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## Core Formation and Mantle Differentiation on Mars

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**Abstract** Geochemical investigation of Martian meteorites (SNC meteorites) yields important constraints on the chemical and geodynamical evolution of Mars. These samples may not be representative of the whole of Mars; however, they provide constraints on the early differentiation processes on Mars. The bulk composition of Martian samples implies the presence of a metallic core that formed concurrently as the planet accreted. The strong depletion of highly siderophile elements in the Martian mantle is only possible if Mars had a large scale magma ocean early in its history allowing efficient separation of a metallic melt from molten silicate. The solidification of the magma ocean created chemical heterogeneities whose ancient origin is manifested in the heterogeneous  $^{142}\text{Nd}$  and  $^{182}\text{W}$  abundances observed in different meteorite groups derived from Mars. The isotope anomalies measured in SNC meteorites imply major chemical fractionation within the Martian mantle during the life time of the short-lived isotopes  $^{146}\text{Sm}$  and  $^{182}\text{Hf}$ . The Hf-W data are consistent with very rapid accretion of Mars within a few million years or, alternatively, a more protracted accretion history involving several large impacts and incomplete metal-silicate equilibration during core formation. In contrast to Earth early-formed chemical heterogeneities are still preserved on Mars, albeit slightly modified by mixing processes. The preservation of such ancient chemical differences is only possible if Mars did not undergo efficient whole mantle convection or vigorous plate tectonic style processes after the first few tens of millions of years of its history.

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## 1 Introduction

Mars is the outermost terrestrial planet in the solar system. Its chemical budget compared to the rocky planets of the inner solar system is characterized by a higher abundance of moderately volatile elements, which most likely is due to its larger distance from the Sun. Mars is the second smallest among the terrestrial planets (Mars has about one ninth the mass of Earth), a feature that has puzzled many generations of scientists. It is now proposed that the early migration inwards then outwards of Jupiter and Saturn at the beginning of the solar system inhibited the full formation of Mars (Walsh et al. 2011; Brasser 2012). Alternatively, a Mars-sized body escaped further accretion by rapid outward migration to the outer region of the inner solar system (Minton and Levison 2011). Whatever the exact formation mechanism of Mars, its accretion time appears to have been shorter than that of Earth (e.g., Kleine et al. 2002, 2009; Dauphas and Pourmand 2011). Understanding the accretion and differentiation history of Mars, therefore, is important not just in its own right, but also because it provides essential insights into the accretion history of rocky planets in the inner solar system. In addition, Mars provides an important analogue of what the Earth and other terrestrial planets may have looked like in their earliest stages of accretion. The objective of this article is to review the accretion and early differentiation history of Mars as constrained mainly from geochemical and isotopic observations.

From mineralogical and chemical studies of Martian meteorites, the measurements of its gravity and magnetic field by orbiting satellites and *in-situ* analyses by exploration rovers, it is known that the planet is chemically differentiated, i.e. it has a metallic core, a heterogeneous silicate mantle and mafic to intermediate crust covered with a layer of weathered material and an atmosphere. Its differentiation processes may have many similarities with the chemical differentiation of the Earth. However, due to the much smaller size of Mars compared to Earth its overall geological activity declined earlier after planetary accretion. This is because to a first approximation smaller bodies lose their primordial heat from accretion, heat generated by radioactive decay of short-lived isotopes and core formation by conduction much more efficiently than larger bodies, which lose significant amounts of heat via convection as expressed in volcanic activity on the surface. Whether convection occurs in addition to conduction also depends on the water-content of the planetary interior. Since Mars seems to have outgassed substantially in its early history, the water content of the Martian mantle is now about 2-5 times lower than on Earth (McCubbin et al. 2012), which disfavors convection as well. However, recent crater counting measurements indicate very young (100 Ma) or possibly even near-recent volcanic activity at the surface of Mars (Neukum et al. 2004, 2010), which imply that not all heat is lost by conduction. Thermodynamical modeling of Mars seems to indicate that its mantle may be convecting at the present time (Li and Kiefer 2007). However, despite possible convection in the mantle, the planet is and has been for the major part of its history in a stagnant-lid regime (Lenardic et al. 2004). Compared to Earth the planet showed vigorous geologic activity only during its very early history (e.g. Breuer and Spohn 2003; O'Neill et al. 2007). As a consequence it can be expected that chemical and isotopic signatures of early planetary differentiation processes may be still well preserved on Mars. In contrast, such signatures are largely lost on Earth due to the vigorous convection of the Earth's mantle which results in the formation of new and the destruction of old oceanic and

continental crust to the present day. This convection drives homogenization of the mantle after an early differentiation event, like core formation or the crystallization of a magma ocean. However, Mars was able to retain some of its primary heterogeneity implying that over time mantle convection was much less vigorous on Mars than on Earth.

The chemical make-up of Mars and the processes leading to a chemically differentiated planetary body can be investigated in some detail because material for chemical, physical, mineralogical and petrological study is available for analysis in the laboratory. Apart from the Earth, Mars is currently the only planet of the solar system from which material is available for direct analysis in the laboratory. Based on images of the Martian surface and spectral analyses of surface rocks, it is clear that the meteorite material is somewhat limited and does not cover all rock types present on Mars. All meteorites are igneous rocks and none have been found so far that derive from the clastic and chemical sediments that cover large parts of the Martian surface. The study of SNC meteorites in combination with *in-situ* analyses on Mars by the rovers Spirit and Opportunity as well as results from earlier missions (particularly the Viking missions in the 1970's and remote sensing data obtained by several orbiting missions) provides insights into the chemical, mineralogical and petrological composition of part of Mars from the micron to the planetary scale. These studies also provide constraints on the chemical composition of the solar nebula since Mars may have sampled a section of the solar system from which we do not have other material for direct study. Together with meteorites mostly derived from smaller bodies located in the asteroid belt, and the terrestrial and lunar material only a small section of the solar system is currently accessible to direct study.

Remote and *in-situ* studies combined with information derived from Martian meteorites can be used to reconstruct the formation of Mars and its evolution through time. This evolution includes aspects of accretion from planetesimals to the final formation of the planet, its core-mantle segregation, the chemical differentiation of the mantle, the formation of the crust and magmatic activity through time. Core formation in particular is the most dramatic chemical differentiation observed in planets and planetesimals, and has profound consequences for their evolution that range from thermal and chemical processes in the silicate part, to surface evolution and the generation of a magnetic field. Magmatism starting with a magma ocean stage and continuing later with volcanic and subvolcanic activities is a key process that influences the chemical composition of the atmosphere and is the dominant vector for the transfer of volatiles from mantle to the atmosphere. The availability of Martian material in the form of meteorites for direct mineralogical, petrological and chemical study, therefore, provides important insights into the composition and evolution of Mars as a planetary body.

## 2 Martian Material and the Composition of Mars

Currently about 100 Martian meteorites are available for direct study in the laboratory (The Meteoritical Bulletin Database, <http://www.lpi.usra.edu/meteor/metbull.php>), but among them, only ~60 are unpaired (<http://www.imca.cc/mars/martian-meteorites.htm>). Almost all samples are finds from hot or cold deserts and show different degrees of terrestrial weathering. Most Martian meteorites collected so far are quite small and only about 20 of them have a mass of more than 500 g. This limits the number of samples that can be studied in detail with currently available destructive geochemical techniques, particularly high precision isotope measurements or trace elements that require large amounts of sample material.

