Sharp et al. 2007). Cl is also strongly incompatible in magmatic systems, which has left the terrestrial mantle depleted with respect to Cl (Sharp and Draper 2013).

Mars is volatile rich and is enriched in chlorine relative to Earth by a factor of three (Dreibus and Wänke 1985; Keller et al. 2006; Filiberto and Treiman 2009; Taylor et al. 2010; Sharp and Draper 2013).

Remote sensing data indicate that the Martian surface has a high Cl concentration ranging from 0.2 to over 1.0 wt%, with an average of 0.49 wt% (Keller et al. 2006). These data also indicate that the highest Cl concentrations can be found in the equatorial region of the Medusae Fossae Formation. This region has been subjected to prolonged volcanic activity, suggesting that volcanic degassing has made a significant contribution to the concentration of Cl at the Martian surface (Keller et al. 2006). In addition, Cl appears to be an important tracer for past surficial water because it is concentrated within topographic lows at the surface, presumably by evaporation of surficial waters in basins and craters (Osterloo et al. 2006, 2010; Tosca and McLennan 2006). The reservoirs of this crustal chlorine, as determined by Martian meteorites and remote sensing observations, are apatite, NaCl, glass, amphiboles, sheet silicates,

scapolite, chloride deposits, Cl-rich dust, and perchlorate (e.g., Bridges and Grady 1999; Keller et al. 2006; Osterloo et al. 2006, 2010; Sautter et al. 2006; Hecht et al. 2009; McCubbin et al. 2009, 2012, 2013, 2016a; Bogard et al. 2010; Filiberto et al. 2014). The absence of plate tectonics on Mars (Spohn et al. 2001; Breuer and Spohn 2003) has kept the mantle isolated from the crust and has preserved distinct crustal and mantle reservoirs of Cl (McCubbin et al. 2016a).

The crust of Mars has also experienced a high degree of alteration resulting from various weathering mechanisms (Chan et al. 2008; Carter et al. 2015; Jain and Chauhan 2015) and has interacted with an atmosphere that is highly fractionated, isotopically (Pepin 1994; Bogard 1997; Gillmann et al. 2011). Numerous studies have documented that atmophile isotopic systems such as Xe, Kr, Ar, and H are fractionated in the atmosphere relative to the composition of the primitive Martian mantle (Owen et al. 1977; Becker and Pepin 1984; Marti et al. 1995; Bogard 1997; Mathew and Marti 2001; Usui et al. 2015). The isotopic evolution of the Martian atmosphere is largely attributed to hydrodynamic escape and interaction with solar wind (Chassefière and Leblanc 2004). However, with the exception of hydrogen, these elements are extremely atmophile and occur in low concentrations in Martian meteorites (e.g., Marti et al. 1995; Bogard 1997). The moderately volatile, lithophile, and hydrophile nature of Cl should allow it to be fractionated similar to the atmophile elements on Mars, yet still be incorporated into Martian surface materials.

Most Martian meteorites represent mantle-derived magmas that experienced varying degrees and types of interactions with the Martian crust and/or atmosphere (Wadhwa 2001; Herd et al. 2002; Borg and Draper 2003; Symes et al. 2008; Papike et al. 2009; Shearer et al. 2013; Peters et al. 2015), so they represent our best opportunity to simultaneously investigate the compositions of mantle, crustal, and atmospheric reservoirs on Mars. In many previous studies, differences in REE geochemistry, radiogenic isotopic systematics, and oxygen fugacity were used to differentiate between various geochemical reservoirs on Mars. The intent of this study is to extend our knowledge of Martian geochemistry by determining the isotopic composition of Cl in a suite of Martian meteorites. The Cl-isotopic data are interpreted within the context of previous studies on Martian meteorite geochemistry and petrology to determine the Cl-isotopic composition of the Martian mantle and crust, the origin of their Cl-isotopic compositions, and the interactions among mantle and crustal reservoirs.

ANALYTICAL METHODS

The distribution of Cl in Martian meteorites and Cl-isotopic compositions of both individual phases and bulk meteorites were examined using electron probe microanalysis (EPMA), secondary ion mass spectrometry (SIMS), and conventional gas source isotope ratio mass spectrometry. The Martian meteorites analyzed for this study are listed in Table 1. The petrography of the individual meteorite samples are discussed in detail in a companion manuscript (Sharp et al. 2016).

Electron Probe Microanalysis and Imaging

Thin sections of selected Martian meteorites were initially documented using backscattered electron (BSE) imaging on the JEOL JXA-8200 Superprobe electron microprobe at UNM. Once suitable areas were identified, wavelength dispersive X-ray maps were collected for Ca, P, Cl, and F and energy dispersive maps were collected for Mg, Al, and Fe. Maps were generated using a 15 kV accelerating voltage, a 100 nA beam current, and a dwell time of 800 ms pixel⁻¹. These X-ray maps identified the distribution of Cl-bearing phases and potential targets for SIMS analyses. Quantitative EPMA analyses were conducted on apatite and glasses using an accelerating voltage of 15 kV, a beam current of 20 nA, and a spot size varying from 1–3 μm . Standards for the apatite point analyses consisted of a suite of C.M. Taylor Company mineral and synthetic standards, as well as select, inhouse, mineral standards. Cl was standardized using an inhouse Sodalite standard (Sharp et al. 1989). Stoichiometric constraints were used to determine the quality of the EPMA analyses, and detection limits were calculated at the 3 σ level.

Bulk Mass Spectrometry Analyses

The method for bulk chlorine extraction and analysis used in this study are modified from Eggenkamp (1994). Samples are crushed to a fine powder and leached with 18M Ω H₂O for a minimum of 4 days to remove water-soluble chlorine, which has a high likelihood of containing terrestrial contamination. There is potential for the water-soluble Cl, especially in falls, to contain a Martian-crustal signature. However, due to the difficulty in distinguishing terrestrial Cl from Martian-crustal Cl, this work will focus only on the structurally bound Cl. The water-soluble chloride is preserved and analyzed. After leaching, the samples are melted in an H₂O vapor stream (Magenheim et al. 1994). The structurally bound chlorine is volatilized,

Table 1. ^{37}Cl values and Cl concentrations of all Martian meteorites measured by bulk rock analysis and secondary ion mass spectrometry analysis.

Petrologic type	Sample	$\delta^{37}\text{Cl}$ (‰ versus SMOC)			Cl (ppm)		
		SIMS	Bulk	Water-soluble	Bulk	Water-soluble	
Olivine-phyric shergottites	Dhofar 019	-1.60			22		
		-0.60					
	RBT 04261	-3.50			-		
		-2.50					
		-2.80					
	LAR 06319	-2.80			-		
		-3.80					
	EETA 79001-A		-2.65		180		
	Tissint Bulk		-0.60		22		
Tissint Glass		-2.04	-0.43	69	136		
Tissint Igneous		-2.89	0.4	30	174		
Basaltic shergottites	NWA 2975		0.10		24		
		Los Angeles	-0.40	-0.30	-0.50	115	10
		-0.60					
	Shergotty		-3.30		108		
	Zagami		-0.09	0.40	49	28	
	EETA 79001-B		0.22		42		
	Augite basalt	NWA 8159		1.5		-	
	Nakhlites	NWA 5790		1.8	0.4	72	11
		NWA 817		0.38		117	
Chassignites	NWA 2737		-3.85				
	Chassigny	0.4			-		
Regolith breccia	NWA 7034	0.3					
		0.4					
		0.4					
		0.5					
		0.5					
		0.5					
		0.5					
		0.6					
		0.6					
		0.7					
		0.7					
		0.7					
		0.9					
		1.1					
		1.1					
		1.4					
		1.5					
0.1							
8.6							
Orthopyroxenite	ALH 84001	1.4				-	

carried by the H_2O vapor stream, and recondensed as chloride into solution. The aqueous chloride solution is reacted with nitric acid for 12 h to volatilize any contaminant sulfur and then reacted with AgNO_3 to form $\text{AgCl}(s)$. The AgCl is vacuum filtered using GF/F glass filter paper and dried at 80°C . The AgCl is reacted with excess CH_3I in evacuated glass tubes at 80°C for 48 h to quantitatively convert AgCl to

CH_3Cl . CH_3I and CH_3Cl contained in the sealed tube are released into a helium stream using a tube cracker. Next, the gasses are cryofocused using liquid nitrogen. The gas is then passed through a custom-made glass GC column at 85°C to separate CH_3Cl from CH_3I . The purified CH_3Cl is measured on a Delta XL plus mass spectrometer in continuous flow mode. The flow of gas is reversed as soon as the CH_3Cl peak has been

analyzed to avoid the introduction of CH_3I into the mass spectrometer. The two CH_3Cl peaks (mass 50 and 52) are integrated, and the ratio is taken relative to a calibrated internal standard. The long-term external reproducibility of ^{37}Cl is $\pm 0.25\%$ based on analysis of an inhouse seawater standard (Barnes et al. 2006; Sharp et al. 2007, 2010a, 2010b; Selverstone and Sharp 2011). Concentrations are determined by measuring external standards that span a range of known concentrations during the analytical session. The integrated peak areas of each sample are then compared to the standards to quantify the Cl concentration.

