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A Review of Volatiles in the Martian Interior

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Abstract

Multiple observations from missions to Mars have revealed compelling evidence for a volatile-rich Martian crust. A leading theory contends that eruption of basaltic magmas was the ultimate mechanism of transfer of volatiles from the mantle toward the surface after an initial outgassing related to the crystallization of a magma ocean. However, the concentrations of volatile species in ascending magmas and in their mantle source regions are highly uncertain. This work and this special issue of Meteoritics and Planetary Science summarize the key findings of the workshop on Volatiles in the Martian Interior (Nov. 3-4, 2014), the primary open questions related to volatiles in Martian magmas and their source regions, and the suggestions of the community at the workshop to address these open questions.

Introduction

The Workshop on Volatiles in the Martian Interior was held Nov. 3 – 4, 2014 at the Lunar and Planetary Institute in Houston, TX (http://www.hou.usra.edu/meetings/volatiles2014/) and gathered together scientists from diverse disciplines to discuss the state of knowledge of volatiles in the interior of Mars (see meeting report Filiberto et al. 2015). The goals of the workshop were to discuss the latest developments in the field, synthesize current knowledge, and identify the primary scientific questions that still need to be addressed. This review and the other papers published in this special issue of Meteoritics and Planetary Science will summarize the key findings of the workshop and primary open questions.

Three general processes determined the history, concentration, and present state of volatiles in the Martian interior: 1) accretion, 2) outgassing during magma ocean solidification, and 3) secondary degassing during later volcanism. Accretion of volatile-bearing material from the protoplanetary disk produced proto-Mars, which is thought to consist of building blocks that formed rapidly (less than 5 million years) at ~ 2 − 3 AU and produced a planetary body that was more enriched in volatiles than Venus or Earth (e.g., Wänke 1981; Wänke and Dreibus 1988; Wänke 1991; Taylor 2001; Lunine et al. 2003; Dauphas and Pourmand 2011).

The halogen content of the Martian interior is thought to be ~ 2 times that of the Earth (Dreibus and Wänke 1985, 1987; Filiberto and Treiman 2009b; Taylor 2013). However, there is a large debate about the past and present water content of the Martian interior (e.g., McSween et al. 2001; Nekvasil et al. 2007; Filiberto and Treiman 2009b; McCubbin et al. 2010; McCubbin et al. 2012; Gross et al. 2013; Taylor 2013; Jones 2015). Further, models suggest that Mars potentially had higher water contents in the interior early in Mars' history (e.g., Médard and Grove 2006) and has subsequently lost volatiles from the interior during two later stages: early outgassing during differentiation (possibly during magma ocean solidification) and later degassing during volcanic eruptions. During crystallization and mantle melting, volatile elements would be enriched in the melt over the early crystallizing mineral phases (e.g., Aubaud et al. 2004; Dalou et al. 2012), depleting the mantle in volatile species. If there was no cap or early crust formation during the magma ocean period, the melt would rise to the surface by vigorous convection. At the surface of the magma ocean, the pressure could be low enough that saturation of some volatiles (specifically H_2O, CO_2, Cl, and S) in the melt would be near zero (e.g., Dixon and Stolper 1995; Dixon et al. 1995; Webster et al. 1999; Gaillard and Scaillet 2014), causing volatile elements to outgas and potentially form an early atmosphere (e.g., Elkins-Tanton 2008; Hirschmann and Withers 2008). Secondary degassing during volcanic eruptions would further deplete the mantle of volatiles, as volatile elements are concentrated in magmas over residual mantle minerals. Without crustal recycling of elements back into the interior (e.g., Magna et al. 2015), the Martian mantle should become more depleted in volatile elements through time (e.g., McCubbin et al. 2008; Fraeman and Korenaga 2010; Grott et al. 2011; Morschhauser et al. 2011; Balta and McSween 2013; Jones 2015).

Approaches to quantifying and understanding the role of volatiles in planetary evolution

Efforts to determine concentrations of volatiles in the Martian interior have focused mainly on investigations of the Martian meteorites. Cosmochemical constraints on the volatile budget of Mars have been obtained from the bulk compositions of Martian meteorites. Mineral chemical constraints on the volatile budget of Martian magmas, and hence the Martian interior, have been obtained from studies of the hydrous phases apatite and amphibole in Martian meteorites. Isotopic studies of H, Cl, and S and noble gases have been used to investigate magmatic secondary volatile loss, variations within mantle source regions, and volatile evolution of the mantle, crust, and atmosphere. These studies have been combined with laboratory experiments and geophysical and geochemical models to constrain the volatile budget of Mars and to determine how the volatile content of the interior has evolved through time. Finally, the models produced have been constrained with planetary-scale observables including crustal thickness, surface and meteorite chemistry (specifically Cl, Th, and K), early formation of the crust, present-day volcanism, and no crustal recycling as implied by Martian meteorites (e.g., Magna et al. 2015). Here we discuss the state of the knowledge and open questions for different volatile species, place these in context of broader open questions about volatiles in the Martian interior, and make inferences about the data and/or samples that would be needed to address these open questions.

Current state of knowledge related to specific volatiles

Water, Fluorine, and Chlorine

Cosmochemical Constraints. The bulk water contents in shergottites are significantly lower than in comparable terrestrial basalts, suggesting that the present Martian interior is drier than the present terrestrial mantle (e.g., Carr and Wänke 1992; Watson et al. 1994a; Filiberto and Treiman 2009b; Jones 2015) and that degassing during the Hesperian and Amazonian may not have provided substantial water to the surface (e.g., Filiberto and Treiman 2009b; McCubbin et al. 2009; Filiberto et al. 2014c; Giesting and Filiberto 2016). However, the D/H ratio of the Martian mantle is similar to that of the terrestrial mantle (Owen et al. 1988; Watson et al. 1994b; Leshin et al. 1996; Leshin 2000; Boctor et al. 2003; Lunine et al. 2003; Usui et al. 2012, 2015; Mane et al. 2016), suggesting that sources of water on the two planets were similar. Models have suggested that the Martian mantle may have degassed its water early in its history (e.g., Médard and Grove 2006; Elkins-Tanton 2008; Grott et al. 2011) and lost its early water-rich atmosphere (e.g., Owen et al. 1988; Carr and Wänke 1992; Carr 1996; Lunine et al. 2003; Carr and Head 2010). However, there is a large debate about the pre-eruptive water content of Martian magmas and their source regions, with estimates as low as nearly-anhydrous (consistent with the bulk rock measurements) and as high as two weight percent dissolved water in the magma before eruption/emplacement (Treiman 1985; Mysen et al. 1998; Dann et al. 2001; McSween et al. 2001; Jones 2004; Herd et al. 2005; Nekvasil et al. 2007; Filiberto 2008; Nekvasil et al. 2009; McCubbin et al. 2010; McCubbin et al. 2012; Usui et al. 2012; Balta and McSween 2013; He et al. 2013; Giesting et al. 2015; Jones 2015; Usui et al. 2015). In comparing literature values for water abundances, it is important to recognize that some authors report results in terms of mantle source region abundance and others in terms of water dissolved in the magma. Because water is incompatible, its abundance in the magma will typically be ~ 10 − 20 times larger than in the mantle source region, depending on the associated melt fraction. In order to constrain the water content of the Martian interior and investigate how the mantle may have changed through time, as well as investigating secondary processes like degassing and alteration, recent studies rely on hydrous minerals (apatite and amphibole) within Martian meteorites to determine the primary volatile contents of Martian magmas and their source regions (e.g., Treiman 1985; Watson et al. 1994b; Boctor et al. 2003; Greenwood et al. 2003; Patiño Douce and Roden 2006; McCubbin and Nekvasil 2008; Filiberto and Treiman 2009b; Patiño Douce et al. 2011; McCubbin et al. 2012; Gross et al. 2013; Filiberto et al. 2014c; Giesting et al. 2015; Howarth et al. 2015; McCubbin and Jones 2015; McCubbin et al. 2015).

Unlike water, since the mid 1980's we have had fairly good constraints on the halogen content, especially Cl, of Martian meteorites and hence their source regions (Dreibus and Wänke 1985, 1987). The Martian interior is thought to be 2 − 3 times enriched in halogens compared with the terrestrial interior (Dreibus and Wänke 1985, 1987; Filiberto and Treiman 2009b; Taylor 2013; Filiberto et al. 2016). This is based on not just comparing the bulk chemistry of Martian meteorites and terrestrial basalts, but comparing ratios of volatile concentrations to a non-volatile element, thereby taking into account primary and secondary processing such as mantle melting, fractional crystallization, degassing, and alteration. The calculated Cl content in the shergottite source region is similar to the terrestrial enriched mantle, while the F content of the shergottite source region is similar to the terrestrial bulk mantle (Filiberto et al. 2016). In order to calculate the H_2O content of the Martian interior, Filiberto et al. (2016) relied on the H_2O/Cl ratio for Martian magmas from apatite and amphibole analyses (see below) and direct measurements of H_2O/Cl concentrations in glass melt inclusions from Usui et al. (2012; 2015).

Filiberto et al. (2016) calculated H_2O contents for the chassignite and nakhlite source region, as well as the source region for Yamato 980459 and LAR 06319. Filiberto et al. (2016) reported that the H_2O abundances of these sources are similar to the depleted terrestrial MORB source (Michael 1988; Saal et al. 2002). However, the large uncertainty in their calculations of an average source region for the Martian meteorites likely reflects heterogeneities in the Martian interior (such as the depleted, intermediate and enriched source regions, as well the chassignite-nakhlite source region) as explored by McCubbin et al. (2016) (see next section).

Volatile-bearing phases- Amphibole and Apatite. Instead of focusing on the bulk chemistry of the Martian meteorites, which may have been affected by secondary processes like degassing and alteration, many previous studies have focused on using the hydrous phases amphibole and apatite to constrain the Martian volatile history and budget (e.g., Treiman 1985; Watson et al. 1994b; Boctor et al. 2003; Greenwood et al. 2003; Patiño Douce and Roden 2006; McCubbin and Nekvasil 2008; Filiberto and Treiman 2009b; Patiño Douce et al. 2011; McCubbin et al. 2012; Gross et al. 2013; Giesting et al. 2015; Howarth et al. 2015; McCubbin et al. 2015; Howarth et al. 2016). The majority of apatites in Martian meteorites (**Figure 1**) are chlorine-rich (Patiño Douce and Roden 2006; Filiberto and Treiman 2009b; McCubbin et al. 2013; Howarth et al. 2015), which has previously led to the suggestion that Martian magmas are chlorine-rich with some magmas potentially having chlorine as the dominant volatile (or at least co-dominant with H_2O; e.g., Filiberto and Treiman, 2009b). However, apatite in Martian meteorites actually ranges from OH- bearing, F- apatite to almost pure end member Cl-apatite (**Figure 1**), which suggests a range in volatile contents of primary magmas with some being rich in H_2O (e.g., McCubbin and Nekvasil 2008; McCubbin et al. 2012; Gross et al. 2013; McCubbin et al. 2016). McCubbin et al. (2016) show a difference in the water content between the rare earth element enriched and depleted sources (51 - 68 ppm vs 14 - 23 ppm H_2O; respectively) consistent with other observed geochemical differences. This work further supports the idea that water is heterogeneously distributed in the mantle. Further, by combining Martian apatite compositions with bulk S and Cl isotopic data, McCubbin et al. (2016) determined that most Martian meteorites have been affected by crustal contamination, and hence estimates of mantle volatile abundances from these samples is quite complicated.