The Martian meteorites are commonly classified as SNC meteorites named after the prominent representative in each group that also represents an observed fall: Shergotty

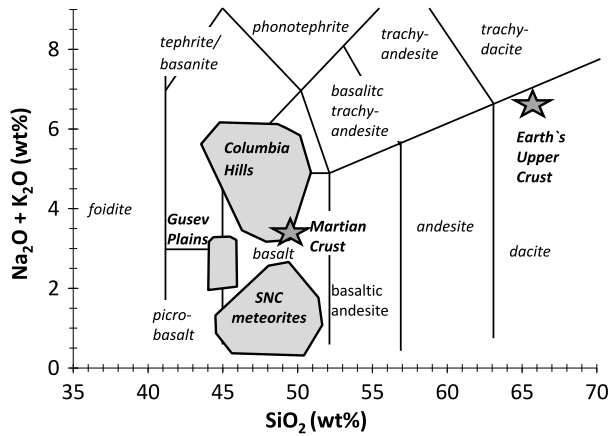
(India, 1865), Nakhla (Egypt, 1911) and Chassigny (France, 1815). All known samples are of magmatic origin (e.g., McSween 1994; Treiman et al. 2000; Nyquist et al. 2001; McSween et al. 2009). The gases contained in almost all SNCs match those measured in situ for the Martian atmosphere by the Viking missions and constitute the absolute proof of their Martian origin (e.g., Bogard and Johnson 1983; Treiman et al. 1986, 2000; Bogard et al. 2001). The gases may have been trapped during shock by impacts of other meteorites prior or during ejection of the Martian samples from near the planetary surface. One exception is the sample Chassigny, which is a cumulate and has different gas abundances that may reflect the abundances in the Martian mantle (Ott and Begemann 1985; Ott 1988).

The *shergottites* are the most common type and represent mafic to ultramafic igneous lithologies with phenocrystic olivine and orthopyroxene and only rarely clinopyroxene. Based on their crystal size and modal mineralogy they are subdivided into basaltic, olivine-phyric, and lherzolitic shergottites and one wehlrite. This mineralogical subdivision more or less reflects another subdivision based on their geochemical composition (depleted, intermediate and enriched in light rare earth elements) (e.g., McSween 1994; Borg et al. 2002; Debaille et al. 2007; Debaille et al. 2008). The remarkable characteristic of the shergottites is their “young” crystallization ages, ranging from 165 to 475 Ma (Nyquist et al. 2001), even though Pb-Pb isotope systematics were used to argue for “old” crystallization ages of around 4.1 Ga (Bouvier et al. 2005; Bouvier et al. 2008). The age significance of the Pb-Pb isotope systematics of shergottites, however, has been questioned and are more commonly interpreted to reflect mixing and contamination with terrestrial Pb (e.g., Borg et al. 2005), or disturbance related to shock (Gaffney et al. 2011). A more complete overview about the ages of shergottites is presented by Grott et al. (2012).

Currently there are about ten known *nakhrites* available; the most prominent of the group is the meteorite Nakhla, which fell in El-Nakhla, Alexandria, Egypt, in 1911. It is an unusually large sample with an estimated weight of 10 kg and the only known fall in this group of meteorites. The members of the Nakhlite group represent clinopyroxenites with 70–80 % augite and about 10 % olivine (Treiman 2005). From the group of the *chassignites* only two samples are currently known (Beck et al. 2005), and they are dunites with cumulative texture that are made up of dominantly olivine and contain minor intercumulus pyroxene, feldspar, and oxides. Nakhrites and chassignites show similar ages, within analytical uncertainties, of  $\sim 1.3$  Ga (Nyquist et al. 2001). Beside the three main groups, a sample in its own group is the meteorite *ALH84001* found in Antarctica. It is a relatively coarse grained orthopyroxenite. This specimen is not only distinct from other Martian meteorites based on its mineralogy, but also due its old age, recently revised from  $\sim 4.5$  Ga (Nyquist et al. 1995) to  $4.091 \pm 0.030$  Ga (Lapen et al. 2010), consistent with the age of  $4.074 \pm 0.099$  Ga obtained by Bouvier et al. (2009).

In addition to chemical analyses of Martian meteorites, numerous major element with selected trace element analyses are available for Martian material analyzed directly on the surface during the Pathfinder, Spirit and Opportunity missions. A striking observation is that almost all Martian rocks on the surface are broadly of basaltic composition (Fig. 1) but not identical to the samples that are available in the meteorite collections (e.g. McSween et al. 2009; Grotzinger et al. 2011). All in-situ analyses show significantly higher total alkali contents than the meteorites. The samples analyzed by Pathfinder have the highest SiO<sub>2</sub> content (e.g. McSween et al. 2009). This may be due to the fact that they represent surface sediments derived from weathered material rather than fresh igneous rocks. Some analyses may also be compromised by dust that covers the surface of Mars (e.g. Wänke et al. 2001; McSween et al. 2009). During the later Spirit and Opportunity missions the rock surface

**Fig. 1** Composition of Martian meteorites, soils and rocks (after Grotzinger et al. 2011)



was generally cleaned with a brush and analyses were made on the solid rock material. Thus the later analyses can be considered more representative of the primary igneous rocks.

Based on the analyses of SNC meteorites and *in-situ* analyses of Martian rocks and sediments by space missions different models for the bulk composition of Mars, its core and its silicate reservoir have been proposed (e.g. Dreibus and Wänke 1985; Ohtani and Kamaya 1992; Bertka and Fei 1997). A striking feature of Mars is that its bulk chemical position is higher in moderately volatile elements than that of the Earth (e.g. Dreibus and Wänke 1985). Compared to igneous rocks on Earth, basaltic rocks from Mars have about twice the FeO content at similar  $\text{SiO}_2$  content (e.g. Halliday et al. 2001). This implies that the Martian mantle is richer in FeO than the Earth's mantle and Mars has a less massive metallic core than the Earth. Indeed, the radius of Mars is 3,400 km and the radius of its core is between 1,480 km (e.g. Kavner et al. 2001) and  $1,794 \pm 65$  km (Sohl and Spohn 1997; Rivoldini et al. 2011). The small size of Mars results in internal pressures that are only about one-third of those in the Earth at any given depth which leads to mineral assemblages in the Martian mantle that are different from the Earth (e.g. Bertka and Fei 1997). As a consequence mantle rheology and melt compositions produced by partial melting of the mantle are also different. From these chemical and physical differences it can be expected that differentiation on Mars will have followed paths that are somewhat different from the Earth (see also Grott et al. 2012).

### 3 Magma Ocean and Core Formation on Mars

Since Mars has a bulk density that is similar to chondrites and its outer parts consist of much lighter silicate rocks it has to have a dense core (e.g., Johnston et al. 1974). Based on results from rotational dynamics of the planet, the size and density distribution as well as the physical state of the core can be determined (e.g. Dehant et al. 2003). Furthermore, chemical analyses of SNC meteorites and *in-situ* analyses during the rover missions on Mars demonstrate that all rocks have Fe contents that are significantly below chondritic abundances. The Martian core, therefore, consists dominantly of metallic Fe, the only abundant element that can produce a large amount of a heavy melt in a planetary body. This metallic melt most likely has dissolved minor amounts of other elements. Due to the high content of moderately volatile elements on Mars and thus its high S-content, it is expected

from studies of the partition behavior of elements between silicate and metal melts that the core contains up to 16 % S (Stewart et al. 2007; Rivoldini et al. 2011). This high S-content also reduces the melting point of the metallic liquid considerably and may result in a present-day partially liquid core on Mars (e.g., Sohl and Spohn 1997; Stewart et al. 2007; Rivoldini et al. 2011). If the core is still molten, it does not generate a significant magnetic field since such a field seems absent since ca. 4 Ga (e.g., Schubert and Spohn 1990; Acuna et al. 1999; Connerney et al. 2004; Lillis et al. 2008; Lapen et al. 2010).

A core can form on a planet only if the planet is at least partially molten to allow for a segregation of a heavy metallic melt from a lighter silicate melt. Efficient core formation requires that the silicate melt dominates the system, because only then the immiscible iron melt can segregate quantitatively. The major evidence for an efficient metal melt segregation on Mars is the abundance of the highly siderophile elements (HSE), particularly Re, Os, Ir, Ru, Pt, Rh, Pd and Au, in its silicate rocks. All Martian rocks are strongly depleted in the HSE as are Earth's mantle rocks (Brandon et al. 2012). Such chemical signatures require an efficient metal-silicate separation that can only be achieved by the segregation of a metallic melt from a silicate melt. In contrast, the separation of molten metal from solid silicate by percolation is less efficient and leaves behind some stranded metal (Yoshino et al. 2004). Moreover, percolation requires dihedral angles of less than  $\sim 60^\circ$  to allow formation of an interconnected network of metal melt. However, throughout the major part of the Martian mantle dihedral angles appear to be larger than  $60^\circ$  (Terasaki et al. 2007), suggesting that percolation has been limited. This implies that efficient metal segregation and differentiation has been possible only with a large degree of silicate melting.