In addition to a bulk rock analysis, a sub split of the meteorite Tissint was separated into two components consisting of glass in one and crystalline material, similar to the materials that comprise the other Martian meteorites, in the other. The glass separate was dominated by a Martian impact glass component (Aoudjehane et al. 2012), but it probably had a small igneous glass component as well. This sample was crushed and then handpicked under a microscope. The glass fraction of Tissint was leached in $18\text{M}\Omega$ H_2O for 2 weeks prior to further extraction to ensure all water-soluble Cl was leached (similar to Sharp et al. [2010a] for the Apollo 17 picritic glass beads).

All Cl isotope measurements (classical mass spectrometry and secondary ion mass spectrometry) are reported in standard delta notation.

The inhouse standard used for chlorine isotope measurements is Carmel seawater, which we have measured and confirmed is indistinguishable from Standard Mean Ocean Chloride (SMOC), hence it has a value of 0% by definition (Kaufmann et al. 1984).

Secondary Ion Mass Spectrometry Analysis

In situ ion microprobe analyses were made on the large radius Cameca ims 1270 ion microprobe at UCLA using a Cs^+ primary beam focused to $\sim 10\text{--}20\ \mu\text{m}$ following procedures outlined in Sharp et al. (2010a). Secondary ions were measured simultaneously for mass 35 and 37 on Faraday cup detectors with equivalent count rates of $2\text{--}5 \times 10^7\text{cps}$ for $^{35}\text{Cl}^-$. The measurements were made at sufficiently high mass resolution so as to eliminate all isobaric interferences, including $^{34}\text{SH}^-$ (Layne et al. 2004). We have developed two apatite standards for calibration: Durango apatite with a concentration of 0.37 wt% Cl and a $\delta^{37}\text{Cl}$ value of $+0.33\%$ and a synthetic Cl-apatite from the University of Heidelberg with a Cl concentration of 5.5% and a ^{37}Cl value of $+2.8\%$. The ^{37}Cl values of these standards were previously determined by gas source mass spectrometry using the method described

above. Precision of individual spot analyses ranged from 0.2% to 1.2% $1\sigma\text{SD}$ depending on concentration of Cl in the apatite. External reproducibility is in the range of 0.5% for apatite with percent-level Cl concentrations like those of typical Martian meteorites (McCubbin et al. 2012, 2013, 2016a).

RESULTS

We collected bulk rock analyses of Cl isotopes and in situ Cl-isotopic data from Cl-rich apatites in a wide range of Martian meteorite petrologic types. Additionally, we divided the olivine-phyric shergottite Tissint into primary crystalline material and a glass component to determine the Cl-isotopic composition of each. The results from both bulk rock and apatite analyses are presented in Tables 1 and 2 and illustrated in Figs. 1 and 2. Bulk rock analyses of all the Martian meteorites range from -3.9% to $+1.8\%$, and individual in situ apatite values range from -3.8% to $+8.6\%$. In the samples in which both bulk rock and apatite measurements were made, they were found to be nearly equal (Fig. 1). For example, bulk rock analyses for Los Angeles and NWA 7034 are -0.3% and $+1.0\%$, respectively, whereas individual apatite analyses range from -0.4% to -0.6% for Los Angeles and $+0.1\%$ to $+8.6\%$ (with an average of $+1.2\%$) for NWA 7034. Based on the agreement between apatite and bulk rock data in the instances where we collected both, we conclude that the in situ data and bulk rock data likely provide similar information, so we can proceed with discussing and grouping data for specific petrologic types when we have collected only in situ or bulk rock data as opposed to both.

Overview of Cl-Isotopic Results with Petrologic Types

When we grouped the meteorites based on their petrologic type, we observed several systematic trends with respect to Cl-isotopic compositions among the various Martian meteorite lithologies, which are illustrated in Fig. 1. (1) Both LREE-enriched and depleted olivine-phyric shergottites Elephant Moraine 79001 lithology A, Roberts Massif 04261, Larkman Nunatak 06319, and Dhofar 019 have low ^{37}Cl values between -2.7% and -3.8% (Fig. 1). The one exception to this range is the bulk rock value for LREE-depleted olivine-phyric shergottite Tissint, which yielded a bulk rock $\delta^{37}\text{Cl}$ value of 0.6% . This anomalously high value is investigated more closely in the Cl-Isotopic Determination of Primary and Secondary Components in Tissint section. (2) The basaltic shergottites analyzed in this study are enriched (Los Angeles, Shergotty, Zagami, NWA 2975) and intermediate (EETA 79001 lithology B)

Table 2. Cl isotope ratios and Cl concentrations from apatite in basaltic breccia NWA 7034 determined from in situ measurements (Cl isotope ratios were measured using SIMS, and Cl concentrations were determined using EPMA). Clast types follow Santos et al. (2015).

Grain (number of spots)	Average $\delta^{37}\text{Cl}$ value (standard deviation)	Average Cl content (standard deviation)	Clast type
1B,2 Grain 1 (4)	0.13 (0.07)‰	5.68 wt%	Mineral fragment
1B,2 Grain 2 (1)	0.49	4.84 (0.20)	FTP clast 1
1B,2 Grain 3 (1)	0.73	5.08	Mineral fragment
1B,2 Grain 4 (2)	0.70 (0.03)	5.11 (0.18)	Mineral fragment
1B,2 Grain 5 (1)	0.43	4.91 (0.05)	Mineral fragment
1B,2 Grain 6 (2)	8.59 (0.59)	4.79	Lithic clast fragment
3A,3 Grain 1 (2)	1.45 (0.10)	5.13	FTP clast 12
3A,3 Grain 2 (1)	0.46	5.14 (0.04)	FTP clast 12
3A,3 Grain 3 (1)	0.60	5.14	FTP clast 12
3A,3 Grain 4 (2)	0.44 (0.10)	4.69 (0.22)	Lithic clast fragment
3A,3 Grain 5 (2)	0.73 (0.03)	5.08 (0.09)	Mineral fragment
3A,3 Grain 6 (1)	0.61	5.05 (0.13)	Melt clast
3A,3 Grain 7 (1)	0.37	5.31	Lithic clast fragment
3A,3 Grain 8 (2)	0.46 (0.09)	4.42 (0.18)	Mineral fragment
3A,3 Grain 9 (1)	0.87	5.01 (0.30)	Mineral fragment
2,3 Grain 1 (1)	1.36	4.78	Mineral fragment
2,3 Grain 2 (1)	1.06	4.83 (0.05)	Mineral fragment
2,3 Grain 3 (2)	1.05 (0.29)	4.80	FTP clast
2,3 Grain 4 (2)	0.48 (0.10)	4.18 (1.07)	Mineral fragment

shergottites. They exhibit only minor variation in the $\delta^{37}\text{Cl}$ values (-0.3 to $+0.2$) with the exception of Shergotty, which has a $\delta^{37}\text{Cl}$ value of -3.3 ‰. The $\delta^{37}\text{Cl}$

value of Shergotty is similar to the olivine-phyric shergottites. (3) Other Martian meteorites, exclusive of the shergottites such as the nakhlites, chassignites, regolith breccia NWA 7034, orthopyroxenite (ALH 84001), and augite basalt (NWA 8159), have positive $\delta^{37}\text{Cl}$ values (Figs. 1 and 2), with the exception of chassignite NWA 2737 (-3.85 ‰), which is similar to the