Amphibole in Martian meteorites, when present, is typically high-Ti kaersutitic amphibole found in olivine-hosted melt inclusions (e.g., Floran et al. 1978; Treiman 1985). Kaersutitic amphibole has been analyzed for halogens and water in Zagami, Shergotty, Chassigny, and Northwest Africa 2737 (Treiman 1985; Watson et al. 1994a; Watson et al. 1994b; Beck et al. 2006; Treiman et al. 2007; McCubbin et al. 2010; He et al. 2013; Giesting et al. 2015). Kaersutite in Martian meteorites is typically oxy-amphibole and contains relatively low water (0.1 – 0.7 wt%) and Cl contents (~0.1 wt%) (Floran et al. 1978; Watson et al. 1994b; Treiman et al. 2007; McCubbin et al. 2010; Giesting et al. 2015). Calculated parental magmas for the kaersutite in the chassignites have H_2O/Cl ratios of 0.5 - 4.0 (Giesting et al. 2015), which are consistent with the parental magma volatile concentrations calculated from apatite analyses (H_2O/Cl ratios of 0.7 - 4.2) (McCubbin and Nekvasil 2008; Filiberto et al. 2016). This suggests a chlorine-rich, hydrous parental magma for the chassignites.

However, the nakhlites MIL 03346, 090030, 090032, 090136, and NWA 5790 do not contain kaersutite like the other Martian meteorites but instead contain potassic-chloro-hastingsite in melt inclusions (e.g., Sautter et al. 2006; McCubbin et al. 2009; McCubbin et al. 2013). Experimental evidence suggests that in order to crystallize such chloro-amphiboles, the activity of water in the melt inclusions must have been extremely low and the system must have had adequate K and Fe to crystallize Cl-rich amphibole (Giesting and Filiberto 2016). This extreme Fe, K, and Cl enrichment may have been caused by exsolution of a saline [$FeCl_2$-rich (Bell and Simon 2011)] aqueous fluid from the late stage melt in the nakhlite pile that was then transported upward from a deeper source region in the nakhlite parent intrusion (McCubbin et al. 2013; Giesting and Filiberto 2016).

D/H ratio. The story of Martian D/H is somewhat in a state of flux. There are at least two water reservoirs on Mars, each having a distinct D/H ratio (**Figure 2**). The Martian mantle probably has a δD of ≤ -100‰, whereas the atmospheric δD is ~+5000‰ ($\delta D = ([(D/H)_{Sample}/(D/H)_{SMOW}] - 1) \times 1000$; where SMOW is D/H ratio of Standard Mean Ocean Water = 0.0001559). Apart from these two, other reservoirs have been suggested (**Figure 2**). Here we will examine the two known reservoirs, the mantle and the atmosphere and briefly discuss a possible reservoir with a δD intermediate to the mantle and atmosphere end-members.

Particularly with respect to volatiles, the most promising sample of the Martian interior in our collections is Chassigny, as determined by the isotopic composition of Xe recorded in Chassigny bulk rock, which has a solar value (see section on Noble Gases) (Ott 1988). Therefore, it appears that the volatiles in Chassigny have not been in contact with the atmosphere, which has a different Xe-isotopic signature and fractionated D/H. Even so, the history of Martian mantle D/H, as mainly viewed from the Chassigny perspective, is still complex. Watson et al. (1994b) used the ion probe to investigate the D/H of olivine-hosted melt inclusions in Chassigny. One of these analyses yielded a δD of ~4000‰, which was in good agreement with Earth-based telescopic measurements of D/H in the Martian atmosphere (Owen et al. 1988). But Leshin et al. (1996) measured δD in stepwise thermal releases, up to 1000°C, and found that there was relatively little variation in δD between 200°C and 1000°C. δD of a combusted Chassigny sample varied between -26‰ and -84‰. A Chassigny pyrolysis release gave δD values between -9 and -60‰. Clearly, these contrasting results from the same research group, using different analytical techniques, are not easily interpretable.

Another set of Martian meteorites that may come close to representing the Martian mantle signatures are the depleted, reduced shergottites, like Yamato 980459 and Tissint. Boctor et al. (2003) carried out an ion probe study that reported D/H ratios in shergottites that were even lower than those of Leshin et al. (1996). However, in this case low δD values could possibly have been due to terrestrial contamination (e.g., epoxy in the thin section). Usui et al. (2012) measured δD in olivine-hosted melt-inclusion glasses from a primitive shergottite, Y980459. Usui et al. (2012) concluded, based on their results and those of Leshin et al. (1996), that the D/H of the Martian mantle was ≤ 275‰ (**Figure 2**). This is consistent with the evidence that even Y980459 has experienced some crustal contamination (Peters et al. 2015). Chen et al. (2015) and Mane et al. (2016) measured impact melts and nominally anhydrous phases like merrillites and maskelynites in Tissint and concluded that the lowest observed δD value in Tissint (~ -100 ‰) represents the Martian interior composition. The merrillites yielded the highest δD values (up to +3682 ‰) and is consistent with merrillite reacting with crustal H_2O on Mars to form a secondary whitlockite component, which can only occur on Mars at submagmatic temperatures (Hughes et al. 2008; McCubbin et al. 2014; Shearer et al. 2015). Although Tissint is not free of crustal contamination, these observations are consistent with the conclusions of Peters et al. (2015) that Tissint had experienced less crustal contamination than Y980459. Hydrogen isotopic composition of nominally anhydrous igneous mineral phases like olivines and pyroxenes in a nakhlite NWA 817 show the δD value -60 to -280 ‰ (Gillet et al. 2002). Similarly apatites from the Nakhla meteorite show a δD value of ~-100‰ (Hallis et al. 2012). So, conservatively, we recommend adopting a δD value of ≤ -100‰ for the Martian mantle. In the sections on S and on Noble Gases, we will show that even Chassigny has experienced minor crustal contamination. Therefore, the lightest Chassigny δD value of Leshin et al. (1996) should probably be considered an upper limit.

It has long been known that the δD ratio of the Martian atmosphere is extremely high (~4000‰; e.g., Owen et al., 1988); and these early measurements were later given support by other Earth-based telescopic/spectroscopic observations (e.g., Krasnopolsky and Feldman 2001). For comparison, the water of the Earth's oceans has a δD of 0‰ (by definition, e.g., Faure 1977), so the absolute D/H ratio of the Martian atmosphere is about 5 times higher than that of the Earth's oceans (**Figure 2**). Subsequently, δD in the Martian atmosphere has been measured directly by the Curiosity rover. The SAM instrument on Curiosity has a tunable laser spectrometer (TLS), which measured the δD of the Martian atmosphere to be 5000±1000‰ (Webster et al. 2013). Therefore, we are confident that the D/H of the tenuous Martian atmosphere is 4000-6000‰. The most likely reason for such a large D/H ratio, generally agreed upon (e.g., Pepin 1991) is preferential loss to space of H relative to D. Most recently, Villanueva et al. (2015) estimated that on Early Mars, water must have been abundant; from their measurements of atmospheric water and DHO across the globe, they calculated the ancient global equivalent layer was as high as 137 m. Mars has not had a dynamo-generated magnetic field since the end of the impact basin-forming epoch roughly 4 billion years ago (e.g., Lillis et al. 2008), and Jeans escape (i.e., loss of species that are not gravitationally bound) from the upper atmosphere and upper-atmospheric erosion by the solar wind can both contribute to preferential loss of lighter isotopes (e.g., Jakosky and Jones 1997).

Recently, Usui et al. (2015) and Mahaffy et al. (2015) have presented evidence for an intermediate δD reservoir of 1000-2000‰ in Martian surficial materials. Usui et al. (2015) found a convergence of intermediate δD analyses from several Martian meteorites and Mahaffy et al. (2015) measured a similar range of δD for a Martian sediment. If these new analyses stand the test of time, it may be that we will have to consider multiple Martian δD reservoirs, not just the mantle and the atmosphere. Although at first glance, it may appear that mixing between mantle and surficial waters is the simplest solution for the origin of the intermediate reservoir, it is not altogether clear that this is true (Usui et al. 2015).

Consequently, Usui et al. (2015) presented two very different models for surficial Martian water. The first model assumed that there was a shallow, buried ice reservoir with an intermediate δD and that this reservoir dominated the surficial water budget. This reservoir was constrained to inefficiently communicate with the atmospheric reservoir. The atmospheric reservoir might also include water ice in the polar caps, which may sublime in response to upper atmospheric H loss. The second model of Usui et al. (2015) was that all surficial condensed waters have an intermediate δD and that the higher δD of the atmosphere has been maintained by a quasi-steady-state of sublimation and atmospheric loss. A third model, not considered by Usui et al. (2015) but explored by Greenwood et al. (2008), is that there was an early δD fractionation (by hydrodynamic escape?) followed by a slow, gradual increase in δD over geologic time. This model implicitly assumes that there is not enough surficial water exchanging with the atmosphere that the atmospheric δD is “buffered.” A probable consequence of this assumption is that the δD of all surficial reservoirs are changing with time.

Although there is uncertainty about how surficial δD reservoirs were established and how they are maintained, it is highly likely that some major δD fractionation occurred very early in Martian history. Of the various models described here, this early fractionation could have produced a global surficial reservoir with a δD of 1000-5000‰.

Cl isotopes. Williams et al. (2016) and Sharp et al. (2016) investigate the Cl-isotopic composition of Martian meteorites to constrain Cl reservoirs in the Martian crust and interior and place the Cl isotopic composition of Mars in context with other planetary materials, the origin of early Solar System Cl-isotopic reservoirs, and the accretion of Mars.

Martian meteorites that are thought to have experienced crustal contamination have positive δ^{37}Cl values up to 8.6 ‰, which suggests a ^{37}Cl enriched crust (Williams et al. 2016; Sharp et al. 2016). Olivine-phyric shergottites and Shergotty have low δ^{37}Cl values (-4 to -2‰), which is thought to represent the primary Martian mantle value (-4 to -3‰). The low δ^{37}Cl values of the Martian mantle may represent the Cl-isotopic value of the primordial bulk composition of Mars inherited during accretion (Sharp et al. 2016). The other basaltic shergottites have δ^{37}Cl from 0 to +1 ‰ which may be due to mixing between a mantle source and a crustal source. Sharp et al. (2016) speculate that preferential loss of ^{35}Cl to space has resulted in a high δ^{37}Cl value for the Martian surface. However, recent results from MSL Curiosity show that the crustal chlorine isotope ratios at Gale Crater are more variable and negative in δ^{37}Cl than typically observed in SNC meteorite analyses, which was attributed to perchlorate fractionating chlorine isotopes (Farley et al. 2016).

Sulfur

Sulfur (in the form of sulfate) alteration and sedimentary minerals dominate what we know of the alteration mineralogy in the Martian crust, particularly in the Hesperian (e.g., Bibring et al. 2006; King and McLennan 2010). This has been used to suggest a change of alteration style from water-dominated alteration in the Noachian to S-dominated alteration in the

Hesperian, potentially caused by a massive outpouring of S-rich volcanism during the formation of Tharsis (e.g., Poulet et al. 2005; Bibring et al. 2006). Therefore, it is vital to understand the sulfur capacity of Martian magmas, as sulfur storage and transport between reservoirs, such as core, mantle, crust, and atmosphere, are tied to igneous processes (e.g., King and McSween 2005; Gaillard and Scaillet 2009; Righter et al. 2009; King and McLennan 2010; Ding et al. 2014; Gaillard and Scaillet 2014; Ding et al. 2015).

Martian meteorites contain up to ~ 3000 ppm S (King and McLennan 2010; Ding et al. 2015), compared with terrestrial basalts which typically contain up to ~ 2000 ppm S (e.g., Wallace and Edmonds 2011). Based on the sulfur content of Martian meteorites, the Martian interior contains 700 − 1000 ppm S (Ding et al. 2015) and 10.6 − 12.7 wt% S in the core (Stewart et al. 2007), although recent estimates based on Fe isotopes places an upper limit of approximately 8 wt.% S in the core (Shahar et al. 2015). The unknown S abundance, or other potential light elements in the core, has an important influence on the density and inferred radius of the Martian core (Mocquet et al. 2011); seismic measurements by the forthcoming Insight mission should improve our knowledge of the core radius and thus may indirectly help to constrain the abundance of S in the core.