The energy required for melting and magma ocean formation may have been provided by the decay of short-lived  $^{26}\text{Al}$  ( $t_{1/2} \approx 0.73$  Ma), if accretion of Mars occurred in the first 1–2 Ma of the solar system (Nimmo and Kleine 2007; Dauphas and Pourmand 2011). Alternatively, large impacts during protracted accretion delivered the energy for widespread melting (e.g., Tonks and Melosh 1993; Elkins-Tanton et al. 2005a). The early loss of a dense atmosphere (Lammer et al. 2008) may be seen as an argument for a large impact. Whether the individual impactors have caused only local heating and the formation of smaller magma oceans (Senshu et al. 2002; Reese and Solomatov 2006) or if alternatively the magma ocean on Mars was global (Elkins-Tanton et al. 2005b) is a matter of current debate, as are the longevity and depth of the magma ocean(s).

Core formation causes almost quantitative removal of the HSE to the core and also leads to the depletion of other siderophile elements in the mantle, including the moderately siderophile W, Cr, P, Co, Ni, Mo, Ga, and V (Kong et al. 1999; Righter and Chabot 2011). The depletion of these moderately siderophile elements can be used to infer the pressure and temperature conditions of metal-silicate equilibration during core formation and, hence, the depth of the Martian magma ocean. Using this approach Righter et al. (1998) suggested a magma ocean depth of 700 to 800 km. However, a more recent study, using new data for the depletion of moderately siderophile elements in the Martian mantle, arrived at a magma ocean depth of about 1300 km (Righter and Chabot 2011). Borg and Draper (2003) used petrogenetic modeling of the lithophile trace element systematics in shergottites to infer a magma ocean depth of at least 1000 km. This depth is also consistent with the requirement that garnet be a liquidus phase. Debaille et al. (2008) used the Sm-Nd and Lu-Hf isotope systematics of depleted shergottites to suggest a magma ocean depth of at least 1350 km. Finally, Elkins-Tanton et al. (2003, 2005a, 2005b) argued on theoretical grounds that Mars could have been entirely molten due to the large amounts of heat present at the beginning of the solar system (see discussion above) and, therefore, proposed the possibility of a magma ocean reaching down all the way to the core-mantle boundary ( $\sim 2000$  km in Mars). Such

a deep magma ocean, however, seems to be inconsistent with the observed depletions of moderately siderophile elements in the Martian mantle (Righter and Chabot 2011), unless metal-silicate equilibration occurred at different depths and models derived from trace element partitioning would thus yield an “average depth” of metal-silicate separation.

The depletion of the highly siderophile elements in the Martian mantle is not only important for constraining the extent of melting during core formation, but also provides essential insights into the temporal relationship of accretion and core formation, and the late accretion history of Mars. The HSE have an extremely high affinity for an iron-melt that is manifested in their metal-silicate partition coefficients that all exceed 10,000 and are different for the different HSEs (e.g., Borisov et al. 1994; Brandon et al. 2000; Holzheid et al. 2000; Brandon et al. 2012). Thus core formation should result in an extreme depletion of these elements and a pattern of HSEs abundances in Martian silicate rocks that are highly fractionated when normalized to chondritic abundances. This is not observed, however. As shown in Brandon et al. (2012) the HSE are depleted by a factor of slightly more than 100 relative to CI chondrites and have an elevated Pd/Pt ratio, but the relative abundances of Re, Os, Ir and Ru are close to chondritic. This element pattern is consistent with a late veneer of ca. 0.08 % (Bottke et al. 2010) of near chondritic material that was added to the Martian mantle after core formation. Thus after the end of core formation there was only minor addition of material and this implies that the time of core formation defines essentially the cessation of planetary growth (see below Sect. 4).

Another important aspect regarding core formation in Mars is that the degree of depletion of some moderately siderophile elements depends on the oxidation state of the magma. From the study of SNC meteorites it is obvious that the Martian mantle is currently more reducing than the Earth’s mantle. However, the higher Fe content of the Martian mantle and the smaller metallic core require that bulk Mars is more oxidized than the bulk Earth. This is consistent with accretion models for terrestrial planets that indicate that the early phase of planet formation involved the accretion of more refractory material that is volatile depleted and reduced, followed by a later addition of more volatile rich material that is also more oxidized (e.g. Ringwood 1977; Dreibus and Wänke 1987; Albarède 2009; Nebel et al. 2011; Rubie et al. 2011). Since bulk Mars has a higher abundance of volatile elements (Dreibus and Wänke 1987) it is also more oxidized than the Earth. As a consequence the depletion of the redox-sensitive moderately siderophile elements by core formation is less severe than on Earth. This resulted in a lesser depletion of W in the Martian mantle than in the terrestrial mantle and thus silicate Mars has a lower Hf/W than silicate Earth. The Hf/W is a crucial parameter for the estimation of core formation ages using the  $^{182}\text{Hf}$ - $^{182}\text{W}$  chronometer, as discussed in the following section.

#### 4 Hf-W Age of Core Formation and the Accretion History of Mars

The  $^{182}\text{Hf}$ - $^{182}\text{W}$  system is a powerful tool for investigating the timescales of planetary accretion and core formation (e.g., Jacobsen 2005; Kleine et al. 2009). The segregation of the Martian core fractionated the highly lithophile Hf from the moderately siderophile W. If this metal-silicate segregation happened during the life time of the short lived isotope  $^{182}\text{Hf}$ , then the Martian mantle should have an excess in  $^{182}\text{W}$  and analyses of SNC meteorites confirm that this signal is preserved in Martian meteorites (Lee and Halliday 1997; Kleine et al. 2004b; Foley et al. 2005). Using the W isotope composition of Martian samples to estimate the timing of core formation requires knowledge of the Hf/W and  $^{182}\text{W}/^{184}\text{W}$  ratios of bulk Mars and the bulk silicate portion of Mars. Furthermore, the degree to which

**Table 1** Parameters used for calculating core formation model ages

$(^{182}\text{Hf}/^{180}\text{Hf})_0$	$(9.72 \pm 0.44) \times 10^{-5}$	Burkhardt et al. (2008, (2012)
$\varepsilon^{182}\text{W}$ Martian mantle	$0.45 \pm 0.15$	Kleine et al. (2009)
$^{180}\text{Hf}/^{184}\text{W}$ Martian mantle	$4.14 \pm 0.53$	Dauphas and Pourmand (2011)
$\varepsilon^{182}\text{W}$ bulk Mars (= carbonaceous chondrites)	$-1.9 \pm 0.1$	Kleine et al. (2002); Schönberg et al. (2002); Yin et al. (2002)
$^{180}\text{Hf}/^{184}\text{W}$ bulk Mars (= carbonaceous chondrites)	$1.23 \pm 0.15$	Kleine et al. (2009)

$$\varepsilon^{182}\text{W} = [(^{182}\text{W}/^{184}\text{W})_{\text{sample}} / (^{182}\text{W}/^{184}\text{W})_{\text{terrestrial standard}} - 1] \times 10^4$$

metal-silicate equilibrium was achieved during core formation must be evaluated (e.g., Kleine et al. 2009).