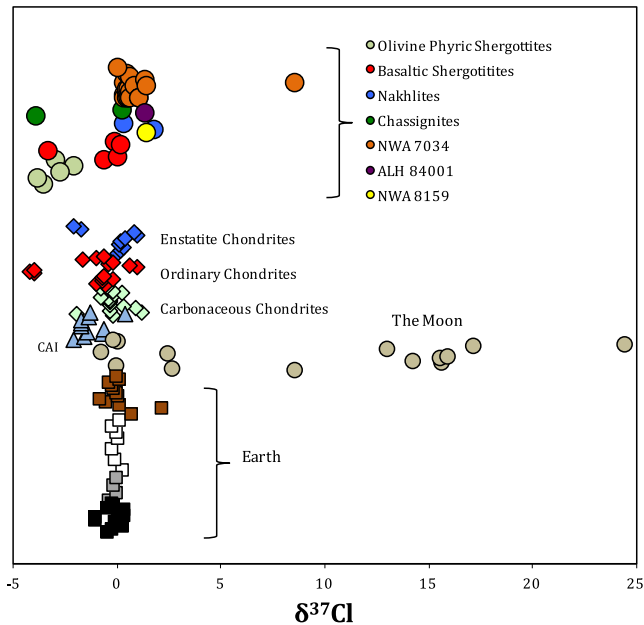


Fig. 1. Cl isotope compositions of planetary bodies (Sharp et al. 2007, 2010a, 2010b, 2013, 2016). Symbols for bulk Earth are: brown = evaporites, white = halite inclusions from kimberlite, gray = carbonite, black = MORB. Averages are used for samples with multiple measurements except for NWA 7034.

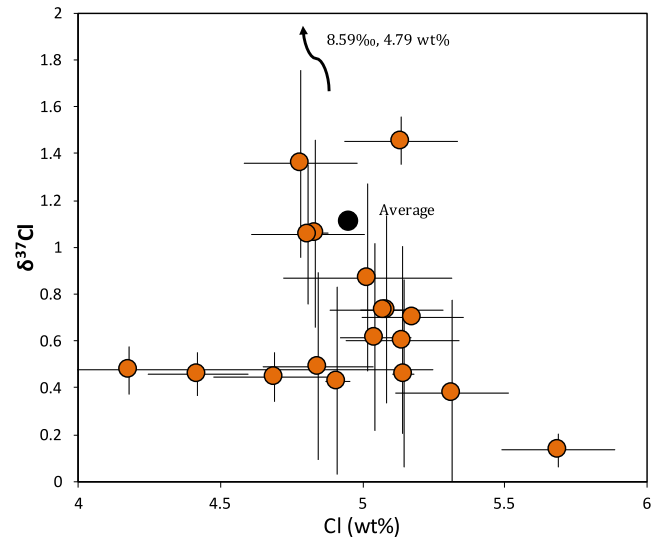


Fig. 2. In situ measurements of apatite grains in all clasts analyzed from NWA 7034. Outlier point at $\delta^{37}\text{Cl} = 8.59$ ‰ not shown in figure. Error bars are 1σ .

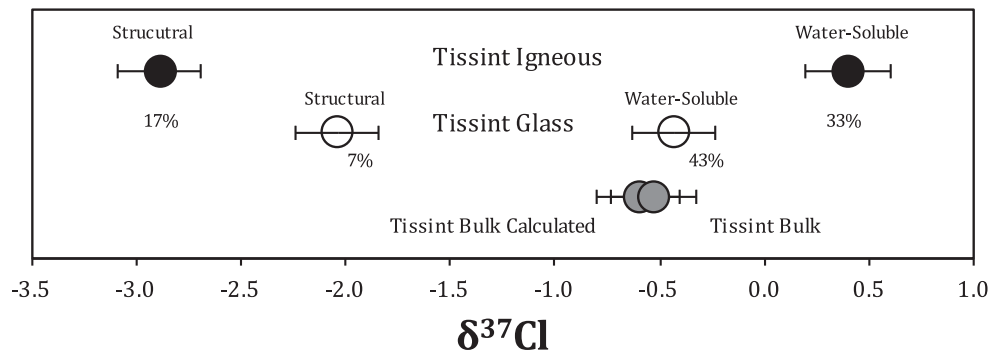


Fig. 3. $\delta^{37}\text{Cl}$ value of all Tissint separates measured as well as the percent of the total Cl from each fraction.

light $\delta^{37}\text{Cl}$ values exhibited by the olivine-phyric shergottites and Shergotty. Exclusive of NWA 2737, Chassigny and the nakhlites we analyzed exhibit ^{37}Cl values between 0.3‰ and 1.8‰ (Table 1). Although NWA 7034 has a bulk rock $\delta^{37}\text{Cl}$ value (1‰) similar to Chassigny and the nakhlites, the in situ analyses of apatite exhibit a large variation in ^{37}Cl values (+0.1‰ to +8.6‰), with an average ^{37}Cl value for apatite of 1.2‰. The range in values in NWA 7034 apatites is likely linked to the different types of clasts incorporated into this sample, which appear to have originated from various types of crustal sources (Santos et al. 2015). The apatites within cumulate orthopyroxenite ALH 84001 have a ^{37}Cl value of 1.4‰. We did not encounter any apatites in augite basalt NWA 8159, but we determined a bulk rock ^{37}Cl value of 1.5‰.

Cl-Isotopic Determination of Primary and Secondary Components in Tissint

The olivine-phyric shergottite Tissint was a witnessed fall in 2011, and it represents our most recent Martian meteorite fall with minimal terrestrial contamination (Aoudjehane et al. 2012). Given the propensity for terrestrial contamination of Cl in meteorites with substantial terrestrial residence times, Tissint presented an opportunity to investigate both the water-soluble and insoluble Cl portions to gain insight into Martian Cl. Furthermore, Tissint is a highly shocked meteorite with numerous black glassy veins interpreted to be impact melt with trapped Martian atmosphere based on excess ^{15}N (Aoudjehane et al. 2012). Consequently, Tissint also provides the opportunity to investigate the Cl-isotopic composition of both the igneous and secondary impact components on Mars.

We did not encounter Cl-rich apatite in Tissint, so we only conducted bulk rock analyses of Cl isotopes. As indicated in the Overview of Cl-Isotopic Results with Petrologic Types section, the bulk rock measurement for Tissint is 0.6‰, which is higher than

the range exhibited by all of the other olivine-phyric shergottites (i.e., $-2.7‰$ and $-3.8‰$; Table 1). However, we also analyzed the Cl-isotopic composition of igneous (crystalline) and impact glass (black glass) separates in Tissint, which exhibit minor, resolvable, variations in Cl isotopes for structurally bound Cl ($-2.9‰$ and $-2.0‰$, respectively) (Table 1, Fig. 3). Given the low degree of terrestrial contamination of Tissint, we also analyzed the water-soluble chlorine of the glass fraction and the igneous fraction, which had $\delta^{37}\text{Cl}$ values of $-0.4‰$ and $0.4‰$, respectively (Table 1).

DISCUSSION

Comparison of Mars to Variations of Cl Isotopes in the Solar System

Over the last decade our group has determined the Cl-isotopic compositions of numerous materials representing a variety of planetary environments including chondrites, the Moon, and the Earth (Fig. 1). Mars provides a unique planetary environment to compare the nature and behavior of Cl isotopes. The differences are discussed in greater detail in our companion paper, Sharp et al. (2016). The bulk Earth has a $\delta^{37}\text{Cl}$ value of 0‰ (Sharp et al. 2007). The Moon has a large variation in $\delta^{37}\text{Cl}$ values, up to +35‰, but the undegassed, “primitive” $\delta^{37}\text{Cl}$ value is thought to be close to 0‰, similar to the Earth (Sharp et al. 2007; Shearer et al. 2014b; Tartèse et al. 2014; McCubbin et al. 2015); however, there is an inexplicably light value of $-4‰$ recorded in apatite from lunar meteorite Miller Range (MIL) 05035 (Boyce et al. 2015). The averages of each chondrite class are indistinguishable from one another and overlap the bulk Earth value. These data were interpreted as evidence for a homogenous solar nebula with respect to Cl isotopes (Sharp et al. 2007, 2010a, 2013).