Even though the Martian interior contains significant S, Martian magmas are not sulfide-saturated because they have relatively high S-solubility (up to ~4000 ppm S) (Righter et al. 2009; Ding et al. 2014), but may reach S-saturation after extensive crystallization (Baumgartner et al. 2015). If Martian magmas did not significantly outgassing sulfur, cumulates in the crust could be an important reservoir of magmatic sulfur (Ding et al. 2015). However, melting of the mantle and subsequent volcanism and degassing of sulfur-rich magmas could explain the abundance of surficial sulfate minerals (Gaillard and Scaillet 2009; Righter et al. 2009). Sulfur released as SO_2

into a volcanic gas from an H and C depleted melt would produce a strongly acidic brine (Gaillard and Scaillet 2009). But Martian sulfur processes are likely to be rather complex. For example, SO_2 degassing is often appealed to as a source for the ubiquitous S (sulfate and jarosite) in Martian soils (Poulet et al. 2005; Bibring et al. 2006; Gaillard and Scaillet 2009). However, the most primitive shergottites, as judged by their Mg# and (ε^{143}Nd), have intrinsic oxygen fugacities that are near the iron-wustite buffer (e.g., Herd et al. 2002; Herd 2003). Under those redox conditions, almost all the S in a shergottite liquid will be speciated as FeS, not as sulfate, and iron sulfides are not particularly volatile — although any trace H_2S would be (Gaillard and Scaillet 2009; King and McLennan 2010; Métrich and Mandeville 2010). Therefore, before volcanism can degas significant amounts of oxidized S, the S must first be oxidized. Alternatively, sulfates could potentially form from weathering of sulfide-bearing basalts in a CO_2-rich environment which produced locally acidic environments (Dehouck et al. 2012). So at a minimum, the outgassing of volcanic S must be, at least, a two-stage process to oxidize the sulfur and form sulfates.

Sulfur Isotopes. Sulfur isotopes have recently been used to track crustal contamination in Martian meteorites and constrain whether the rare earth element enrichment seen in many Martian meteorites is due to crustal assimilation or different mantle source regions (Franz et al. 2014). Franz et al. (2014) showed that assimilation of sulfur-rich crustal material into Martian magmas was a common occurrence during the eruption and emplacement of the parental magmas to the Martian meteorites. Further, the range of sulfur-isotopic values in sulfides and sulfates in Martian meteorites cannot be explained with terrestrial analog processes, which would suggest a fundamental difference between sulfur chemical processes in the Martian atmosphere/crust and that of the Earth (Franz et al. 2014).

Carbon

The C content of the Martian interior is currently not well constrained with estimates varying over more than 3 orders of magnitude (e.g., Dasgupta et al. 2014). In addition, there is evidence that portions of the Martian mantle may be graphite saturated, which further complicates abundance estimates of C in the Martian mantle (e.g., Hirschmann and Withers 2008; Righter et al. 2008). Understanding the Martian carbon budget and any putative carbon cycle is vital because dissolved C will reduce the Martian mantle solidus, potentially drive volcanism, and is key for habitability of surficial environments (Steele et al. 2012a; Steele et al. 2012b; Dasgupta et al. 2014). Carbon solubility in Martian basaltic melts is small [0.34 – 2.12 wt% CO_2 for the Gusev Crater basalt "Humphrey" composition or 0.45 – 1.26 wt% CO_2 for a Yamato 908459 composition at ~1 − 3 GPa] and is relatively insensitive to bulk composition (Stanley et al. 2011; Stanley et al. 2012). However, carbon solubility in a magma changes as a function of temperature, pressure, oxygen fugacity, and H_2/H_2O fugacity (Hirschmann and Withers 2008; Ardia et al. 2013; Dasgupta et al. 2014; Li et al. 2014; Li et al. 2015). Carbon solubility in silicate melts generally increases with increasing temperature and oxygen fugacity; however, there is a complex interplay between fO_2 and fH_2 on the solubility of C in silicate melts. Carbon solubility typically increases with increasing fO_2 (e.g., Pawley et al. 1992; Holloway 1998; Stanley et al. 2014; Li et al. 2015); however, at extremely low fO_2 in H-rich systems, carbon solubility increases with increasing fH_2 and decreasing fO_2 (Hirschmann and Withers 2008; Ardia et al. 2013; Stanley et al. 2014; Li et al. 2015). The reason for this reversal is that the solution mechanism for C in silicate liquids changes as a function of H_2 fugacity, which in turn changes as a function of O_2 fugacity: as fO_2 decreases in the O-H system, the H_2/H_2O fugacity ratio increases (e.g., Elkins-Tanton and Grove 2011; Hirschmann et al. 2012;

Sharp et al. 2013). At high fO_2, carbon dissolves as carbonate in the melt, while at low fO_2 and high fH_2 carbon dissolves as C-H species (e.g., Mysen et al., 2009; Li et al., 2014; Ardia et al., 2013). Consequently, both the fO_2 and fH_2 of the Martian interior will control the primary C-species that would have been degassed from Martian magmas. Furthermore, it illustrates the potential link between low fO_2, high fH_2 magmas on Mars and the possible abiotic production of methane during episodes of Martian volcanism.

Carbon dissolution in a reduced magma ocean was likely limited (< 500 ppm C) and a magma-ocean post core formation was likely C-free with a core with ~1 wt.% C, if a single stage core-mantle equilibration model is applicable (Chi et al. 2014; Dasgupta et al. 2014). Assuming a magma ocean with low C contents and a reduced oxygen fugacity, degassing of a Martian magma ocean may have released methane to the atmosphere (Li et al. 2014); however degassed carbon alone may not be sufficient to maintain a warm surface of early Mars (e.g., Stanley et al. 2011; Li et al. 2014).

Reduced macromolecular carbon has been discovered in a number of Martian meteorites, both as inclusions within igneous mineral phases (Steele et al. 2012a; Agee et al. 2013), as well as macromolecular carbon and graphitic carbon associated with hydrothermally precipitated carbonate globules in Allan Hills 84001 (Steele et al. 2007; Steele et al. 2012b; Steele et al. 2016). Based on the petrologic context of this macromolecular carbon, it is interpreted as forming through abiotic synthesis under low fO_2, high fH_2 conditions. In fact, the presence of macromolecular carbon and polycyclic aromatic hydrocarbons in association with spinel inclusions in olivine from a number of Martian meteorites has been used as evidence to support that at least portions of the Martian mantle are graphite saturated (Steele et al. 2012a).

Noble Gases

Noble gases have been measured in the Martian atmosphere by the Viking lander (Owen et al. 1977) and Curiosity rover (Atreya et al. 2013; Mahaffy et al. 2013; Mahaffy et al. 2015; Conrad et al. 2016), in rock samples collected at Gale Crater by the Curiosity rover (Farley et al. 2014), and in the Martian meteorites (e.g., Swindle 2002 and references therein). In fact, noble gas measurements in shock melt glass pockets in EETA79001 provided the first clear evidence that the SNC meteorites are indeed from Mars (e.g., Bogard and Johnson 1983).

Noble gases in Martian meteorites represent a mixture of a variety of Martian and terrestrial components (**Figure 3**). On Mars, atmosphere, interior, and fractionated atmospheric components occur and specific isotopes are formed as radiogenic/nucleogenic products, including fission and spallation processes (e.g., Swindle 2002). During space travel, cosmogenic isotopes are formed. Once on Earth, terrestrial atmosphere, elementally fractionated in most cases, further complicate the picture (e.g., Mohapatra et al. 2009; Schwenzer et al. 2013).

From a noble gas perspective, Chassigny appears to be our best example of the interior (Ott 1988). It has a ^{129}Xe/^{132}Xe ratio of approximately 1, which means it contains no radiogenic ^{129}Xe and has a solar-like Xe-isotopic composition (Ott 1988). A second (^{136}Xe-enriched) reservoir has also been found in Chassigny (Mathew and Marti 2001). This ^{136}Xe-enriched component cannot be detected in bulk Chassigny analyses (e.g., Ott 1988), and can only be discerned by detailed, step-wise thermal releases (e.g., Mathew and Marti 2001). The second reservoir is thought to be an interior reservoir containing a contribution from Pu fission (e.g., Mathew and Marti 2001; Swindle 2002). This might be connected to the observation of two D/H reservoirs at different spatial resolution of the analyses (see above), and support the existence of inhomogeneity of the mantle volatile reservoir. Similarly, Ar isotopes are distinctive in the

Martian interior, but a second reservoir could exist (Schwenzer et al. 2007). Shergottite samples generally fall onto a trend between the atmospheric endmember measured by Viking (Owen et al. 1977), noble gases measured by Curiosity (Atreya et al. 2013; Conrad et al. 2016) , and a Martian interior component represented by Chassigny (e.g., Becker and Pepin 1984; Ott 1988).

Interestingly, at some point on Mars (possibly during crustal processes), elementally-fractionated atmospheric noble gas signatures were incorporated into the ALH 84001 and nakhlite Martian meteorites, complicating their noble gas signature and leading to a range of incorporation hypotheses (Ott 1988; Drake et al. 1994; Swindle et al. 1995; Gilmour et al. 1998; Mathew et al. 1998; Gilmour et al. 1999, 2001; Mathew and Marti 2001; Musselwhite and Swindle 2001; Mathew and Marti 2002; Swindle 2002; Mathew et al. 2003; Mathew and Marti 2005; Schwenzer and Ott 2006; Ott 2008; Mohapatra et al. 2009; Swindle et al. 2009; Cartwright et al. 2013). Further measurements of Martian rocks - preferably on Mars to avoid complications through later additions of isotopes, and careful investigations of fractionation effects, e.g., through experiments (Bullock et al. 2015; Schwenzer et al. 2016), are necessary to fully understand sources, pathways and sinks of the noble gases.

Effect on magma genesis and evolution of specific volatiles

Effect of water on magma genesis

Extensive work has investigated the effect of water on liquidus temperature, mantle solidus temperatures, and magma (basalt through granite) crystallization for terrestrial compositions (e.g., Burnham and Davis 1974; Mysen and Boettcher 1975; Danyushevsky 2001; Grove et al. 2002; Katz et al. 2003; Nekvasil et al. 2004; Feig et al. 2006; Grove et al. 2006;

Almeev et al. 2007; Médard and Grove 2008; Whitaker et al. 2008; Feig et al. 2010; Balta et al. 2011; Parman et al. 2011), with much less work focusing on the effect of water on magma crystallization and genesis for Martian compositions (e.g., Dann et al. 2001; Médard and Grove 2006; Nekvasil et al. 2007; Filiberto 2008; McCubbin et al. 2008; Nekvasil et al. 2009; Pommier et al. 2012). Water is known to depress basalt liquidus temperatures by breaking bridging oxygen bonds and thereby destabilizing plagioclase (e.g., Burnham and Davis 1974; Silver et al. 1990; Giordano et al. 2004; Mysen and Cody 2004). Water also has a large effect on the solidus temperature of the Martian mantle, which decreases from 975 °C at 1 GPa down to 800 °C at 3 GPa under water saturated conditions (e.g., Médard and Grove 2006). These solidus temperatures may be compared to the ones inferred for the dry primitive mantle of Mars, 1187 – 1220 °C at 1 GPa and 1396 – 1443 °C at 3 GPa (values estimated or calculated from Bertka and Holloway 1994; Filiberto and Dasgupta 2011; Matsukage et al. 2013; Kiefer et al., 2015; and Collinet et al. 2015). However, for concentrations below a few hundreds of ppm, water will have little effect on the position of the solidus despite having a potentially important effect on the rheology of the mantle.