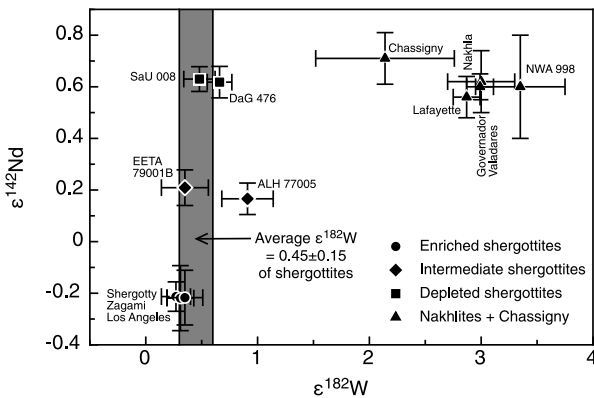
#### 4.1 Hf-W Systematics of the Martian Mantle

Since both Hf and W are refractory it can be assumed that bulk Mars has chondritic relative abundances of Hf and W, and that its  $^{182}\text{W}/^{184}\text{W}$  is similar to that found in chondrites. However, as a result of metal-silicate fractionation in the early solar nebula, the Hf/W ratio is different among the various groups of chondrites. The average  $^{180}\text{Hf}/^{184}\text{W}$  ratio of carbonaceous chondrites is  $1.23 \pm 0.15$ , corresponding to a present-day  $^{182}\text{W}/^{184}\text{W}$  ratio of  $-1.9 \pm 0.1$   $\varepsilon^{182}\text{W}$  (Kleine et al. 2002; Schoenberg et al. 2002; Yin et al. 2002;  $\varepsilon^{182}\text{W}$  is the deviation of  $^{182}\text{W}/^{184}\text{W}$  from the terrestrial standard value in parts per  $10^4$ , see Table 1). Ordinary chondrites have more variable  $^{180}\text{Hf}/^{184}\text{W}$  ratios ranging from  $\sim 0.6$  to  $\sim 1.1$  for H chondrites and from  $\sim 1.6$  to  $\sim 2.1$  for LL chondrites, and corresponding  $\varepsilon^{182}\text{W}$  values between  $\sim -2.5$  and  $\sim -2.0$  and  $\sim -1.7$  and  $\sim -1.5$ , respectively (Kleine et al. 2008, 2009). Calculating a Hf-W age of core formation, therefore, requires estimating which of these chondritic Hf-W compositions is most appropriate for Mars.

Estimating the Hf/W and  $^{182}\text{W}/^{184}\text{W}$  ratios of the bulk Martian mantle is more complicated. Unlike the Earth and Moon, the mantle of Mars does not have a uniform  $^{182}\text{W}/^{184}\text{W}$  ratio but exhibits  $^{182}\text{W}$  heterogeneities (Lee and Halliday 1997; Kleine et al. 2004b; Foley et al. 2005). The shergottites are characterized by  $\varepsilon^{182}\text{W}$  values of  $\sim 0.2$  to  $\sim 0.8$ , whereas the nakhlites and Chassigny have  $\varepsilon^{182}\text{W}$  values of around  $\sim 3$  (Fig. 2). These  $^{182}\text{W}$  variations most probably reflect early silicate differentiation processes, which led to a fractionation of highly incompatible W from less incompatible Hf (Righter and Shearer 2003). Using the W isotopic data to infer the timescales of core formation in Mars, therefore, requires distinguishing  $^{182}\text{W}$  variations caused by silicate differentiation processes from those that reflect Hf/W fractionation due to early core formation. As a consequence of an early silicate differentiation, Martian meteorites also show variations in  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios. While all nakhlites are characterized by large  $^{142}\text{Nd}$  excesses of  $\sim 0.6$   $\varepsilon$ -units, shergottites show more variable  $^{142}\text{Nd}/^{144}\text{Nd}$  ranging from  $\sim -0.2$  to  $\sim +0.6$   $\varepsilon^{142}\text{Nd}$  (Debaille et al. 2007; Caro et al. 2008). The  $^{142}\text{Nd}$  variations in shergottites and nakhlites were interpreted to reflect an early silicate differentiation in Mars between  $\sim 30$  and  $\sim 100$  Ma after solar system formation (see Sect. 5.1), early enough to also have caused variations in  $^{182}\text{W}/^{184}\text{W}$  ratios.

Kleine et al. (2004b) and Foley et al. (2005) argued that the  $^{182}\text{W}/^{184}\text{W}$  ratio of shergottites best represents the W isotopic composition of bulk silicate Mars. In spite of their variable  $^{142}\text{Nd}/^{144}\text{Nd}$ , shergottites exhibit a limited range in  $\varepsilon^{182}\text{W}$  values from  $\sim 0.3$  to





**Fig. 2**  $\varepsilon^{182}\text{W}$ - $\varepsilon^{142}\text{Nd}$  systematics of SNC meteorites (data from Lee and Halliday 1997, Kleine et al. 2004b; Foley et al. 2005; Debaille et al. 2007; Caro et al. 2008). The isotope variation implies the preservation of distinct mantle reservoirs that formed during the initial stages of chemical differentiation on Mars.  $\varepsilon^{182}\text{W} = [({}^{182}\text{W}/{}^{184}\text{W})_{\text{sample}}/({}^{182}\text{W}/{}^{184}\text{W})_{\text{terrestrial standard}} - 1] \times 10^4$ ,  $\varepsilon^{142}\text{Nd} = [({}^{142}\text{Nd}/{}^{144}\text{Nd})_{\text{sample}}/({}^{142}\text{Nd}/{}^{144}\text{Nd})_{\text{terrestrial standard}} - 1] \times 10^4$

$\sim 0.6$  (Kleine et al. 2004b; Foley et al. 2005). Only ALH 77005 has a somewhat higher  $\varepsilon^{182}\text{W}$  value of  $0.9 \pm 0.3$  (Foley et al. 2005). The limited range in  ${}^{182}\text{W}/{}^{184}\text{W}$  of the shergottites indicates that the early silicate differentiation processes that led to the  ${}^{142}\text{Nd}$  variations did not result in significant  ${}^{182}\text{W}$  variations. Furthermore, several of the shergottites exhibit  ${}^{142}\text{Nd}/{}^{144}\text{Nd}$  ratios close to the estimated Nd isotopic composition of bulk Mars (i.e.,  $\varepsilon^{142}\text{Nd}$  between  $\sim -0.2$  and 0 (Debaille et al. 2007; Caro et al. 2008). The average  ${}^{182}\text{W}/{}^{184}\text{W}$  of shergottites of  $\varepsilon^{182}\text{W} = 0.45 \pm 0.15$  (Kleine et al. 2009), therefore, provides the current best estimate for the W isotopic composition of bulk silicate Mars.

The Hf/W ratio of the bulk Martian mantle cannot be measured directly because the Hf/W ratios of available Martian meteorites are the result of complex melting histories (Treiman et al. 1986; Kleine et al. 2004b; Nimmo and Kleine 2007). During silicate melting W is more incompatible than Hf, resulting in large Hf/W fractionations during partial melting. The Hf/W ratio characteristic for the entire Martian mantle must, therefore, be inferred by comparing the W concentrations in Martian meteorites to those of a refractory lithophile element, whose incompatibility is similar to that of W and whose abundance relative to Hf is known. Trace element studies on lunar and terrestrial basalts show that this condition is most closely met by U and Th (Palme and Rammensee 1981; Newsom et al. 1996; Arevalo and McDonough 2008). Owing to the more oxidized nature of the Martian mantle, its Hf/W ratio is much lower than that of the bulk silicate Earth. Nimmo and Kleine (2007) pointed out that the Hf/W ratio is only slightly elevated compared to chondrites and that this ratio, therefore, must be known precisely to obtain useful information on the timescale of Martian core formation. Based on an improved determination of the chondritic Hf/Th ratio, Dauphas and Pourmand (2011) used the constant Th/W ratio of Martian meteorites to estimate a Hf/W ratio of  $3.51 \pm 0.45$  for the bulk mantle of Mars. This estimate is consistent with, but more precise than previous estimates.