The bulk Martian meteorites and apatites have a much larger variation in $\delta^{37}\text{Cl}$ values (-3.85 to $+8.6‰$) than observed in deep-sourced rocks from the Earth,

but not as broad as lunar samples (Fig. 1). However, many of the mantle-derived olivine-phyric shergottites, the chassignite NWA 2737, and Shergotty are distinctly isotopically light compared to the terrestrial mantle, most chondrites, and all lunar samples (sans MIL 05035). The negative $\delta^{37}\text{Cl}$ values are difficult to explain in terms of known fractionation or mixing processes as discussed in the companion paper Sharp et al. (2016). Although previous studies had reported that most chondrites, presumed to represent the solar nebula, have a $\delta^{37}\text{Cl}$ value of $\sim 0\text{‰}$ (Sharp et al. 2007, 2013), Sharp et al. (2016) point out that the samples studied previously had all been thermally altered to varying degrees and may not represent the primary Cl-isotopic composition of the solar nebula. Consequently, Sharp et al. (2016) analyzed an unaltered 3.00 chondrite, NWA 8276 (a pairing with NWA 7731), which yielded a $\delta^{37}\text{Cl}$ value of -4.5‰ , similar to the chondrite Parnallee (Sharp et al. 2013). Sharp et al. (2016) interpret the values from NWA 8276 and Parnallee as representative of the primitive solar nebula and posit that this primary nebula value has been recorded by a subset of the Martian meteorites analyzed in the present study. Furthermore, it could explain the anomalously light $\delta^{37}\text{Cl}$ value of -4‰ reported for apatite within lunar meteorite MIL 05035 (Boyce et al. 2015). Given that Mars is known to have accreted exceptionally fast compared to the other terrestrial planets (Dauphas and Pourmand 2011), it could have recorded a primary nebular value within its interior during accretion, hence these light values are likely to represent the value of the Martian mantle.

The heavy Cl-isotopic enrichments measured in Martian samples representative of the Martian crust, such as apatite grains in NWA 7034 (regolith breccia), are unlike those observed at the Earth's surface but similar in their ^{37}Cl enrichment to soils and breccias from the Moon (Fig. 1; Sharp et al. 2010a; Shearer et al. 2014b). Furthermore, they are similar to the heavy Cl-isotopic reservoir of the urKREEP component that is recorded in KREEP-rich basalts and highlands magnesian- and alkali-suite rocks (Sharp et al. 2010a; Boyce et al. 2015; McCubbin et al. 2015; Shearer et al. 2015a).

Martian Mantle and Crustal Chlorine Reservoirs

Martian Crust

With respect to many geochemical parameters, the bulk composition of NWA 7034 mimics that of the bulk composition of the Martian crust as portrayed by the 2001 Mars Odyssey Gamma Ray Spectroscopy (MOGRS) data (Keller et al. 2006; Boynton et al. 2007; Agee et al. 2013). The bulk composition of NWA 7034

also mimics many of the proposed geochemical and spectral characteristics of the Martian crust (e.g., Norman 1999; McLennan 2001; McSween et al. 2009; Taylor and McLennan 2009; Cannon et al. 2015). For example, REE patterns for NWA 7034 have similar slopes and concentrations to those predicted for the Martian crust (Nyquist et al. 2016). Further, this sample has recently been shown to contain the first Martian sedimentary clast (Wittmann et al. 2015; McCubbin et al. 2016b). The high Cl concentration of 2200 ppm for NWA 7034 is the highest measured in any Martian sample, but still at the lower end of the Cl concentration range of the surface of Mars (Agee et al. 2013; Shearer et al. 2014a). Based on the presence of crustal materials and the chemical similarities to bulk Martian crust, we find it appropriate to use the isotopic composition of this sample as representative of the Martian crust.

The $\delta^{37}\text{Cl}$ values determined by in situ analysis of NWA 7034 apatites indicate that the Martian crust is enriched in heavy Cl relative to the Martian mantle, which will be discussed later in detail. The variability in this enrichment ($^{37}\text{Cl} = 0.1\text{--}8.6\text{‰}$) could indicate differences in the amount of crustal Cl assimilated in various clasts, or more likely, that the crust of Mars is heterogeneously enriched in the heavy isotope of Cl. Figure 2 plots all in situ measurements of $\delta^{37}\text{Cl}$ values versus measured Cl concentrations. The majority of apatites in this breccia have a narrow range of Cl-isotopic compositions and concentrations. One clast, 1B,2 Grain 6 (lithic clast fragment), has an apatite with a $\delta^{37}\text{Cl}$ of 8.60‰ and a concentration of 4.79 wt% Cl. This suggests that the Martian crust was highly isotopically fractionated, relative to the mantle, since at least 1.5–1.7 Ga (Bellucci et al. 2015; Cartwright et al. 2014; McCubbin et al. 2016b). The 1.5–1.7 Ga ages are for U-Pb in apatite, metamict zircon, and bulk rock K-Ar, which has been interpreted as the age of breccia lithification originating from a thermal event (Humayun et al. 2013; Cartwright et al. 2014; Muttik et al. 2014; Bellucci et al. 2015; McCubbin et al. 2016b). The igneous components in NWA 7034 are older, up to 4.4 Ga (Humayun et al. 2013; Nemchin et al. 2014; McCubbin et al. 2016b; Nyquist et al. 2016).

The process that caused the heavy $\delta^{37}\text{Cl}$ value of the crust could be related to the same mechanism responsible for the heavy isotopic composition of Martian atmosphere elements, which would imply interaction between the Martian atmosphere and crust. Mars has lost a significant portion of its atmosphere through billions of years of interaction with solar wind (Chassefière and Leblanc 2004). Mars is susceptible to this loss in the absence of a magnetosphere. This interaction effectively strips the atmosphere and causes

large mass-dependent fractionation by preferential loss of the light isotope to space. D/H, $^{15}\text{N}/^{14}\text{N}$, and $^{38}\text{Ar}/^{36}\text{Ar}$ show large enrichments in the heavy isotope partly attributed to this sputtering reaction (e.g., Owen et al. 1977; Becker and Pepin 1984; Mathew and Marti 2001). Chlorine is likely concentrated in the Martian crust and atmosphere through volcanic degassing of HCl. HCl gas could also be produced by low-temperature fluid-rock interaction. Jarosite has been identified by the Mars Exploration Rover (MER) Opportunity (Klingelhofer et al. 2004) and within Martian meteorites (McCubbin et al. 2009). This is strong evidence that the hydrosphere of Mars may have been acidic, at least locally. If an acidic fluid interacts with NaCl it can volatilize Cl through the following reaction: $\text{NaCl (s)} + \text{H}_2\text{SO}_4 \rightarrow \text{HCl (g)} + \text{NaHSO}_4 \text{ (aq)}$. Perchlorate formation has also been shown to produce a significant volatile species of Cl (Hecht et al. 2009). Preferential loss of H^{35}Cl relative to H^{37}Cl to space through time would cause a large positive shift in the $\delta^{37}\text{Cl}$ of the atmosphere and ultimately, the crustal reservoir, leaving a isotopically light mantle reservoir ($\delta^{37}\text{Cl} \sim -3$ to -4‰) and a isotopically heavy crustal reservoir ($\delta^{37}\text{Cl} \geq 1\text{‰}$). As a first order analog, argon shows similar heavy isotope enrichment for the same overall molecular mass, so there can be little doubt that HCl gas is able to escape Martian gravity.