Effect of water on magma crystallization and liquidus temperatures

In order to investigate the effect of H_2O on basaltic liquidus depression, experiments have been run on many different compositions at different pressures, temperatures, and using different techniques (e.g., Danyushevsky 2001; Katz et al. 2003; Feig et al. 2006; Almeev et al. 2007; Médard and Grove 2008; Feig et al. 2010). The resulting models of liquidus/solidus depression are all rather similar (Katz et al. 2003; Almeev et al. 2007; Médard and Grove 2008), except for that of Danyushevsky (2001) (**Figure 4**). Danyushevsky (2001) investigated the effect of small amounts of H_2O on crystallization of terrestrial mid-ocean ridge and back-arc basin magmas and observed a greater liquidus depression (for the same water content) than the other studies, which suggests a bulk compositional dependence. Médard and Grove (2008) noted an effect of the bulk MgO content of the magma on the effect of H_2O on liquidus depression. They noted that magmas with higher MgO content have greater liquidus depression for the same weight percent water. Most Martian magmas have MgO contents similar to those of terrestrial magmas, which justifies using these models to explain Martian basalt genesis and crystallization. However, some Martian basalts have significantly higher MgO contents, and the parameterization of the effect of water on liquidus and solidus depression may break down for these compositions (**Figure 4**). In fact, preliminary results from hydrous experiments conducted on Martian meteorite Yamato 980459 with <0.5 wt% H_2O, 0.5 wt% H_2O, and 2 wt% H_2O (Norris and Herd 2006; Dalton et al. 2007; Draper 2007) have greater liquidus depression for the same water content than typical terrestrial basalts (**Figure 4**). It is important to note that the Yamato 980459 bulk composition has ~18 wt% MgO, significantly more than typical terrestrial basalts (< 12 wt%).

Effect of halogens on magma genesis

Experimental work on halogens in magmatic systems has mainly focused on its solubility in magmas, solution mechanisms, and effect on viscosity of evolved melt compositions for fluorine and basaltic systems for chlorine (e.g., Webster 1990; Webster 1997; Aiuppa et al. 2009; Filiberto and Treiman 2009a; Bell and Simon 2011; Dalou et al. 2012; Filiberto et al. 2014a; Dalou and Mysen 2015; Webster et al. 2015; Farcy et al. 2016). Halogens are known to have a large effect on the physical properties of a silicate melt; however, the effect of halogens on melt properties is largely dependent on melt chemistry (e.g., Metrich and Rutherford 1992; Dingwell and Hess 1998; Zimova and Webb 2006; Baasner et al. 2013a; Filiberto et al. 2014a), which can result in wide-ranging implications for basalt genesis in both Earth and Mars. F and Cl are thought to form complexes with network modifying cations within a silicate melt, forming ion clusters that are distinct from the silicate network (Malinin et al. 1989; Webster and De Vivo 2002; Sandland et al. 2004; Evans et al. 2008; Filiberto and Treiman 2009a). F is thought to complex mainly with Mg in basaltic systems, but may also form complexes with Ca, K, and Al depending on the melt chemistry (Foley et al. 1986; Luth 1988b; Luth 1988a; Zeng and Stebbins 2000; Kiczenski et al. 2004; Filiberto et al. 2012). Studies of simplified silica-rich compositions (aluminosilicate glasses with and without sodium), have shown that fluorine preferentially complexes mainly with Al and Na but possibly Si as well (Schaller et al. 1992; Zeng et al. 1999; Zeng and Stebbins 2000; Liu and Nekvasil 2002; Liu and Tossell 2003; Mysen et al. 2004). Cl is thought to mainly form complexes with Fe^{2+} in basaltic systems, though it may complex with Ca or Mg as well (Metrich and Rutherford 1992; Webster and De Vivo 2002; Sandland et al. 2004; Zimova and Webb 2006; Filiberto and Treiman 2009a; Bell and Simon 2011; Filiberto et al. 2014a; Farcy et al. 2016).

These complexes affect silicate melts by decreasing their viscosity (though for certain bulk compositions, dissolved halogens may actually initially increase viscosity), by changing the polymerization of the silicate network (Dingwell et al. 1985; Dingwell 1989; Dingwell and Hess 1998; Giordano et al. 2004; Zimova and Webb 2006; Zimova and Webb 2007; Baasner et al. 2013a, b). As halogens form complexes with 2+ cations in the melt, the behavior of Fe and Mg partitioning between minerals and melt and therefore crystallizing mineral chemistry are affected (Filiberto and Treiman 2009a; Bell and Simon 2011; Filiberto et al. 2014a; Farcy et al. 2016). Finally, dissolved F and Cl will depress the liquidus temperature (Manning 1981; Luth 1988a;

Filiberto and Treiman 2009a; Filiberto et al. 2014a; Giehl et al. 2014; Farcy et al. 2016); however, the amount of liquidus depression is dependent on bulk composition (e.g., Filiberto et al. 2014a; Farcy et al. 2016).

Effect of moderately volatile elements on the mantle solidus

Although the primary focus of this review is on highly volatile elements and compounds, it is worth noting that moderately volatile elements (such as Na, K, and P) are also thought to be enriched in Mars relative to Earth (Dreibus and Wänke 1985; Taylor, 2013), and these enrichments have important effects on the Martian mantle solidus temperature. Sodium lowers the primitive mantle solidus by ~20 °C on Mars relative to Earth (Kiefer et al., 2015); its effect on the solidus will decline through Martian history as Na is partitioned from the mantle into the crust. Phosphorous and potassium will also act to lower the Martian solidus, although their effects will be smaller due to their smaller overall abundances in the Martian mantle. Kiefer et al. (2015) found that the elevated abundances of Na and K on Mars enhanced the time-integrated crustal production on Mars by 10-15% relative to models with Earth-like Na and K.

Geodynamical Modelling

The distribution of heat-producing elements (K, Th, U) and volatiles in crustal and mantle reservoirs is strongly connected with the thermal evolution of the planet. The concentration and distribution of K, Th, and U controls the heat budget and the vigor of convection, whereas water and other volatile elements control the rheology of the mantle, which also affects the vigor of convection. The efficiency of convection controls the heat transfer and heat loss, the thermal evolution of the mantle, and the rate of magmatic output or crustal production, and therefore the formation of distinct reservoirs depleted or enriched in incompatible elements. Modeling of the thermal evolution of Mars addresses the coupling between these various processes with the objective of producing scenarios consistent with available observations, including petrological/geochemical/cosmochemical constraints, or constraints on the structure and dynamics of the Martian interior (e.g., crust thickness, existence of magnetic dynamos).

The thermal evolution of a terrestrial planet like Mars depends strongly on the rheology (viscosity) of the mantle material, which depends on temperature, pressure, and water content. Even a few tens of ppm water can be rheologically significant (Hirth and Kohlstedt 1996; Karato and Jung 1998; Mei and Kohlstedt 2000). Water, at an abundance of 200 ppm in the mantle source region, will reduce the viscosity by a factor of 36 relative to a nominally dry (10 ppm water) mantle (Mei and Kohlstedt 2000; Li et al. 2008), and the associated increase in convective vigor will increase the characteristic convective velocity by a factor of 11. As limiting cases, viscosities of 10^{19} and 10^{21} Pa s at a temperature of 1600 K and a pressure of 3 GPa are generally assumed to represent wet and dry mantle rheologies, respectively. The effects of water on the magma production rate are smaller. Comparison of magma production in dry mantle plume melting (Li and Kiefer 2007) and in water-undersaturated mantle plume melting (Kiefer and Li, this issue) shows that 200 ppm of water in the mantle source region increases the magma production rate by a factor of 3 under conditions appropriate to present-day Mars. Balta and McSween (2013) proposed that the shergottites represent melting from a hydrated mantle source, which would reduce the needed mantle melting temperature, while Filiberto and Dasgupta (2015) proposed that the shergottites represent localized dry mantle plume sources. Because water is incompatible in the minerals that dominate the mantle, it preferentially partitions into the melt and escapes from the mantle to the crust. It is therefore crucial to include the effect of water on the solidus when modeling the coupled feedback loops between thermal evolution, mantle viscosity, magma production, and degassing.

Crustal production and implications for the heat budget and water concentration in the mantle

As a consequence of crustal formation, the mantle becomes depleted in water. Thermal evolution models typically predict a water depletion in the mantle by about 40-80 % (e.g., Fraeman and Korenaga 2010; Morschhauser et al. 2011; Sandu and Kiefer 2012). An example water degassing history is shown in **Figure 5**. The model (based on the "Mars Na+K" model in Figure 5 of Kiefer et al. (2015)) initially has 500 ppm of water in the primitive mantle. Two-thirds of this water degasses from the mantle, which is likely within the uncertainty of the geochemical constraints on volatile loss summarized below. Approximately 155 ppm of water remains in the mantle at present, consistent with the models of McCubbin et al. (2010; this issue) and Filiberto et al. (this issue) based on hydrous phases in Martian meteorites and Chen et al.'s (2015) study of hydrogen isotopes in the shergottite Tissint. Assuming that about 40 % of the water in the crust-forming melt is released into the atmosphere (Grott et al. 2011), a total of about 60-120 m of water is delivered to the surface for an initial amount of water in the mantle of 100 ppm. Most of the degassing occurs in the first billion years of Martian history, which is consistent with the concentration of valley networks in early Martian history (Hynek et al. 2010; Bouley et al. 2016), which might have contributed to an early Martian ocean (Clifford and Parker 2001; Perron et al. 2007). The crustal production for the model in Figure 5 (51 km globally averaged, Kiefer et al., 2015) is also consistent with observational constraints (Wieczorek and

Zuber, 2004). Some of the water that escapes from the mantle may remain trapped in the crust, resulting in a rheologically wet crust, which can lead to a mechanical decoupling of the crust and mantle (Grott and Breuer 2008, 2009). This may be necessary to explain the observed elastic lithosphere thickness in the Noachian with values smaller than about 20 km (e.g., McGovern et al. 2002; McGovern et al. 2004).

The water depletion in the mantle is consistent with the observation that about half of Mars' radioactive elements are in the crust (Norman 1999; McLennan 2001; Taylor et al. 2006; Hahn et al. 2011). Radioactive elements and H_2O are incompatible with similar partition coefficients ($D \sim 0.01$-0.002) (Salters et al. 2002; Borg and Draper 2003; Aubaud et al. 2004), which implies that at least half of the total Mars water was released from the mantle – part of it is enriched in the crust and part of it degassed into the atmosphere. Note, however, that the concentration of radioactive heat sources in the crust is an estimate and in particular its vertical distribution is not well known. The results of the crustal radioactivity calculations were interpreted with the precaution that they would represent an upper limit if the Martian crust had developed a vertically heterogeneous chemistry with upward enrichment (Hahn et al. 2011) as in the case of the terrestrial continental crust.

However, the recent findings of feldspar-rich lithologies from orbital spectroscopy (Bandfield 2006; Carter and Poulet 2013; Wray et al. 2013), in-situ analyses at Gale crater (Sautter et al. 2014; Sautter et al. 2015), and within Martian meteorites (Filiberto et al. 2014b; Gross and Filiberto 2014; Santos et al. 2015) suggests that the structure of the Martian crust could be more complex than even a simple upward enrichment. The suggestion of silica-rich lithologies in ancient crustal material implies that lithologies enriched in heat-producing elements are not necessarily well exposed at the surface and may be eroded or buried by

Hesperian or Amazonian volcanic material, which is dominated by tholeiitic basalts (McSween et al. 2003; McSween et al. 2006). It has been indeed argued that a low-density component may be essentially buried (Pauer and Breuer 2008; Baratoux et al. 2014; Sautter et al. 2015). On the other hand, these supposed feldspar/silica-rich igneous rocks may represent plagioclase-enriched basaltic eruptive products and not silica-rich lithologies, and may represent localized outcrops that are not representative of a significant portion of the Martian crust (Rogers and Nekvasil 2015). Therefore, a better understanding of the architecture of the Martian crust, and of the relative contribution of light felsic intrusive components, or dense olivine-bearing tholeiitic basalts, is needed before K, Th, and U surface concentrations may be extrapolated to the entire crust and used to constrain the volatile and remaining heat budget of the crust and interior.