#### 4.2 W Isotope Evolution in Different Accretion and Core Formation Models

Table 1 summarizes the Hf-W parameter used to calculate model ages for core formation in Mars. In the simplest model of core formation it is assumed that the entire core segregated

instantaneously from a fully formed planet. The instantaneous core formation model age for Mars is  $4.2^{+3.0}_{-3.3}$  Ma after CAI formation, assuming that the Hf-W systematics of bulk Mars are similar to those of carbonaceous chondrites. If a bulk composition similar to that of H chondrites is used instead, the instantaneous core formation age changes to  $3.4^{+2.7}_{-3.0}$  Ma after CAI formation, indistinguishable from the model age calculated using a carbonaceous chondrite composition. The particular choice of different bulk compositions for Mars, therefore, does not have a significant effect on the calculated ages. A more severe problem exists if the core did not form instantaneously but rather segregated continuously during accretion of Mars, which may be a more likely core formation scenario. Calculating realistic core formation ages, therefore, requires modeling the W isotopic evolution of the Martian mantle during accretion and concomitant core formation.

Information regarding the accretion history of Mars may be obtained from numerical simulations of terrestrial planet accretion but in these models the small size of Mars has been a persistent problem. However, two different models have been proposed recently that successfully reproduce the size of Mars. Walsh et al. (2011) modeled the small size of Mars by invoking an early migration of Jupiter that removed planetesimals from the inner solar system. In this model the accretion history of Mars was protracted and probably involved some giant impacts. In an alternative model, Minton and Levison (2011) proposed that a Mars-sized body escaped further accretion by rapid outward migration to the outer region of the inner solar system. This model predicts a rapid accretion of Mars within less than 1 Ma. Given the different accretion timescales predicted in the two models, the  $^{182}\text{Hf}$ - $^{182}\text{W}$  chronometer could provide the necessary constraint to distinguish between the two models.

A widely used model for using W isotopic data to constrain the timescales of planetary accretion and core formation is the exponential growth model (Halliday et al. 1996; Harper and Jacobsen 1996; Jacobsen 2005). This model assumes that accretion occurred at an exponentially decaying rate, such that:

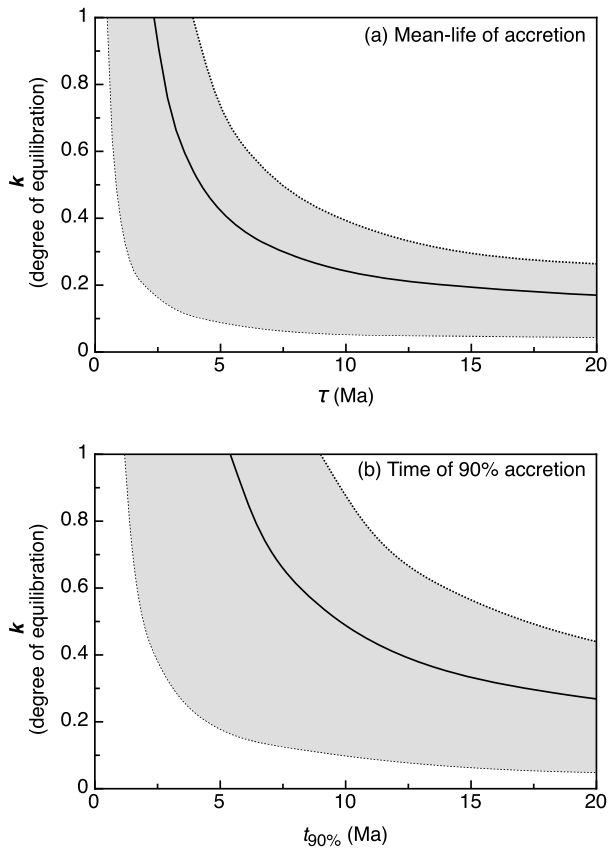
$$M_{\text{Mars}}(t)/M_{\text{Mars}} = 1 - e^{-t/\tau}$$

where  $M_{\text{Mars}}(t)/M_{\text{Mars}}$  is the cumulative fractional mass of Mars at time  $t$ , and  $\tau$  is the mean time of accretion, corresponding to the time at which 63 % growth was achieved. The exponential model assumes that accretion occurred by the addition of numerous small planetesimals to the growing Mars. While such a scenario might be appropriate if Mars is a stranded planetary embryo, accretion may have also occurred by a few distinct giant impacts that delivered large masses of material at once. In this case the exponential model nevertheless provides useful age information, because these giant impacts probably also occurred at an approximately exponentially decaying rate.

In the exponential model, the end of accretion and core formation is poorly constrained and so the timescale of core formation is given by  $\tau$ , the time taken to achieve 63 % growth. In addition, the time of 90 % accretion,  $t_{90\%}$ , is often used. Using the parameter listed in Table 1, accretion timescales of  $\tau = 2.3^{+1.6}_{-1.8}$  Ma and  $t_{90\%} = 5.4^{+3.6}_{-4.2}$  Ma are obtained, similar to  $\tau = 1.8^{+0.9}_{-1.0}$  Ma obtained by Dauphas and Pourmand (2011) using a slightly different accretion model. Therefore, in the case of exponential accretion Mars may have reached 90 % of its mass as early as  $\sim 1.2$  Ma or as late as  $\sim 9$  Ma after CAI formation. The large uncertainty on this age estimate primarily reflects the low Hf/W of the Martian mantle, leading to only slightly elevated  $^{182}\text{W}/^{184}\text{W}$  relative to chondrites.

An additional variable that has a strong influence on the estimated accretion and core formation timescales is the degree of metal-silicate equilibration during metal segregation (Halliday 2004; Kleine et al. 2004a; Kleine et al. 2009; Nimmo et al. 2010; Rudge et al. 2010; Kleine and Rudge 2011). Figure 3 shows the effect of metal-silicate disequilibrium

**Fig. 3** Dependence of calculated Hf-W ages on the assumed degree of metal-silicate equilibration. For full metal-silicate equilibration  $k = 1$ . **(a)** Mean life of accretion  $\tau$  vs.  $k$ . In the exponential accretion model  $\tau$  corresponds to the time of 63 % accretion. **(b)** Same as **(a)** but for the time of 90 % accretion,  $t_{90\%}$



on the calculated Hf-W ages. For instance, the time of 90 % accretion,  $t_{90\%}$ , changes from  $\sim 5.4$  Ma for complete equilibration to  $\sim 12.2$  Ma for 40 % equilibration (corresponding to a shift in  $\tau$  from  $\sim 2.3$  Ma to  $\sim 5.3$  Ma). Thus, precisely defining the accretion timescale for Mars requires knowledge of the degree of equilibration of newly accreted metal cores with the silicate mantle of Mars. However, while there is strong evidence, particularly from the abundances of the HSE, for efficient metal segregation and core formation on Mars (see above Sect. 3), it is less clear if mantle and core have always been in isotopic equilibrium. Full equilibrium can only be assumed if Mars accreted predominantly by collisions with small planetesimals. Collisions in which the impactor is much smaller than the target lead to vaporization of the impactor and subsequent efficient equilibration of the impactor with the mantle of proto-Mars. However, the fate of the impactor material during collisions involving larger bodies is less well understood. During giant impacts (i.e., for target/impactor ratios of  $\sim 0.1$ ) fragments of the metal core of the impactor may have rapidly merged with the core of the target, leaving no opportunity for equilibration with the mantle of the target (Dahl and Stevenson 2010; Deguen et al. 2011). Thus, if accretion of Mars involved giant impacts, incomplete metal-silicate equilibration might be expected. We are, therefore, left with the dilemma that the Hf-W data are equally consistent with (i) a very rapid accretion of Mars as a stranded embryo (Dauphas and Pourmand 2011), in which efficient metal-silicate equilibration occurred during metal segregation, as well as with (ii) a more protracted accretion history involving several giant impacts and metal-silicate disequilibrium during

core formation. The exact timing of core formation in Mars as well as its accretion history thus remains uncertain.