Additional evidence for the heavy Cl-isotopic signature being related to a surface-atmospheric component is its correlation with the sulfur isotopic composition of Martian meteorites. Sulfur is an ideal system for tracking the incorporation of material that has been at the surface of Mars. There are four stable isotopes of sulfur (^{32}S , ^{33}S , ^{34}S , and ^{36}S). Mass-independent fractionation for sulfur occurs during photochemical reactions (Thiemens 1999) and has been documented for a number of reactions involving sulfur isotopes (Farquhar et al. 2000, 2001). The most significant source of sulfur mass-independent fractionation (S-MIF) is gas phase photochemistry driven by ultraviolet (UV) radiation (Cooper et al. 1997; Farquhar et al. 2001; Rai et al. 2005; Rai and Thiemens 2007). The resulting sulfur species, characterized by an anomalous isotopic composition due to this fractionation, may subsequently transfer this fingerprint from the atmosphere to solid phases. This effect, which results in $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values that do not lie on a predicted mass-dependent array, has been documented in terrestrial sedimentary deposits and in some meteorites (Cooper et al. 1997; Farquhar et al. 2001; Rai et al. 2005; Rai and Thiemens 2007). Franz et al. (2014) reported on the $\Delta^{33}\text{S}$ anomalies in some Martian meteorites. Franz et al. (2014) interpreted these

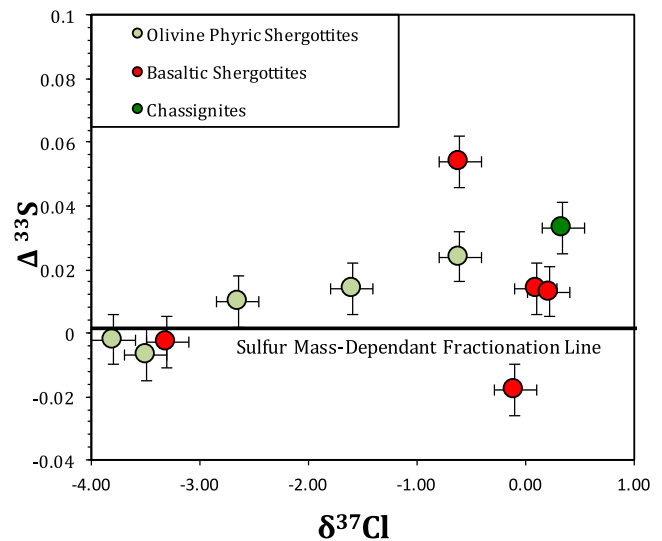


Fig. 4. Plot of $\Delta^{33}\text{S}$ versus $\delta^{37}\text{Cl}$. The sulfur mass dependant fractionation line is defined by equations in Farquhar et al. (2000, 2001). Sulfur data is from Franz et al. (2014). Error bars are 1σ . Averages are used for samples with multiple measurements.

observations as evidence for cycling of sulfur between an atmospheric reservoir where photochemical processing of sulfur-bearing gases occurred and a surface reservoir in which photochemical products were ultimately deposited. The incorporation of these S-MIF fingerprints into products of Martian magmatism implies mixing of sulfur from the Martian surface into the basalts through assimilation by lavas/magmas or interaction with crustal fluids.

A plot of ^{37}Cl versus $\Delta^{33}\text{S}$ (Fig. 4) shows that the olivine-phyric shergottites with $\delta^{37}\text{Cl}$ values of less than -3‰ (RBT 04261 and LAR06319) and basaltic shergottite Shergotty do not have a $\Delta^{33}\text{S}$ anomaly. All samples with more positive $\delta^{37}\text{Cl}$ values also have a $\Delta^{33}\text{S}$ anomaly, which is consistent with our hypothesis that positive $\delta^{37}\text{Cl}$ values are indicative of crustal assimilation. This correlation suggests that use of these isotopic systems tangentially distinguish between the primitive isotopic composition of the mantle and the crust. It further suggests that the crustal signature is characteristic of the crust for at least 1.5–1.7 billion years and, if based solely on Cl, perhaps as long as 4.1 billion years. ALH 84001 is the oldest unbrecciated sample measured with an age of 4.09 Ga (Lapen et al. 2010). Even if the metamorphic age of ALH 84001 (3.9 Ga; Borg et al. 1999) is used as the constraint for the timing of $\delta^{37}\text{Cl}$ incorporation, the results imply the previously mentioned crustal chlorine fractionation occurred within the first 500 Ma of Mars history.

Taylor et al. (2010) suggested that bulk Mars has a chondritic Cl/K ratio based on the average of orbital data from the 2001 Mars Odyssey Gamma Ray Spectrometer. However, this ratio is relatively heterogeneous and can be geographically isolated (Taylor et al. 2010). Our suggestion that the Cl-isotopic composition of the crust is representative of fractionation through mass-dependent dynamic escape suggests that the bulk Martian crust should have a sub-chondritic Cl/K if a significant proportion of Cl was lost to space. A first-order calculation assuming Grahams law diffusion ($\alpha = \frac{\text{MassH}^{35}\text{Cl}}{\text{MassH}^{37}\text{Cl}}$) with the Raleigh fractionation equation suggests approximately 36% of the crustal Cl would have to be lost to change the chlorine isotopic composition by 12‰; although if the crustal value is representative of the bulk rock value of the regolith breccia (i.e., 1‰; Table 1), it would still imply a loss of approximately 14% crustal chlorine. These calculations imply that Mars had an initial super-chondritic Cl/K because the surface is presently near chondritic (Taylor et al. 2010). Another possibility is that the Cl/K observed on the Martian surface has been influenced by degassing of Cl and hydrothermal activity that would raise the apparent Cl/K on the surface relative to its source due to the hydrophilic nature of Cl compared to K.

Recent Cl-isotopic measurements of the Martian surface have been made by the SAM instrument aboard the Curiosity rover (Farley et al. 2016). These findings suggest that the Martian crust is far lighter ($\sim -60\%$) than any other object yet measured in the solar system. This is in striking contrast to our crustal $\delta^{37}\text{Cl}$ values, which are heavier than most materials. It is unclear what the source of this discrepancy is. One possibility may be an issue in instrumental fractionation related to the difficulty of standardization by the SAM instrument. Further research needs to be done to address this issue.

Martian Mantle

The olivine-phyric shergottites, including Yamato 980459 and ALH 77005 (intermediate lherzolite), are thought to represent our closest approximations of crystallization products of primary Martian basalts. Both the olivine-phyric shergottites and basaltic shergottites exhibit an enormous range in several isotopic and geochemical signatures compared to Earth. For example, a prominent geochemical feature of the shergottites is the large range in initial Sr isotopic ratios and initial ^{14}Nd values (Nyquist et al. 1979, 2000, 2001, 2006; Shih et al. 1982, 2003, 2004, 2005; Borg et al. 1997, 2001, 2003, 2005, 2012; Brandon et al. 2004, 2012; Shearer et al. 2005, 2006, 2008; Symes et al. 2008). This range far exceeds the range observed in all terrestrial

mantle-derived basalts (Borg et al. 2005, 2012). Within this range, the shergottites do not form a radiogenic isotopic continuum, but instead, they fall into three discreet subgroups. These subgroups have distinct characteristics such as the bulk rock REE patterns, mineral chemistries (i.e., phosphate REE patterns, Ni, Co, V in olivine), and oxygen fugacity during crystallization (Wadhwa 2001; Herd et al. 2002; Borg et al. 2003, 2005; Herd 2003, 2006; Borg and Drake 2005; Shearer et al. 2006, 2008, 2015b; Symes et al. 2008).

Although there are significant geochemical differences among the depleted (Tissint), intermediate (Elephant Moraine 79001 lithology A), and enriched (Roberts Massif 04261, Larkman Nunatak 06319, Dhofar 019) olivine-phyric shergottites, these samples all have low $\delta^{37}\text{Cl}$ values, ranging from -3.8% to -2.04% . As Cl does not fractionate during high-temperature processes such as fractional crystallization and partial melting (i.e., Sharp et al. 2007; Sharp and Draper 2013), and because these samples have no direct petrographic evidence for fluid alteration, our interpretation is that these light Cl isotope values are representative of the Martian mantle (see Sharp et al. 2016). This conclusion is further supported by the S isotopic composition of these basalts. As noted earlier, the $\Delta^{33}\text{S}$ of these samples are 0‰ (Franz et al. 2014) indicating that they have not interacted with S derived from crustal-atmosphere interactions at the Martian surface (Fig. 4).