A much lower mantle water depletion (5-10 %) has been suggested by Hauck and Phillips (2002), which is likely because they used a partition coefficient for water (0.1) that is too large and thus underestimated the amount of water transport to the crust. A smaller depletion is also obtained when the change in mantle density due to crustal formation results in a layered mantle structure with an upper mantle being less dense and more depleted in incompatible elements than the lower mantle (Ruedas et al. 2013; Plesa and Breuer 2014). Subsequent melting of the depleted upper mantle results in a reduced outgassing rate in comparison to a well-mixed and homogeneous mantle and water is heterogeneously distributed. On the other hand, outgassing is strongly enhanced for efficient crustal recycling via delamination of the lower crust (Morschhauser et al. 2011; Ogawa and Yanagisawa 2012). Although crustal mixing is suggested to be inconsistent with the geochemical data (Mezger et al. 2013; Magna et al. 2015), this argument may not hold when Martian eclogite (e.g., Papike et al. 2013), i.e., dense rock resulting from high-pressure metamorphism of basalt, sinks to the core-mantle boundary to form a separate reservoir. Nevertheless, this mechanism will not change the depletion of radioactive elements in the mantle but results in a more heterogeneous distribution of incompatible elements in the mantle with the co-existence of enriched and depleted reservoirs.

Heterogeneous mantle

Thermal evolution models consider a well-mixed homogeneous convecting mantle, while isotopic signatures in the Martian meteorites suggest the existence of distinct geochemical reservoirs that formed about 4.4-4.5 Ga ago and have not mixed since (e.g., Chen and Wasserburg 1986; Borg et al. 1997; Brandon et al. 2000; Halliday et al. 2001; Humayun et al. 2013; Bellucci et al. 2015; Nyquist et al. 2016). Distinct long-lived reservoirs are difficult to reconcile with a homogenously convecting mantle, unless these reservoirs have been ‘captured’ early in the stagnant lid. Alternatively, fractional crystallization of a magma ocean has been suggested to explain the isotopic heterogeneities in the Martian meteorites (e.g., Elkins-Tanton et al. 2003; Elkins-Tanton 2008). In this scenario, the crystallization sequence of the magma ocean leads to a non-monotonic density increase and an exponential increase of incompatible elements towards the surface. Such a gravitationally unstable configuration implies a global mantle overturn resulting in a density stratification that is stable against thermal convection, assuming the most recent density profiles of fractional crystallization for Mars derived by Elkins-Tanton et al. (2005). It has been shown that such a scenario is not consistent with the subsequent volcanic history of Mars and also suggests extensive melting of the lower mantle (Plesa et al. 2014). A similar study, which instead assumed a much smaller density contrast was caused by fractional crystallization, suggests sufficient entrainment from the lower mantle after the overturn by thermal convection to permit the formation of small-scale domains of isotopically distinct materials in the upper mantle (Scheinberg et al. 2014). However, a global mantle overturn would also suggest a more water-rich lower mantle and a depleted upper mantle after the overturn. Outgassing subsequent to the magma ocean crystallization is therefore likely to be very inefficient and a thin elastic lithosphere in the Noachian is difficult to obtain (see the review about the different thermal evolution scenarios of Mars; Breuer et al. 2016).

Degassing and atmospheric evolution

For a homogeneous mantle, most mantle water and CO_2 is released in the early evolution, i.e., during the first 500 Ma to 1 Ga when the bulk of the crust is also produced (**Figure 5**). A total of 0.9–1 bar CO_2 is outgassed during this time period if a mantle oxygen fugacity corresponding to one log10 unit above the iron–wustite buffer is assumed (Hirschmann and Withers 2008; Grott et al. 2011). It is, however, controversial whether an atmosphere with a much higher pressure of several bars can result in surface temperatures reaching above the freezing point of water, necessary for the presence of long-standing global liquid surface water (Forget and Pierrehumbert 1997; Kasting 1997; Forget et al. 2013). In addition, atmospheric loss of H, due to thermal escape as a consequence of a high EUV flux of the young Sun during the first few hundred million years resulted in an entire loss of the early atmosphere (e.g., Tian et al. 2009; Lammer et al. 2013). Therefore, only volcanic activity and associated degassing after this initial loss phase may have contributed to the Martian atmosphere.

Constraints from the magnetic field

To explain the early magnetic field of Mars, a superheated core of a few hundred degrees has been commonly assumed to induce strong core cooling, sufficient to initiate a thermal dynamo (e.g., Hauck and Phillips 2002; Breuer and Spohn 2003; Breuer and Spohn 2006; Morschhauser et al. 2011). This initial temperature distribution allows the generation of a thermal dynamo for up to a few hundred million years independent of the mantle rheology – although the duration of a magnetic field increases with the strength of mantle convection and thus the decrease in mantle viscosity. The dynamo then stops as a consequence of core cooling below a critical heat flow, i.e., the heat flow along the core adiabat (e.g., Breuer et al. 2010). The existence of a superheated core depends strongly on the core formation mechanism and is not well understood for Mars (Golabek et al. 2009). Sandu and Kiefer (2012) have shown that a thermal dynamo can be generated even without a superheated core if water is present because it strongly reduces the viscosity. The reduction in the convective vigor in the mantle due to mantle degassing reduces the heat flux out of the core and terminates a dynamo. Although many studies have suggested that the thermal effects of large impact basin formation are the cause of dynamo termination on Mars (e.g., Roberts et al. 2009), it is in fact possible to terminate the dynamo in the observed time period solely by mantle degassing and the associated reduction in heat flux out of the core. Moreover, it is possible that both internal and impact processes played a role in terminating the dynamo, because the impact mechanism works best if the heat flux out of the core has already been reduced to a level that is close to the critical flux for supporting dynamo generation.

Primary Open Questions

Discussion at the workshop focused on both our current state of knowledge (above) as well as the primary open questions about each volatile species and key higher level questions that are potentially answerable using either geophysics, additional studies of meteorite samples, studies of samples returned by Mars sample return mission(s), or in situ measurements from missions like the MSL Curiosity rover, Mars2020 rover, and/or ExoMars. As with the discussion above about the current state of knowledge of volatiles in the Martian interior, here we discuss the open questions for different volatile species before placing these in context of broader open questions about volatiles in the Martian interior.

Water

Current studies have placed limits on the amount of water in the shergottite source region, but there are still many critical unknowns about water in the Martian interior. Without ancient samples of Martian basalts, it is difficult to constrain how water in the interior has evolved through time. Further, Martian meteorites come from a limited number of unknown locations on the Martian surface, so without context and with variable locations it is difficult to constrain the heterogeneities of water in the Martian interior. This all leads to a critical unknown of the input of magmatically degassed water to the Martian water cycle, which is vital to make a habitable planet and explain the alteration minerals seen from orbit. Further, early serpentinization of the Martian crust may help explain the remnant magnetic field intensity and its distributions, and the present D/H ratio of the crust and atmosphere, but the input of water to the surface and the global water concentrations need to be constrained. Therefore, what is the role played by subsurface clathrates (or other crustal minerals) in trapping/releasing volatiles in the Martian interior?

Further, how does water influence magma genesis, magma crystallization, and interior dynamics? In particular, have volatiles aided in generating a diversity of Martian magmas, now that new studies suggest possible occurrences of evolved rocks in the Martian crust? Does the extensive work done on water in terrestrial systems apply to Martian magmas and the interior with significantly different chemistry? How does water (and other volatile species) influence Martian interior dynamics? Finally, how much water has been lost from the interior due to volcanism?

Halogens

We have a fairly good constraint on the concentration of chlorine in the Martian interior, but estimates for fluorine vary by an order of magnitude. We also have limited constraints on the halogen bearing phases in the Martian interior and how these halogen-bearing phases affect mantle properties including rheology, structure, and melting. Finally, what is the relative abundance of F:Cl:H_2O in Martian magmas and how do halogens and water combine to affect magma genesis, crystallization, and eruption?

Carbon

The largest unknown in the volatile budget of the Martian interior is: what is the bulk C concentration of Mars and is it higher or lower than the Earth? This is vital in order to establish the initial inventory of mantle carbon and understand the Martian carbon cycle from mantle to crust and finally atmosphere.

Isotopes and Noble Gases

The main question that came out of the workshop is the apparent non-correlation between H, S, and Cl isotopes. If all three are recording crustal contamination and secondary processes, then the analyses should correlate with each other, but the current data sets do not fully correlate.

Further, they do not correlate with the noble gas signatures, which also record secondary processes. How many reservoirs (e.g., more than one interior reservoir) do the isotopic and noble gas measurements represent? Which processes or factors (e.g., alteration mineral formation, T regime, redox, degassing) influence specific isotopic systems predominantly (but maybe not others to the same degree)? Finally, why do surface rocks not have the isotopic composition of the Martian atmosphere?

Geophysics

What is the relative importance of batch and fractional melting in Martian mantle plumes? Fractional melting tends to remove incompatible elements such as water early in the melting process, which means that water has less of an effect on the melt production rate in the fractional melting case. What role did mantle degassing and the associated reduction in mantle convection vigor play in terminating magnetic dynamo activity and producing discreet reservoirs in early Mars? How did/do volatiles influence the interior dynamics? Mantle water content has a large influence on the mantle solidus and mantle viscosity. Models of partial melting are quite dependent on interpretations of volatiles in the mantle. Will seismic observations from INSIGHT help resolve any of the issues discussed here?

Strategies moving forward

The community at the workshop concluded that in order to constrain bulk volatile and isotopic composition, and importantly the heterogeneity of the Martian interior, it is vital to increase the diversity of the sample collection, ideally including sophisticated in-situ measurements and through Mars sample return. Detailed experimental petrologic studies are required to understand how volatiles affect mantle melting, magma genesis, and crustal evolution. The results of these experiments should be taken into consideration for the interpretation of global surface mineralogical or chemical trends in terms of planetary cooling and/or mantle chemical evolution and heterogeneity. Finally, geophysical models will have to include these experimental results along with the constraints from Martian samples.