## 5 Magma Ocean Solidification and Mantle Differentiation

Silicate differentiation on terrestrial planets is thought to be related to the presence of a magma ocean. While direct evidence for the existence of magma oceans has now disappeared, it can be inferred indirectly on geochemical and theoretical grounds (see above Sect. 3). A magma ocean on Mars was not only important for facilitating efficient metal segregation during core formation, but also played a key role in establishing compositionally distinct mantle source regions that later melted to give rise to Martian basaltic meteorites. For instance, Borg and Draper (2003) showed that the trace element and isotope systematics of shergottites are most easily accounted for by mixing variable proportions of ancient reservoirs formed during crystallization of a magma ocean. The compositional variability of basaltic Martian meteorites can alternatively be explained by assimilation of evolved Martian crust (Jones 1989; Herd et al. 2002). However, this latter model falls short of explaining the isotope systematics of the shergottites, in particular their Os isotope compositions (Brandon et al. 2000; Borg and Draper 2003; Brandon et al. 2012).

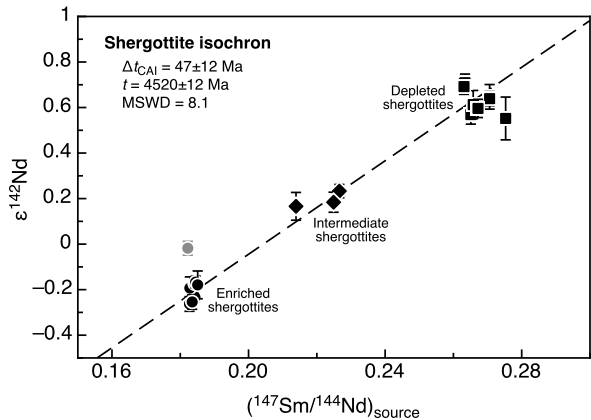
Understanding magma ocean evolution and solidification, therefore, is key for constraining the evolution of Mars through time. Isotope studies are particularly useful in this regard as they provide constraints on the nature and timing of magma ocean solidification and mantle differentiation, on the mineralogical composition of the mantle, and on the dynamics of the magma ocean.

### 5.1 Duration of a Martian Magma Ocean

The duration of the magma ocean stage on Mars largely depends on the presence or absence of an insulating cover, like a thick solid lid or a thick atmosphere (Abe 1997; Elkins-Tanton 2008). In the absence of an insulating cover, the magma ocean would have crystallized rapidly in less than to  $10^5$  years (Elkins-Tanton 2008). In contrast, the presence of an insulating atmosphere may have increased substantially the lifetime of a magma ocean. For instance, a thick atmosphere rich in  $H_2O$  and  $H_2$  could have led to surface temperatures exceeding the silicate solidus, such that the residual shallow portion of a magma ocean may have persisted up to a few hundred Ma (Abe 1997). In the case of a volatile element-rich planet like Mars, such an atmosphere may have formed due to degassing of the mantle during crystallization of the magma ocean. After it was eroded due to solar wind, hydrodynamic escape or later large impact, the planet finally crystallized (e.g., Lammer et al. 2008).

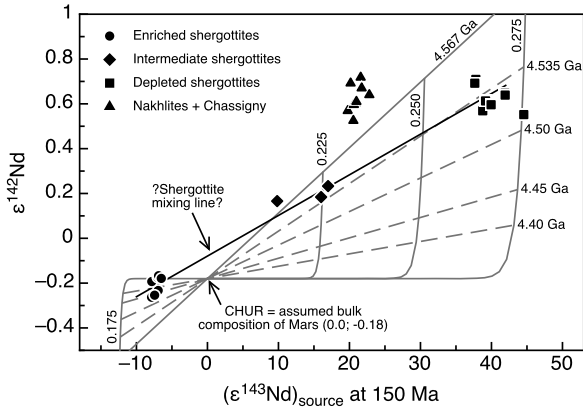
Information on the lifetime of a magma ocean on Mars can be obtained from the study of various long- and short-lived isotope systems. Evidence for an early global differentiation of Mars comes from the fact that Martian meteorites define a  $\sim 4.5$  Ga Rb-Sr whole-rock isochron (e.g., Shih et al. 1982), and from Pb-Pb isotope systematics of shergottites that define an upper intercept at  $\sim 4.5$  Ga on the U-Pb Concordia diagram (Chen and Wasserburg 1986). While these isotope systematics provide clear evidence for an early differentiation of the Martian mantle, they cannot constrain the duration of magma ocean solidification precisely. Much tighter age constraints can instead be obtained from short-lived radionuclide systems such as the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  decay system [ $t_{1/2} \sim 68$  Ma; note that all ages presented in the following were recalculated using the revised decay constant of  $^{146}\text{Sm}$  and the revised

**Fig. 4**  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  isochron for shergottites. The source  $^{147}\text{Sm}/^{144}\text{Nd}$  are calculated using the approach outlined in Caro et al. (2008). Data are from Debaille et al. (2007) and Caro et al. (2008). The age of differentiation is calculated relative to a solar system initial  $^{146}\text{Sm}/^{144}\text{Sm}$  of 0.0094 (Kinoshita et al. 2012)



solar system initial  $^{146}\text{Sm}/^{144}\text{Sm}$  (Kinoshita et al. 2012)]. The radionuclide  $^{146}\text{Sm}$  was extant only during the first  $\sim 350$  Ma of the solar system and so measurable  $^{142}\text{Nd}$  variations could only have been produced during this brief period of time. This makes the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  system uniquely useful for investigating early silicate differentiation processes. Another strength of this system is that it is coupled to the long-lived  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  decay system ( $t_{1/2} \sim 106$  Ga), which permits a precise determination of the early Sm/Nd fractionations that led to the  $^{142}\text{Nd}$  variations measured today.

Martian meteorites show large variations in  $^{142}\text{Nd}/^{144}\text{Nd}$ , ranging from  $\epsilon^{142}\text{Nd}$  values of  $\sim -0.2$  for enriched shergottites to  $\sim +0.6$  for depleted shergottites and nakhlites (Fig. 2) (Borg et al. 1997; Borg et al. 2003; Debaille et al. 2007; Caro et al. 2008). The  $^{142}\text{Nd}$  variation in the Martian mantle is thus much larger than that observed in the Earth and Moon, indicating a very early differentiation of the Martian mantle. The coupled  $^{142}\text{Nd}$ - $^{143}\text{Nd}$  systematics of shergottites suggest that the mantle sources of all shergottites were generated simultaneously by a major fractionation within the Martian mantle at  $47 \pm 12$  Ma after solar system formation (Fig. 4) (Borg et al. 2003; Foley et al. 2005; Caro et al. 2008). However, the identification of small  $^{142}\text{Nd}$  deficits in chondrites (Boyet and Carlson 2005) has complicated the interpretation of the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  record of Mars. Debaille et al. (2007) observed that chondrites do not plot on the  $^{142}\text{Nd}$ - $^{143}\text{Nd}$  correlation line defined by the shergottites and on this basis suggested that this correlation line is not an isochron but rather a mixing line (Fig. 5). This would imply that the depleted and enriched shergottites sample two different Martian reservoirs that formed at different times during solidification of a magma ocean characterized by chondritic Sm/Nd and  $^{142}\text{Nd}/^{144}\text{Nd}$ . Debaille et al. (2007) proposed that the depleted shergottites derive from an upper mantle reservoir that crystallized  $\sim 37$  Ma after solar system formation, while the enriched shergottites sample an incompatible trace element-enriched component (similar to the lunar KREEP) representing the residual liquid of the Martian magma ocean that crystallized  $\sim 90$  Ma after solar system formation (Fig. 5). An alternative interpretation of the  $^{142}\text{Nd}$ - $^{143}\text{Nd}$  systematics of shergottites was advanced by Caro et al. (2008), who argued that bulk Mars (as well as the Earth and Moon) is characterized by super-chondritic Sm/Nd and  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios. In this case chondrites should not plot on the shergottite isochron and the  $^{142}\text{Nd}$ - $^{143}\text{Nd}$  systematics of shergottites could still be interpreted as a single differentiation event in the Martian mantle that occurred at  $47 \pm 12$  Ma after solar system formation (Fig. 4) (Borg et al. 2003; Foley et al. 2005; Caro et al. 2008).