Dhofar 019 has a slightly higher $\delta^{37}\text{Cl}$ value than other olivine-phyric shergottites, $\delta^{37}\text{Cl} = -1.6\%$. However, this higher value can be attributable to secondary processes. Dhofar 019 displays strong evidence for secondary alteration including the formation of calcite and gypsum, and it exhibits extreme enrichment of Sr (Folk et al. 2001). It has been suggested that this alteration is terrestrial, as this meteorite was a find in the Oman dessert (Folk et al. 2001). However, Taylor et al. (2002) have also suggested that this alteration may have formed on the surface of Mars. It is unclear whether or not the chlorine isotopic composition of Dhofar 019 is reflective of terrestrial or Martian weathering, but it is probably not reflective of the primitive Martian mantle.

Both Shergotty (basaltic shergottite) and NWA 2737 (chassignite) exhibit light Cl-isotopic compositions (Table 1), similar to the olivine-phyric shergottites, indicating that they may record a Cl-isotopic signature from the same source as the olivine-phyric shergottites, which we attribute to a mantle signature. Shergotty is petrologically similar to the enriched basaltic shergottites Zagami and Los Angeles, and all three are geochemically enriched and relatively oxidized, but

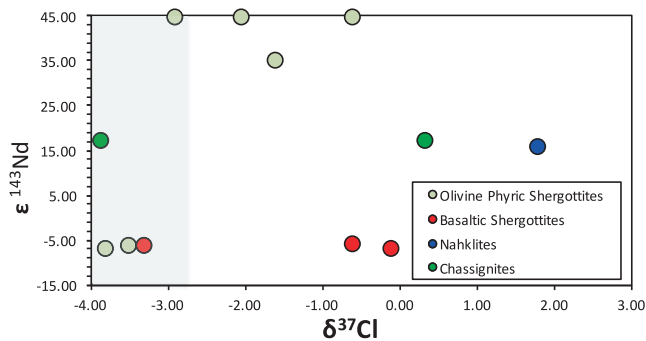


Fig. 5. Plot of $\delta^{37}\text{Cl}$ versus $\epsilon^{143}\text{Nd}$ demonstrating that across the isotopically different reservoirs, the Martian mantle has low chlorine isotope ratios. There is no difference between enriched and depleted shergottites. Nd data taken from Jagoutz and Wänke (1986); Borg et al. (2001); Nyquist et al. (2001); McCubbin et al. (2013). Averages are used for samples with multiple measurements.

Shergotty contrasts strongly with Zagami and Los Angeles in Cl isotopes (Table 1). The mantle-like $\delta^{37}\text{Cl}$ value for Shergotty corresponds to a $\Delta^{33}\text{S}$ value of 0‰, which supports the interpretation that the Cl-isotopic composition of Shergotty represents a mantle signature. In contrast, Zagami and Los Angeles both have isotopically heavy $\delta^{37}\text{Cl}$ values and both exhibit positive $\Delta^{33}\text{S}$ anomalies (Table 1; Franz et al. 2014). NWA 2737 is a cumulate igneous rock that records extensive secondary shock effects that have disrupted noble gas systematics (Marty et al. 2006) as well as D/H systematics (e.g., Giesting et al. 2015), which renders questionable a mantle interpretation for the $\delta^{37}\text{Cl}$ value of NWA 2737. However, loss of Cl through volatilization of HCl or metal chlorides typically does not affect or drives to higher values the initial $\delta^{37}\text{Cl}$ value of a sample (Sharp et al. 2010a, 2010b; McCubbin et al. 2015), so we do not attribute the low mantle-like $\delta^{37}\text{Cl}$ value of NWA 2737 (-3.85‰ , Table 1) to secondary shock effects and support the interpretation of a mantle signature.

Studies of radiogenic isotopic systems such as Sm-Nd and Rb-Sr have shown that the Martian mantle is heterogeneous and that the Martian meteorites sample at least two mantle reservoirs and perhaps more (Nyquist et al. 1979, 2000, 2001, 2006; Shih et al. 1982, 2003, 2004, 2005; Borg et al. 1997, 2001, 2003, 2005, 2012; Brandon et al. 2004, 2012; Shearer et al. 2005, 2006, 2008; Symes et al. 2008; Sarbadhikari et al. 2009, 2011). Figure 5 further demonstrates how the Cl-isotopic compositions of Martian meteorites relate to geochemical enrichment indicated by $\epsilon^{143}\text{Nd}$ values. Figure 5 illustrates that isotopically light Cl values in the range of -2.8‰ to -4‰ are recorded in Martian meteorites that span geochemically enriched,

intermediate, and depleted sources. If our interpretation that the primitive Martian mantle is homogeneously light with respect to Cl isotopes, deviations from a mantle Cl-isotopic value likely result from secondary mixing with heavier components like the Martian crust. Furthermore, our interpretation supports the idea that there are geochemically depleted, intermediate, and enriched reservoirs in the Martian mantle, and Cl isotopes could be utilized as a tracer for crustal contamination in Martian meteorites.

The homogeneity of the Martian mantle with regard to Cl isotopes and the heavy Cl isotope composition of the Martian crust have profound implications for petrogenetic models for Martian magmatism. Many of the REE and isotopic characteristics of the shergottites have been linked to different reservoirs in the crust and mantle and their interactions during the petrogenesis of shergottite magmatism. Two endmember petrogenetic models have been suggested to account for the location and interaction of these reservoirs and the variation in shergottite compositions. All of these reservoirs seem to have formed within the first 30–50 Myr of the formation of the solar system (Borg and Draper 2003; Bouvier et al. 2009). In one model, the shergottite compositional array is a product of melting (and mixing) of two distinctly different mantle sources; a reduced (IW–1 to IW+1), depleted mantle and enriched mantle that is either oxidized or its melting products have undergone secondary oxidation during or prior to crystallization (Blinova and Herd 2009; Papike et al. 2009; Shearer et al. 2013). An alternative model is that the shergottites that are reduced and depleted reflect the Martian mantle, whereas the more oxidized and enriched shergottites indicate interaction between mantle-derived basalts and the Martian crust. To distinguish between these two models, a fuller understanding of the petrologic linkages among all of these geochemical characteristics and intensive parameters ($f\text{O}_2$) must be reached. One approach to deciphering these petrogenetic linkages is unraveling the crystallization history preserved in olivine megacrysts in the more primitive shergottites (olivine-phyric shergottites). The isotopically light $\delta^{37}\text{Cl}$ values of both the enriched and depleted mantle sources indicate that the formation of these reservoirs is not a product of mixing of a crustal component. The nature of mixing of the two Cl isotope reservoirs will be examined in the next section.