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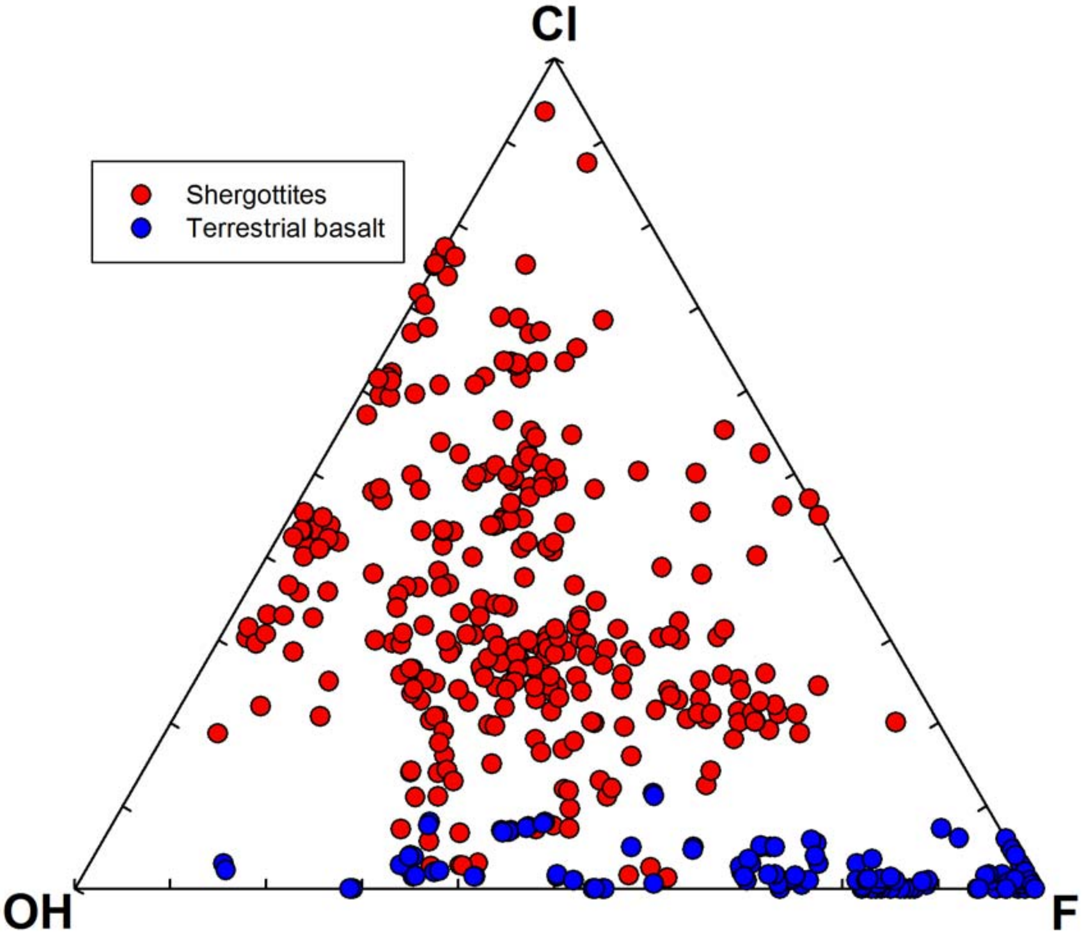


Figure 1. Ternary plot of apatite X-site occupancy (mol%) from shergottites (red) and terrestrial basalts (blue). The shergottite data include basaltic, lherzolitic, and olivine-phyric shergottites, and data are from Gross et al. (2013) and McCubbin et al. (submitted; 2012). Terrestrial apatites are from basaltic systems that have not been reported to have interacted with hydrothermal fluids (Brown and Peckett 1977; Spengler and Garcia 1988; Liu and Comodi 1993; Stoppa and Liu 1995; Coulson and Chambers 1996; O'Reilly and Griffin 2000; Dymek and Owens 2001; Piccoli and Candela 2002; Casey et al. 2007; Filiberto and Treiman 2009b; Rossi et al. 2011).

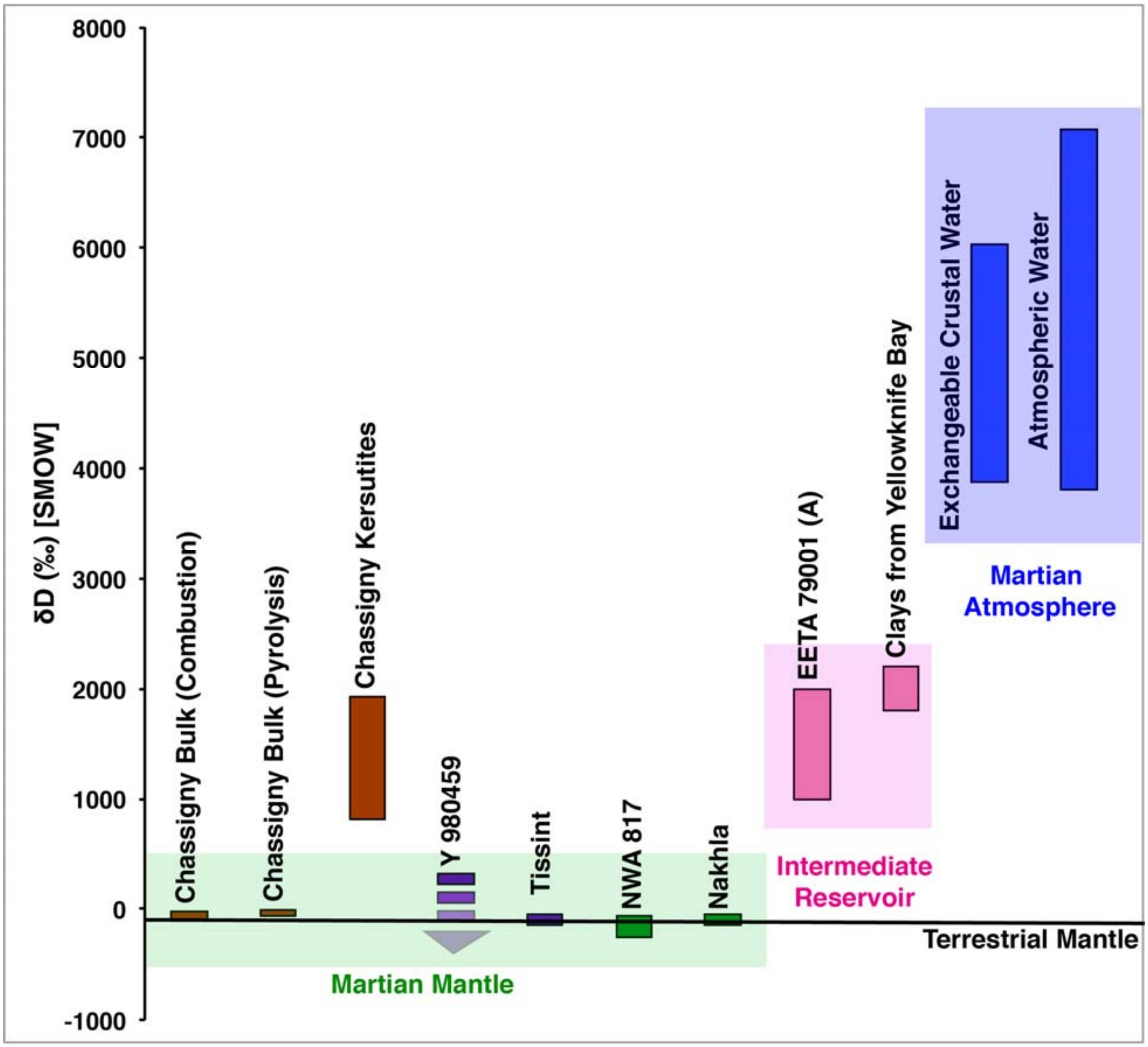


Figure 2: Hydrogen isotopic compositions of Martian water reservoirs, modified and updated from Usui et al. (2012). Data sources: Martian mantle (Chassigny: Leshin et al., 1996, Watson et al., 1994) Depleted Shergottites; Y980459 from Usui et al., 2012; Tissint from Mane et al., submitted. Nakhlites: Nakhla from Hallis et al., (2012); NWA 817 from Gillet et al., (2002). Intermediate reservoir: EETA 79001 (A) from Usui et al., (2015); Clays from Yellowknife Bay from Mahaffy et al., (2015). Atmospheric reservoir (Leshin et al., 2013; Webster et al., 2013).

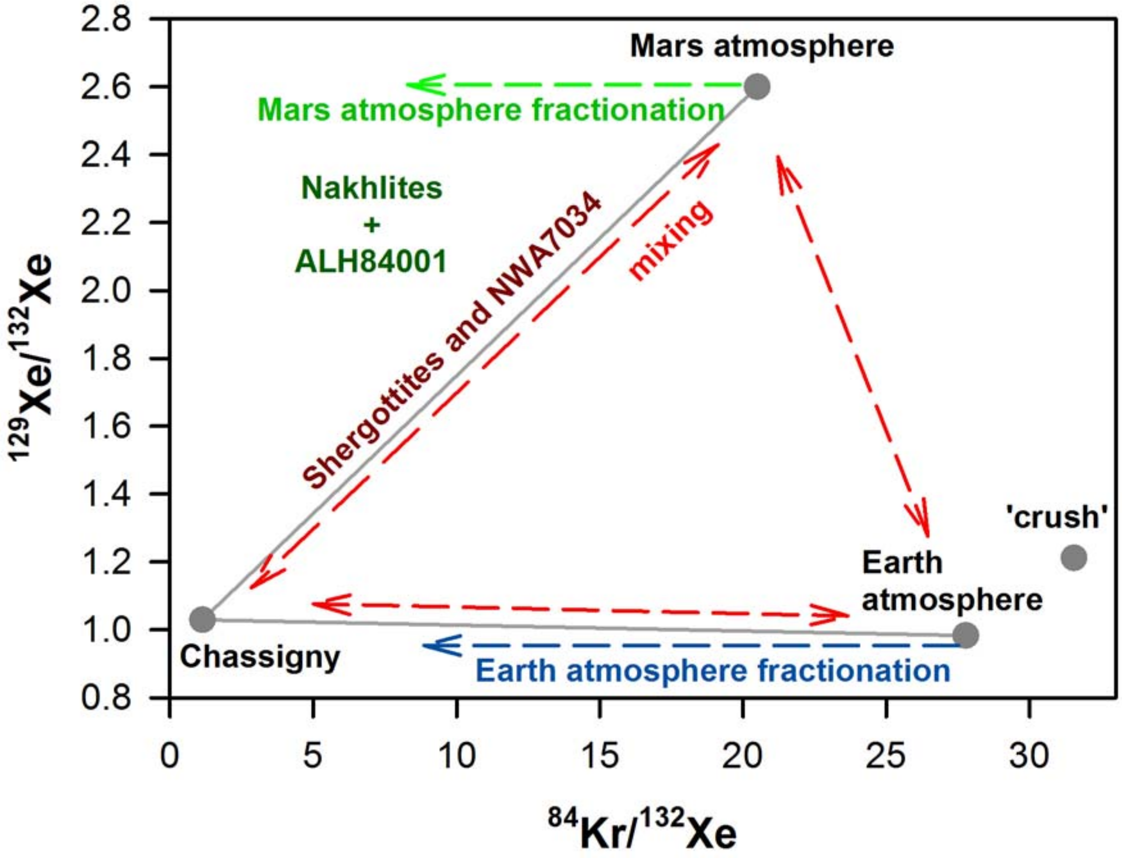


Figure 3. Schematic diagram locating the different gas reservoirs found in Martian meteorites and processes shaping them. For endmembers Martian atmosphere from Bogard and Johnson (1983), Chassigny from Ott (1988), but see also Swindle (2002). Terrestrial atmosphere from (Ozima and Podosek 2002). Earth atmosphere is fractionated when dissolved in water (e.g. Ozima and Podosek 2002 for discussion) but also when incorporated in minerals (Mohapatra et al. 2009; Schwenzer et al. 2013). The meteorites show the following signatures: Chassigny noble gases are thought to represent the Martian interior (e.g., Ott 1988, Matthew and Marti 2001), the Shergottites a mixture of implanted Martian atmosphere and Martian interior (often with some admixed terrestrial air contamination; Bogard and Johnson 1983, Ott 1988, Swindle 2002), and the nakhlites and ALH84001 (Ott 1988, Swindle 2002, and see text). NWA 7034 from

Cartwright et al. (2014). Meteorite measurements often return a mixture of two or more components as indicated by the red arrows. The ‘crush’ component was found by Wiens (1988) and has not been understood yet.