**Fig. 5** Two-stage Nd isotope evolution model for the Martian meteorites. Only samples plotting inside the field defined by solid gray lines are consistent with a two-stage evolution. In this model an initially chondritic Martian magma ocean (stage 1) undergoes differentiation (stage 2). *Solid (near vertical) lines* represent constant  $^{147}\text{Sm}/^{144}\text{Nd}$  in the source, *dashed lines* are calculated model isochrons. Note that this two-stage model assumes that bulk Mars has the same Nd isotope composition than ordinary chondrites, as given by the central point of the graph (0.0; -0.18). The graph would shift to a higher central point and the slope of the isochrons would change if Mars is characterized by a non-chondritic Sm/Nd (Caro et al. 2008; Caro and Bourdon 2010). Data from Debaille et al. (2007), Caro et al. (2008), Debaille et al. (2009)

The  $^{142}\text{Nd}$ - $^{143}\text{Nd}$  record of the nakhilites is even more difficult to interpret than that of the shergottites. The elevated  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio of the nakhilites corresponds to a two-stage model age of  $\sim 25$  Ma after CAI formation (Harper et al. 1995; Foley et al. 2005). This age is also consistent with that obtained from combined  $^{142}\text{Nd}$ - $^{182}\text{W}$  systematics for Sm/Nd and Hf/W fractionation in a garnet-bearing shallow mantle (Kleine et al. 2004b; Foley et al. 2005). However, the nakhilites plot outside the two-stage evolutionary field in the  $^{142}\text{Nd}$  vs.  $^{143}\text{Nd}$  diagram (Fig. 5), indicating that the two-stage model ages might be meaningless and that a more complex model may be required to constrain the age of the nakhilite source (Borg et al. 2003; Debaille et al. 2009). The  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  systematics of the nakhilites are similar to those of the depleted shergottites, whereas the  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  systematics reveal differences. This could indicate a disturbance of the Sm-Nd system after extinction of  $^{146}\text{Sm}$ , possibly related to the addition of a LREE-enriched fluid (Borg et al. 2003; Foley et al. 2005). Wadhwa and Crozaz (1995) argued that the REE in nakhilites evolved as a closed system, however, making post-crystallization addition of LREE-enriched fluids unlikely. Debaille et al. (2009) proposed that the  $^{146}\text{Sm}$ - $^{142}\text{Nd}$ ,  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  and  $^{182}\text{Hf}$ - $^{182}\text{W}$  systematics of the nakhilites are best explained by a multistage process during crystallization of the Martian magma ocean, involving garnet segregation during cumulate overturn soon after magma ocean solidification  $\sim 90$  Ma after solar system formation (see Sect. 5.2).

The  $^{146,147}\text{Sm}$ - $^{142,143}\text{Nd}$  systematics of the SNC meteorites provide clear evidence for differentiation of the Martian mantle in the first few ten to hundred Ma after solar system formation, the exact timescale of magma ocean solidification remains uncertain and depends on the differentiation model and bulk Sm-Nd isotope composition assumed for Mars. Either the shergottites witness a major single-event crystallization of the magma ocean at  $47 \pm 12$  Ma after solar system formation (Borg et al. 2003; Foley et al. 2005; Caro et al. 2008), or a protracted shallow magma ocean that finished crystallizing  $\sim 90$  Ma after solar system formation (Debaille et al. 2007). Clearly, tighter constraints on the timescales and processes involved in the primordial differentiation of Mars will require a better knowledge of the bulk

composition of Mars, and the genetic relationships among the different groups of Martian meteorites.

## 5.2 Magma Ocean Crystallization and Cumulate Overturn

Crystallization of a magma ocean will occur from the bottom up, because the thermal adiabat crosses the liquidus curve first at the base of the mantle (e.g., Elkins-Tanton et al. 2003). Segregation of minerals from the magma will occur only if these crystals are denser than the melt and large enough to overcome the forces generated by the convecting magma ocean. The settling velocity depends on the density difference between mineral and melt, the viscosity of the melt and the velocity of convection (Solomatonov 2000). The dominant factors controlling the mineralogical composition of the crystallizing assemblages are the bulk composition of the magma ocean and the depth and temperature dependence of the stability of the minerals. On Mars the crystallization sequence of the magma ocean was roughly as follows: majorite and  $\gamma$ -olivine crystallized from the bottom of the magma ocean, followed by an assemblage of garnet, olivine and pyroxene, which in turn was followed by crystallization of olivine and pyroxene above the low-pressure end of garnet stability (Borg et al. 2003; Borg and Draper 2003; Elkins-Tanton et al. 2003; Elkins-Tanton et al. 2005b; Debaille et al. 2008).

Crystallization of a magma ocean ultimately generates a chemical gradient. The content in incompatible trace elements in the remaining melt will progressively increase with the percentage of solidification, because the first minerals formed at the bottom of the mantle are depleted in incompatible trace elements. Furthermore, the first minerals to crystallize from the magma ocean are Mg-rich, causing a progressive Fe enrichment in the liquid. This ultimately leads to the formation of an unstable density stratification, where early-formed Mg-rich minerals are overlying later-formed, more dense Fe-rich minerals located at the top of the mantle (Elkins-Tanton et al. 2003, 2005a, 2005b). Such a gravitationally unstable stratigraphy will overturn via Rayleigh-Taylor instabilities, where denser cumulates sink to the bottom of the mantle and deeper cumulates rise to shallower levels, resulting in a stable density stratification (Elkins-Tanton et al. 2003, 2005a, 2005b).

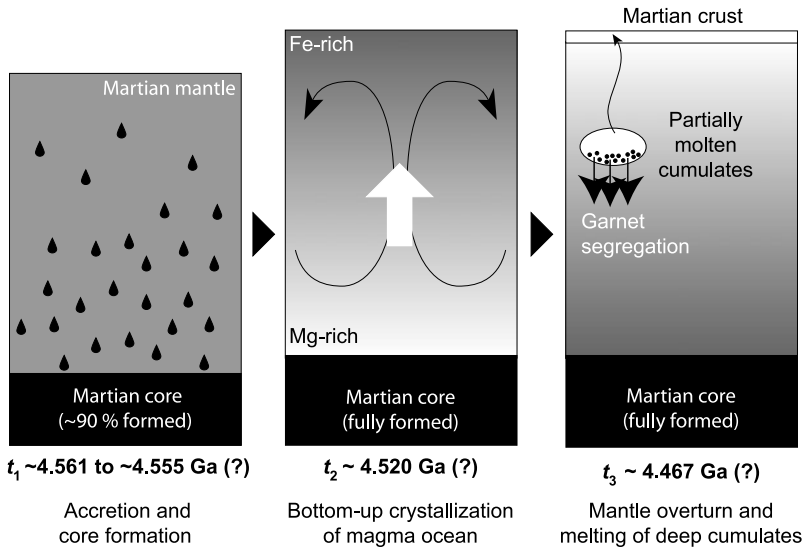
The isotope and trace element systematics of Martian meteorites provide important constraints on the crystallization and dynamics of the magma ocean, as well as on its mineralogical composition. For instance, the Rb-Sr and Sm-Nd isotopic systematics of Martian meteorites indicate that Martian mantle sources were generated during crystallization of a magma ocean (Borg et al. 1997, 2003; Borg and Draper 2003). More specifically, the trace element and isotopic variations observed among shergottites is successfully modeled as a mixture between a depleted mantle component, represented by mafic cumulates of the magma ocean, and a strongly enriched component, most likely represented by the late-stage residual liquid of the magma ocean (Borg et al. 2003; Borg and Draper 2003; Elkins-Tanton et al. 2003, 2005b; Debaille et al. 2008). Debaille et al. (2008) observed that equilibrium crystallization is more appropriate to generate the observed chemical compositions of the shergottites, while they acknowledged that the crystallization of a magma ocean is certainly a hybrid process, where some crystals have time to equilibrate with the magma while others sink directly to the bottom of the magma ocean without equilibration. This observation is consistent with the expected dynamics of a turbulent magma ocean, because turbulence can keep the minerals suspended long enough for equilibration to occur. However, as soon as the fraction of residual melt becomes lower than 20 %, fractional crystallization is more appropriate to model the chemical evolution of the remaining magma ocean (Snyder et al. 1992; Borg and Draper 2003). Elkins-Tanton et al. (2003, 2005a) also argued, on theoretical

grounds, for some fractional crystallization of the magma ocean. At pressures exceeding  $\sim 7.5$  GPa ( $\sim 600$  km depth in Mars), olivine and pyroxene become positively buoyant with respect to the coexisting liquid and float, while garnet is denser than the liquid and sinks to the bottom of the magma ocean. Thus, in this pressure regime, garnet is fractionated from the magma ocean and is segregated from olivine and pyroxene (Elkins-Tanton et al. 2003, 2005a).