Mechanisms of Mantle-Crust Interactions

Placing the Cl isotope signatures of the Martian meteorites into the context of their textures, mineralogy,

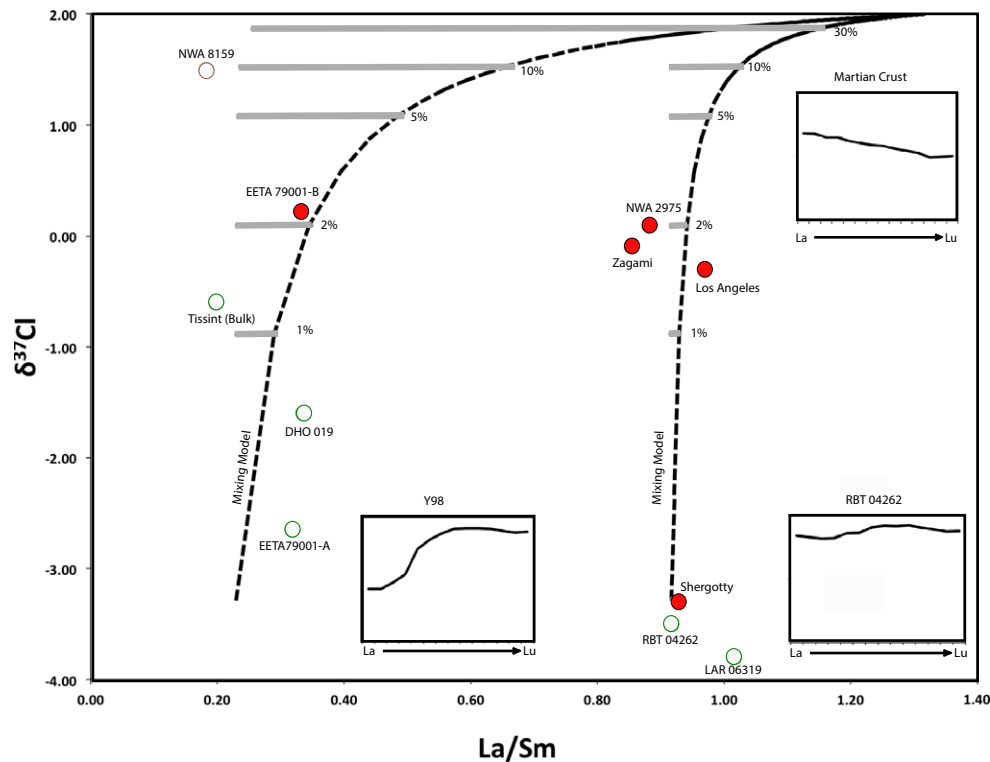


Fig. 6. Assimilation-fractional crystallization model (black line) and mixing model (dashed black lines) showing interaction effects from depleted and enriched Martian reservoirs with an estimated Martian-crustal composition (Taylor et al. 2010). Values next to model lines represent the amount of assimilated material. Partition coefficients used assume olivine is removed from the system (McKenzie and O’Nions 1991). Averages are used for samples with multiple measurements.

and geochemistry provides evidence for a variety of mechanisms for interactions between mantle-derived magmas and the Martian crust. These mechanisms include mechanical mixing during impact and other surface processes, interactions between crystallized basalts and crustal fluids, and assimilation of the crust by mantle-derived basaltic melts. Here, we give examples of each process and consider the relative likelihood of each in reproducing the observed changes in Cl-isotopic composition.

Assimilation and Fractional Crystallization

The importance of crustal assimilation for the generation of shergottites is unsettled (see Papike et al. 2009; Shearer et al. 2013). We can address the degree of assimilation using the isotopes of Cl, S, and Li because the crustal and mantle endmember values are so different. These light element isotopic systems may be more sensitive than REE systematics in tracing low degrees of crustal assimilation.

The chlorine concentration in olivine-phyric shergottites ranges from 20 to 50 ppm but the concentration in the crust has been shown to be significantly higher and variable, between 2000 ppm and

1 wt% (Wänke and Dreibus 1994; Keller et al. 2006; Bogard et al. 2010; Taylor et al. 2010; McCubbin et al. 2016a). It is also likely that the isotopic composition of the crust is highly variable as discussed earlier. As shown in Sharp et al. (2016), a simple mixing model indicates that all of the measured Cl-isotopic compositions of the basaltic shergottites (other than Shergotty, which exhibits anomalously light Cl values) can be explained by an addition of less than 2% crustal assimilation.

Assimilation of crustal material would also have important implication for other elemental systems. To assess this effect, Fig. 6 shows an assimilation-fractional crystallization (AFC) model for varying degrees of assimilation. The two dashed lines represent a simple mixing model of Cl isotopes and the La/Sm ratio from both the LREE-depleted (Yamato 980459) and LREE-enriched (Roberts Massif 04261) mantle reservoirs with a highly LREE-enriched Martian crust (Taylor and McLennan 2009). The gray lines track the change in the La/Sm as olivine crystallizes; we assume that this process does not affect the ^{37}Cl values. Appropriate partition coefficients (from McKenzie and O’Nions 1991) were chosen under the assumption that only

olivine would be removed from the system. It is important to note that AFC from the LREE-depleted reservoir does not appear to explain the LREE-enriched shergottites and therefore evolution from a previously enriched reservoir is required to explain their chemistry.

The low degrees of AFC indicated by the ^{37}Cl values has little effect on the REE patterns, which clearly demonstrates the insensitivity of REE to low degrees of crustal assimilation. For example, the sample Shergotty (enriched shergottite) is largely indistinguishable from Los Angeles (enriched shergottite) in REE space (Fig. 6). Los Angeles is only slightly more enriched with respect to REE patterns. However, the Cl isotope composition of these samples shows a significant difference (Fig. 6). Shergotty appears to be representative of an unaltered mantle-derived basalt, and Los Angeles has been affected by a Cl-rich, isotopically heavy, crustal assimilate.

This AFC model provides valuable insights into Martian geochemistry and petrology. It demonstrates the usefulness of Cl isotopes as a sensitive indicator for crustal assimilation where other elemental systems, such as REE, fail to elucidate these interactions. More importantly, Cl isotopes reveal a new window into differentiating between samples that are representative of geochemically enriched mantle versus samples that have been contaminated by enriched crust on Mars. Cl isotopes have the potential to become an important petrogenetic discriminator on Mars, especially in combination with REE geochemistry, estimates of oxygen fugacity, and other stable isotopic systems, including S and Li.

Mechanical Mixing

Several Martian meteorites consist of an igneous component and pods, pockets, and/or veins of impact-derived glass materials (e.g., EETA 79001 lithologies A, B, and C; Tissint). In Tissint, the bulk composition of the impact glass appears to be a mixture of the igneous component and a soil and/or crustal component (Aoudjehane et al. 2012; Magna et al. 2015). Tissint igneous and impact glass separates show minor, resolvable, variations in $\delta^{37}\text{Cl}$ of structurally bound Cl (-2.9% and -2.0% , respectively) (Table 1, Fig. 3). Compared to the bulk measurement for Tissint of -0.6% in Table 1, a third component is required for mass balance. This third component is the water-soluble chlorine of the glass fraction, with a measured value of -0.4% . This fraction contains 33% of the total Cl. This component most likely represents the influence of weathering near the surface of Mars that has been documented by Aoudjehane et al. (2012). The impact glass found throughout Tissint makes up approximately 20% of the meteorite. A mass balance of all fractions

analyzed yields a $\delta^{37}\text{Cl}$ of -0.5% per mil, identical within error to the previous bulk measurement of -0.6% (see Table 1, Fig. 3). Therefore, this agreement supports the idea that the glass found in Tissint may source a crustal, potentially soil-like, material (Aoudjehane et al. 2012). Furthermore, this result indicates how impact processes may potentially alter primary Cl-isotopic signatures of a sample through mechanical mixing processes.

Fluid Interaction

It has been long recognized that low-temperature mineral assemblages of Martian origin are preserved in some Martian meteorites. These assemblages are largely interpreted as alteration products from Martian fluids and brines. They include Fe-rich smectite, serpentine, fluid inclusions, and amorphous gels among others and are generally found along veins (Bridges and Grady 2000; Changela and Bridges 2010; Bridges and Schwenzer 2012; Hallis et al. 2014).

In addition to low-temperature alteration, the Martian meteorites also exhibit evidence of high-temperature hydrothermal activity and magma-fluid interaction. The most well-documented evidence for high-temperature hydrothermal activity has been with the chassignites and nakhlites. The nakhlites and chassignites are generally interpreted as comprising a cumulate igneous pile (Harvey and McSween 1992; Lentz et al. 1999; Mikouchi et al. 2003, 2012; Imae et al. 2005; Treiman 2005; Day et al. 2006; Treiman and Irving 2008; Hallis and Taylor 2011), and they have recently been proposed to be of co-magmatic origin (McCubbin et al. 2013). The chassignites are dunites consisting of cumulus olivine and chromite and are thought to be at the base of this cumulate pile. The nakhlites are clinopyroxenites with cumulus clinopyroxene and olivine grains, thought to be stratigraphically higher than the chassignites (Floran et al. 1978; Treiman 2005; Beck et al. 2006; Mikouchi et al. 2012; McCubbin et al. 2013). Both meteorite groups are very Cl-rich with respect to other Martian meteorites and show evidence for aqueous/hydrothermal alteration by Cl-rich fluids/brines (McCubbin and Nekvasil 2008; McCubbin et al. 2009, 2013; Bridges and Schwenzer 2012; Filiberto et al. 2014).