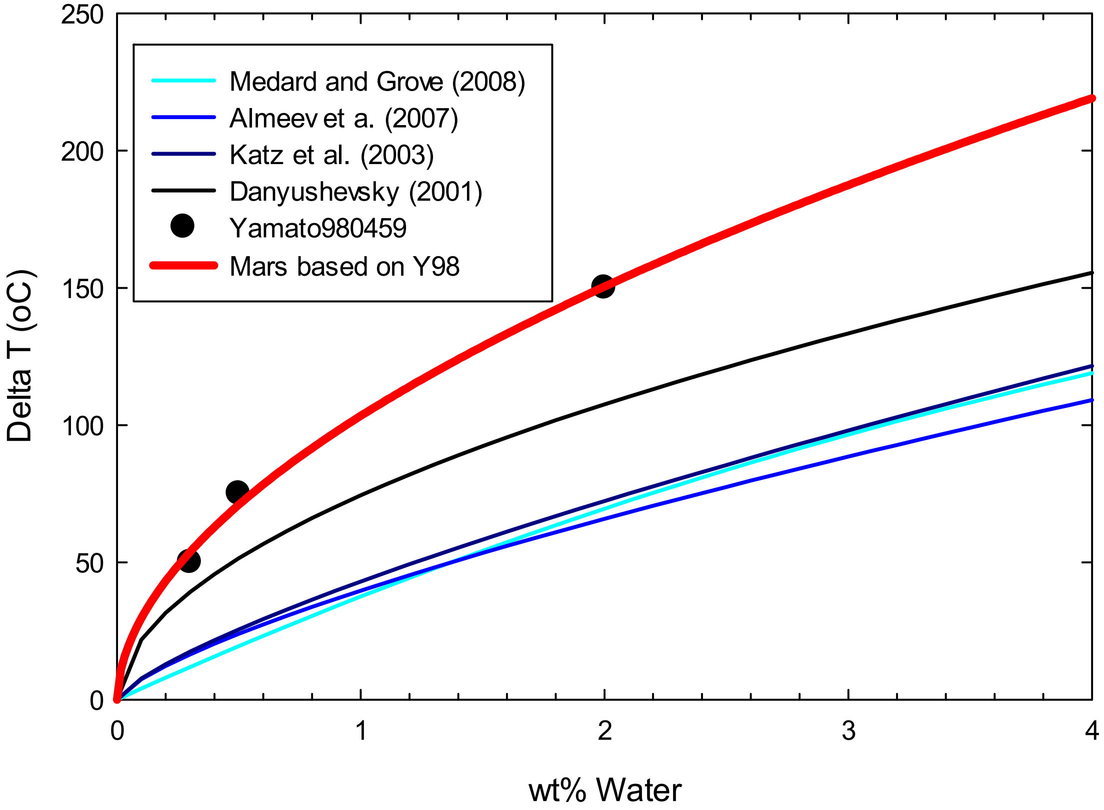


Figure 4. Liquidus depression (Δ T^{o}C) as a function of wt% water in the melt from terrestrial experiments over a range of pressures and experimental techniques Medard and Grove (2008); Almeev et al. (2007); Katz et al. (2003); and Danyushevsky (2001). Also, plotted is the calculated liquidus depression (red curve) for experiments on the Martian meteorite Yamato 980459 with <0.5, 0.5, and 2 wt% water (Norris and Herd 2006; Dalton et al. 2007; Draper 2007 respectively) calculated relative to the anhydrous experiments of Musselwhite et al. (2006).

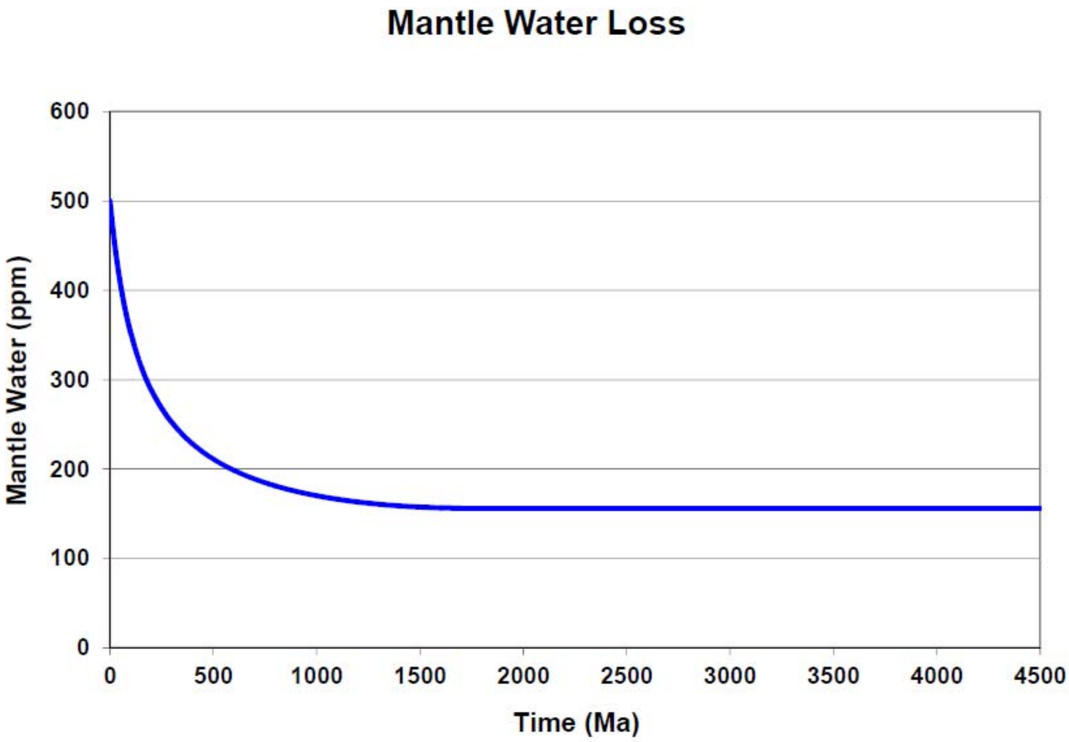
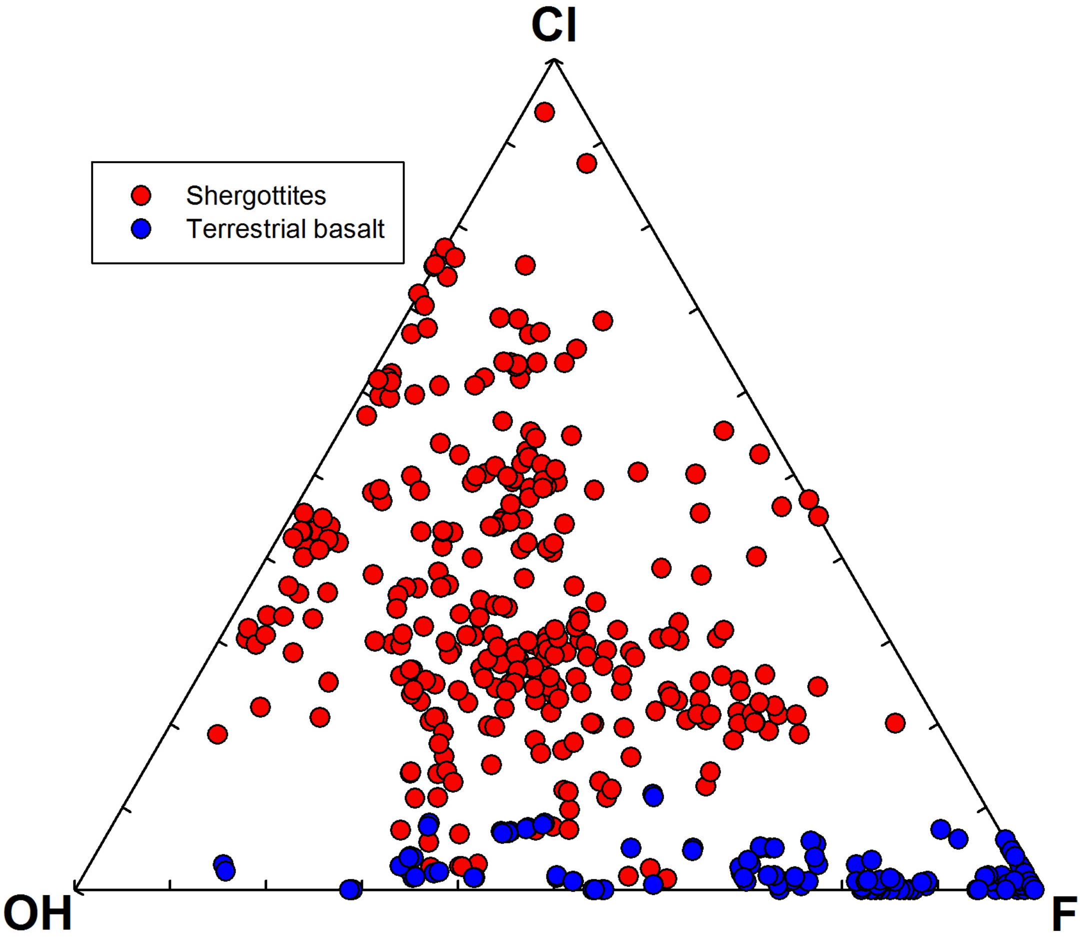
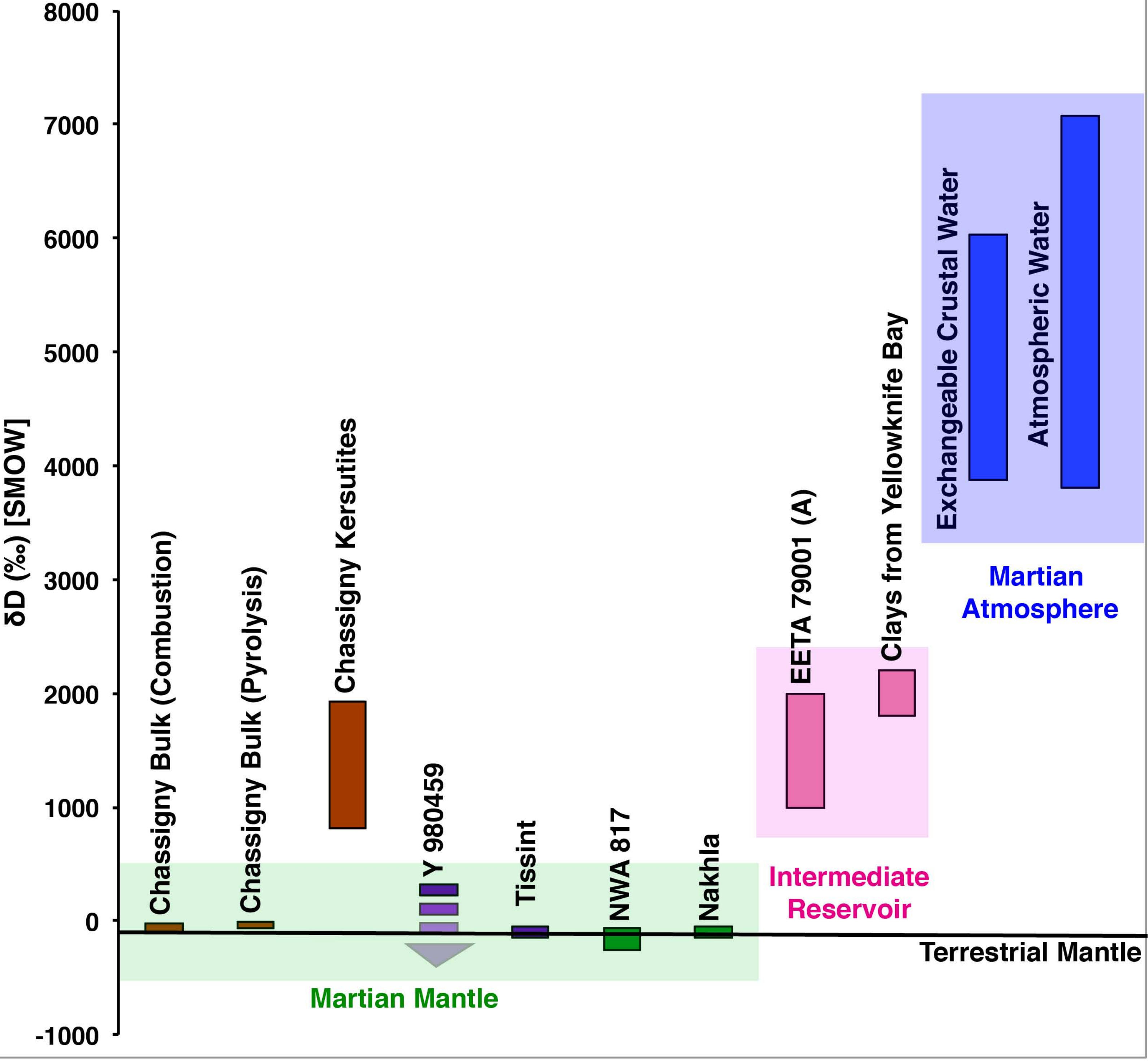
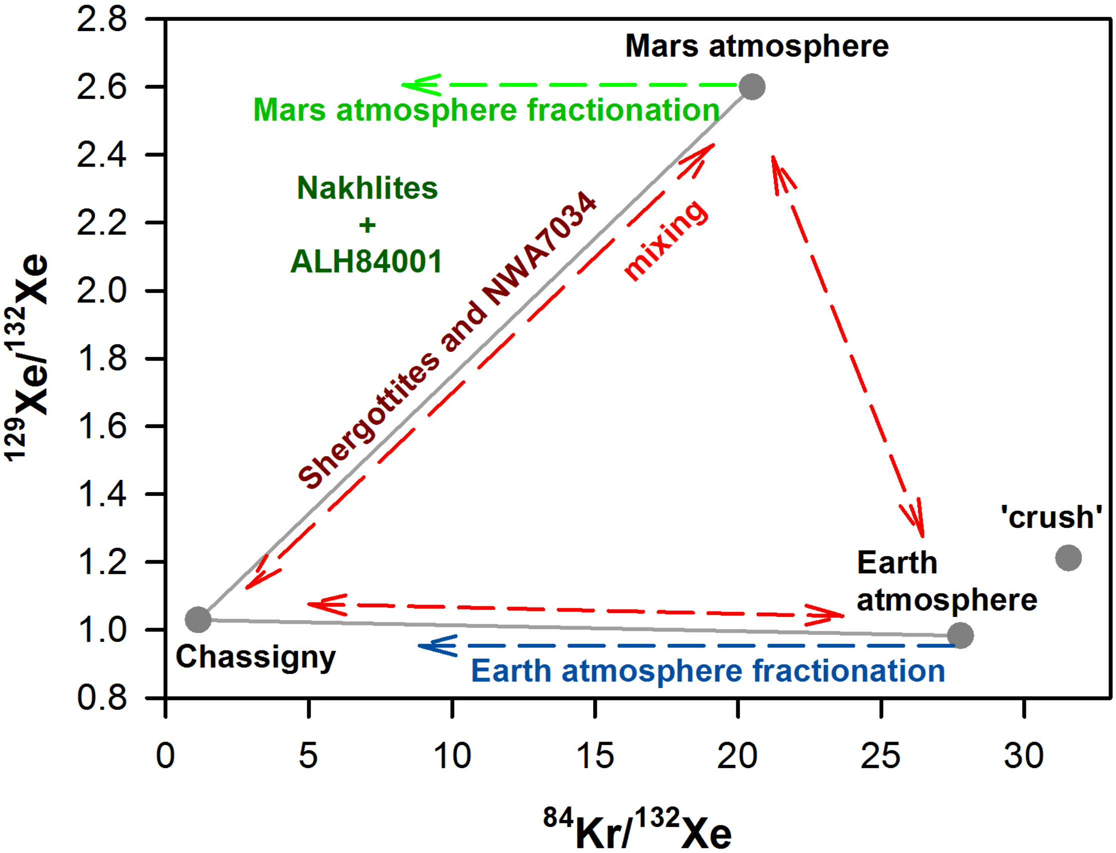