Combined Hf and Nd isotope studies show that at some stage of their evolution garnet must have been present in the source of the shergottites (Blichert-Toft et al. 1999; Debaille et al. 2007). However, experimental work suggests that garnet is not a liquidus phase of primary shergottite melts. This would be consistent with the garnet segregation model of Elkins-Tanton et al. (2003, 2005a), because fractional crystallization of garnet would impart a strong signature on the relative REE abundances of the remaining melt, which would then later crystallize as the shergottite source region. Nevertheless, based on combined Hf and Nd isotopic data, Debaille et al. (2007) argued that the shergottite magmas formed by partial melting of a garnet-bearing source.

The formation of the source of nakhlites by magma ocean processes has proven more difficult to interpret. This is partly due to the fact that nakhlites plot outside the two-stage evolutionary field in  $\epsilon^{142}\text{Nd}$ - $\epsilon^{143}\text{Nd}$  space (Fig. 5), indicating a more complex evolution (see above, Sect. 5.1). Furthermore, nakhlites show relative large  $^{182}\text{W}$  excesses, which are difficult to interpret as a result of core formation alone, because the Hf/W ratio of the Martian mantle appears to be too low to have generated the radiogenic  $\epsilon^{182}\text{W}$  of  $\sim +3$  observed for the nakhlites. The Hf-W systematics of the nakhlites rather seem to indicate an early Hf/W fractionation in a garnet-bearing source (Righter and Shearer 2003; Kleine et al. 2004a, 2004b; Foley et al. 2005). Recently, Debaille et al. (2009) proposed a detailed model for the evolution of the nakhlite source, based on  $^{176}\text{Lu}$ - $^{176}\text{Hf}$ ,  $^{146,147}\text{Sm}$ - $^{142,143}\text{Nd}$  and  $^{182}\text{Hf}$ - $^{182}\text{W}$  systematics. These authors argued that the combined Hf-Nd isotope systematics of the nakhlites require segregation of garnet/majoritic garnet from their source and proposed the following model evolution (Fig. 6): after Hf/W fractionation during global metal-silicate separation at  $t_1$ , the source of nakhlites differentiated from the magma ocean at some time  $t_2$ , involving crystallization of garnet/majoritic garnet. This led to high Sm/Nd, Lu/Hf and Hf/W in the nakhlite source and can account for the radiogenic  $\epsilon^{142}\text{Nd}$  and  $\epsilon^{182}\text{W}$  of the nakhlites. Then, at  $t_3$ , garnet/majorite was removed from the mantle source of the nakhlites. This event may have occurred when  $^{182}\text{Hf}$  was already extinct but while  $^{146}\text{Sm}$  was still extant, resulting in a decoupling of  $\epsilon^{142}\text{Nd}$  and  $\epsilon^{182}\text{W}$ . Due to its high Sm/Nd ratio, garnet segregation has a significant effect on the Sm/Nd ratio of the nakhlite source. This event, therefore, is consistent with the observation that the combined  $\epsilon^{142}\text{Nd}$ - $\epsilon^{143}\text{Nd}$  systematics of the nakhlites require a more complex history than a two-stage evolution. Segregation of garnet is only possible in a highly molten source at shallow depth, where garnet is negatively buoyant while olivine and pyroxene are positive buoyant (see above). Debaille et al. (2009), therefore, suggested that the episode of re-melting required for garnet segregation that occurred at  $t_3$  and allowed for garnet segregation is related to a major mantle cumulate overturn in the Martian mantle. During such overturn, where hot material is brought up to shallower levels, up to 60 % melting can occur by adiabatic decompression (Elkins-Tanton et al. 2003, 2005a). The generation of large volumes of melt related to the overturn may have created the primary crust of Mars, and possibly participated to the generation of the crustal dichotomy (Elkins-Tanton et al. 2005b).





**Fig. 6** Cartoon model for the major differentiation events and processes on Mars and the evolution of a Martian magma ocean (after Debaille et al. 2009). The metallic core (in black) segregated from the silicate portion of Mars at  $t_1$ . The timing of this event is not precisely known and depends on the assumed degree of metal-silicate equilibration during core formation. Here the time of 90% accretion for complete metal-silicate equilibration is given. After core formation, the magma ocean crystallized from the bottom up (white arrow) at  $t_2$ . The timing and duration of this event can be constrained by combined  $^{142}\text{Nd}$ - $^{143}\text{Nd}$  systematics, but the interpretation of the Nd isotope data strongly depends on the assumed composition of bulk Mars. Here, a differentiation age of 4.520 Ga (i.e., 47 Ma after solar system formation) based on Nd isotopic for shergottites is shown. Note that the same data have been used to argue for protracted crystallization of the magma ocean between  $\sim 30$  and  $\sim 100$  Ma after solar system formation. Note further that the source of the nakhlites may have formed even earlier (see text for details). Crystallization of the magma ocean resulted in an unstable density stratification where dense Fe-rich cumulates are located on top of less dense, Mg-rich cumulates. This resulted in mantle overturn at  $t_3$ . Based on Nd and W isotopic data for nakhlites it has been argued that this event occurred at  $\sim 100$  Ma after solar system formation (see text). During overturn upwelling of deep cumulates caused melting by adiabatic decompression, leading to segregation of garnet. Magmas generated by adiabatic decompression may have also resulted in forming the early Martian crust (Elkins-Tanton et al. 2005a)

## 6 Conclusions

Due to the broad chemical similarity of Earth and Mars, the two planets show great similarities in their basic building plan. Both have a metallic core, a silicate mantle and crust and an atmosphere. However, in detail there are striking differences in their evolution and current state.

Compared to Earth, Mars has a smaller core, a heterogeneous mantle inherited from differentiation processes in the first few tens of millions of years, only a basaltic crust, no felsic igneous rocks. The relatively small core is due to the higher oxidation state of the whole planet. The preservation of ancient chemical heterogeneities attests to the existence of a magma ocean and is also strong evidence against vigorous whole mantle convection and plate tectonic processes, although some convective mixing immediately following the magma ocean stage is likely. The lack of evolved felsic melts precludes hydrous melts, which are a common feature of terrestrial subduction zone related magmatism. The limitation to mafic and ultramafic volcanic and subvolcanic rocks from the near surface of Mars is more

consistent with plume triggered volcanism above hot spots, which in turn is consistent with the observation that Mars is host to individual shield type volcanoes and lacks pronounced linear arrays showing magmatic activity similar to mid-oceanic ridges and subduction zones on Earth that generate the vast majority of mantle derived melts. However, some lateral crustal mobility may have occurred locally as indicated by magnetic lineaments (Connerney et al. 2005). The trace element and isotope systematic of currently available Martian samples show that the chemical heterogeneity of the Martian mantle is directly inherited from the crystallization of a magma ocean with some later, albeit limited, mixing. The existence of a magma ocean step was important, not only for the core segregation, but also for the chemical evolution of the planet and its atmosphere.

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