The $\delta^{37}\text{Cl}$ values of both nakhlites (NWA 5790 and NWA 817) and matrix apatites (i.e., not found in melt inclusions in olivine) in Chassigny have positive ^{37}Cl values. This suggests that a Cl-rich brine of crustal origin interacted with these samples, which is consistent with previous models proposed for the Chassigny meteorite (McCubbin and Nekvasil 2008). The range in Cl isotope compositions seen in these samples may give

an indication as to the degree of fluid interaction, where NWA 5790 has exchanged most with the crustal fluid. One interesting difference is seen in the two measured chassignites, NWA 2737 and Chassigny. The matrix apatites measured in Chassigny have ^{37}Cl values between 0.3 and 0.4‰ but the bulk rock measurement from NWA 2737 has a ^{37}Cl value of -3.85 ‰. It has been observed that NWA 2737 experienced a lesser degree of Cl-enrichment in apatite than Chassigny (McCubbin et al. 2013). The Cl-isotopic composition of NWA 2737 further supports this idea as it has retained a mantle-like Cl signature despite the apparent shock effects and isotopic resetting seen in other systems (Beck et al. 2006; Marty et al. 2006; Treiman et al. 2007; Pieters et al. 2008; He et al. 2013; Giesting et al. 2015). Chassigny, on the other hand, appears to have exchanged with a crustal fluid to some extent at least within the portions of the meteorite that are interstitial to the cumulus olivine grains.

The noble gas composition of Chassigny is representative of the Martian mantle and has not exchanged with a crustal or atmospheric reservoir (Mathew et al. 1998; Mathew and Marti 2001). Therefore, it might be expected that the Cl-isotopic composition would also support the same conclusion. In fact, McCubbin and Nekvasil (2008) reported that apatites within olivine-hosted melt inclusions in Chassigny are depleted in Cl relative to the intercumulus apatites. We hypothesize that the Cl-isotopic composition reflected in the matrix apatites indicates fluid exchange and alteration but that the fluorine-rich apatites hosted in melt inclusions may reflect an unaltered mantle-derived ^{37}Cl value, which is reflected in the noble gas composition of the cumulus olivines, although additional analyses of apatites from the olivine-hosted melt inclusions in Chassigny are required to test this hypothesis.

Lithium has been used in many systems to track fluid interactions and low-temperature alteration (e.g., in MORB; Elliott et al. 2006; Tomascak et al. 2008). Li isotope fractionation has been shown to occur in low-temperature processes. During weathering and fluid interaction, secondary phases preferentially incorporate the light isotope, leaving a heavy residue (Pistiner and Henderson 2003; Rudnick et al. 2004; Vigier et al. 2008; Wimpenny et al. 2010; Magna et al. 2015). Magna et al. (2015) showed that Li isotopes in Martian meteorites have a large variation ($+5.0$ to -0.2 ‰). The Bulk Silicate Mars, as represented by the olivine-phyric shergottites and other unweathered samples, has a ^7Li value of $+4.2$ ‰, but the Martian-crustal Li isotopic composition has a much lighter value, potentially reflected by NWA 7034 of -0.2 ‰. Figure 7 displays the Li isotopic compositions against

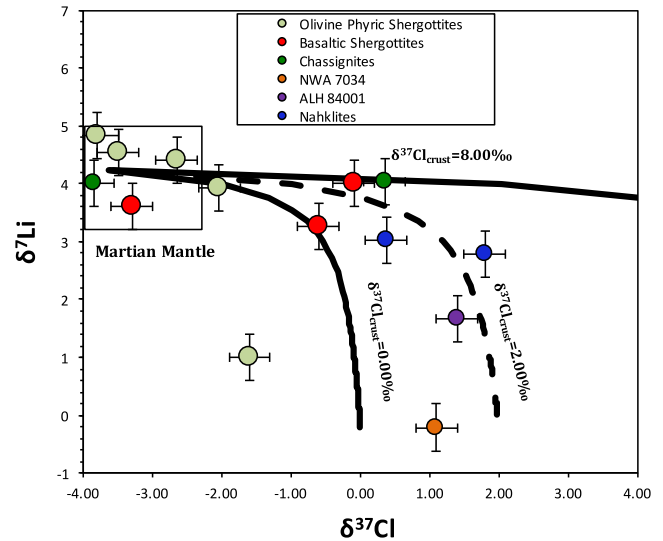


Fig. 7. Plot of ^7Li versus $\delta^{37}\text{Cl}$ (Magna et al. 2015). Model lines are simple mixing models as discussed in text. Error bars are 1σ . ^7Li value for Dhofar 019 taken from Reynolds et al. (2006). Averages are used for samples with multiple measurements.

the Cl-isotopic compositions as shown by Magna et al. (2015). Figure 7 shows a general negative correlation with a much tighter clustering around the primitive Martian mantle signatures of both isotopic systems: ^7Li of 4.2 ‰ and ^{37}Cl value of -3.8 ‰. Mixing curves between mantle and crust for these two isotope systems were calculated for three different assumed $\delta^{37}\text{Cl}$ values of crust; all other parameters were kept constant: Mantle – $^7\text{Li} = +4.2$ ‰, Li conc. = 2 ppm (Magna et al. 2015), $\delta^{37}\text{Cl} = -4$ ‰, Cl conc. = 20 ppm; Crust – $^7\text{Li} = -0.21$ ‰, Li conc. = 12 ppm, $\delta^{37}\text{Cl} = 0$ ‰, $+2$ ‰, and $+8$ ‰ (three separate curves), Cl conc. = 2000 ppm. Li isotope composition and concentrations have little effect in these models due to the much narrower difference in the concentrations and isotopic compositions of the mantle and crustal reservoirs compared to Cl. The mantle concentration of Li is near 2 ppm, indicated by the meteorite record (Magna et al. 2015); in contrast, the crust has been suggested to have a concentration of around 10 ppm as measured by the Mars Science Laboratory (MSL) rover Curiosity and the meteorite record (McLennan et al. 2014; Ollila et al. 2014; Magna et al. 2015). As a consequence, only the Cl isotope composition of the Martian crust was varied in these models. All samples, with the exception of Dhofar 019, fall into the array defined by $\delta^{37}\text{Cl}$ crustal values between 0 and 8‰. This is a further indication that the crustal Cl-isotopic reservoir is highly variable and may be spatially dependent.

CONCLUSION

Our study found that Mars has at least two isotopically distinct chlorine reservoirs, the mantle and the crust. The ^{37}Cl value of the Martian mantle, as represented by the olivine-phyric shergottites, NWA 2737, and Shergotty, is lighter than all other known planetary bodies with a ^{37}Cl value of approximately -3.8‰ . The ^{37}Cl value of the Martian crust is reflective of a highly isotopically fractionated atmosphere and is potentially heterogeneously enriched in the heavy isotope of Cl. Due to the large concentration difference of Cl in the mantle and crust, the Cl isotope system acts as a sensitive recorder of crust-mantle interaction. It appears that the petrologic linkages among the SNC meteorite reservoirs cannot be explained solely by assimilation of crustal material, as all mantle reservoirs (depleted, intermediate, and enriched) are homogenous with respect to Cl isotopes, despite variations in Sm-Nd and Rb-Sr isotopic systematics as well as LREE enrichment. This observation further supports the idea that there are geochemically enriched reservoirs within the Martian mantle. Assimilation of crustal material into these reservoirs would have caused a positive shift in the ^{37}Cl values. The meteorite record contains samples that lie upon a continuum of exchange with the Martian crust after extraction from mantle reservoirs. The nature of this interaction can be mechanical, fluid/brine interaction, and assimilation-fractional crystallization.

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Editorial Handling—Dr. Justin Filiberto

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