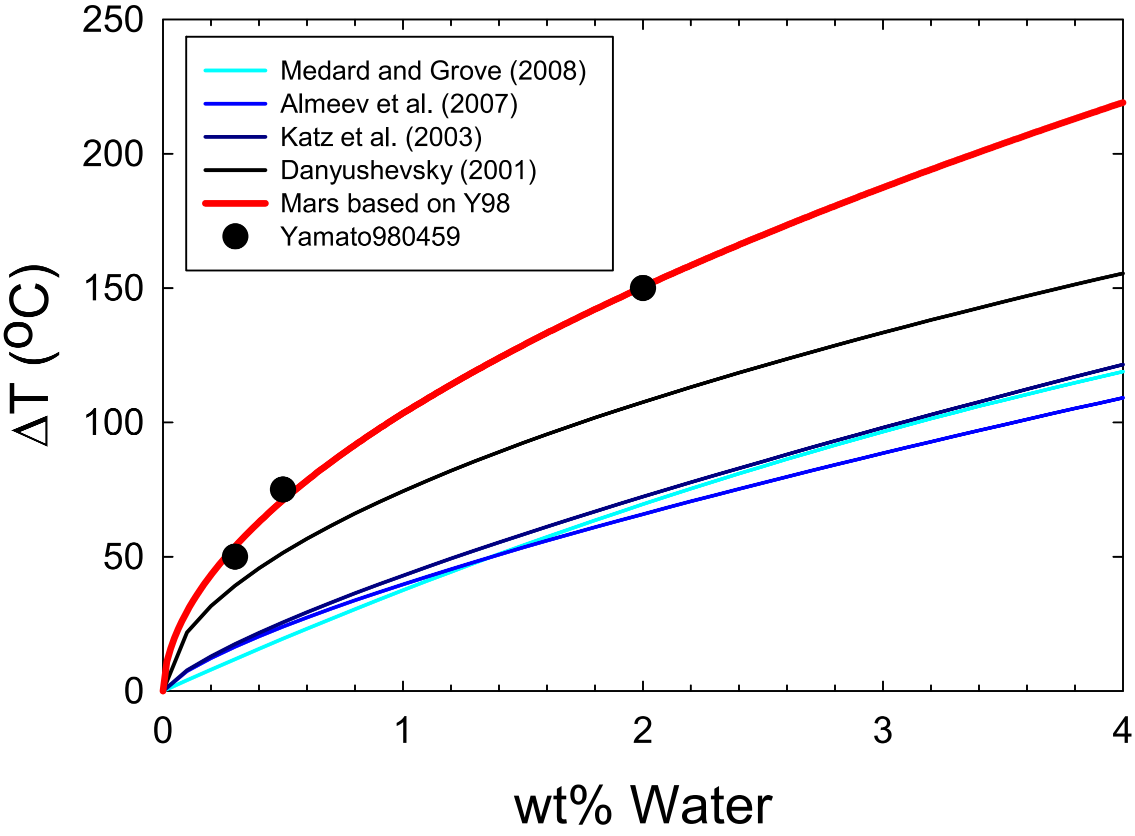
Figure 5. An example calculation of mantle degassing and water loss on Mars, shown as a function of time since accretion. In this simulation, two-thirds of the original mantle water is lost from the mantle, primarily in the first billion years of Martian history.

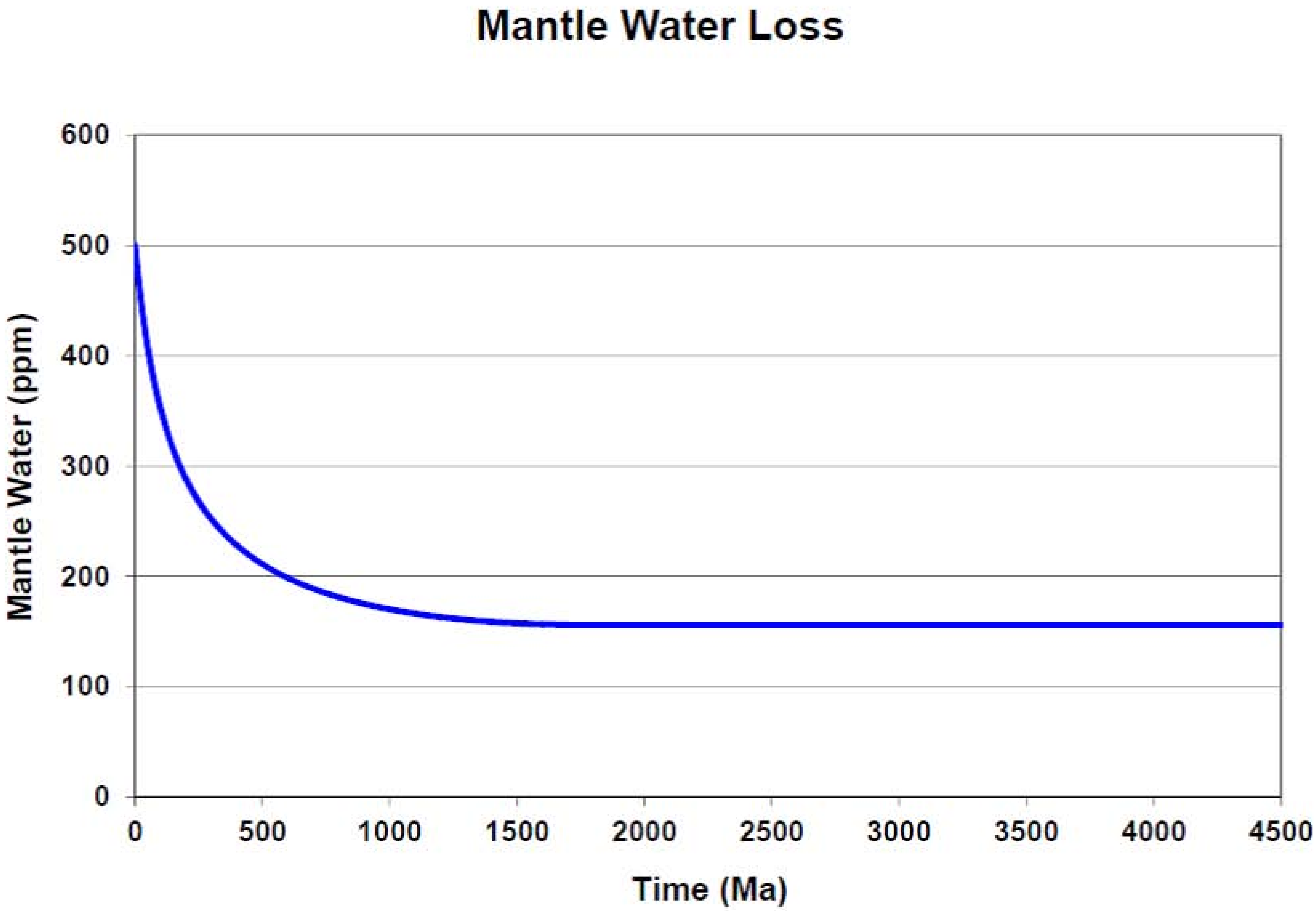

Cl
OH
F
Shergottites
Terrestrial basalt



8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
δD (‰) [SMOW]
Chassigny Bulk (Combustion)
Chassigny Bulk (Pyrolysis)
Chassigny Kersutites
Y 980459
Tissint
NWA 817
Nakhla
EETA 79001 (A)
Clays from Yellowknife Bay
Exchangeable Crustal Water
Atmospheric Water
Martian Atmosphere
Intermediate Reservoir
Martian Mantle
Terrestrial Mantle


Mars atmosphere
Mars atmosphere fractionation
Nakhlites
+
ALH84001
Shergottites and NWA7034
mixing
'crush'
Earth
atmosphere
Chassigny
Earth atmosphere fractionation
$^{129}Xe/^{132}Xe$
$^{84}Kr/^{132}Xe$
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0
5
10
15
20
25
30


250
200
150
100
50
0
ΔT (°C)
0
1
2
3
4
wt% Water
Medard and Grove (2008)
Almeev et al. (2007)
Katz et al. (2003)
Danyushevsky (2001)
Mars based on Y98
● Yamato980459


Mantle Water Loss
Mantle Water (ppm)
600
500
400
300
200
100
0
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Time (Ma)