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Pb evolution in the Martian mantle

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Abstract

The initial Pb compositions of one enriched shergottite, one intermediate shergottite, two depleted shergottites, and Nakhla have been measured by Secondary Ion Mass Spectrometry (SIMS). These values, in addition to data from previous studies using an identical analytical method performed on three enriched shergottites, ALH 84001, and Chassigny, are used to construct a unified and internally consistent model for the differentiation history of the Martian mantle and crystallization ages for Martian meteorites is presented. The differentiation history of the shergottites and Nakhla/Chassigny are fundamentally different, which is in agreement with short-lived radiogenic isotope systematics. The initial Pb compositions of Nakhla/Chassigny are best explained by late addition of a Pb-enriched component with a primitive, non-radiogenic composition. In contrast, the Pb isotopic compositions of the shergottite group indicate a relatively simple evolutionary history of the Martian mantle that can be modeled based on recent results from the Sm-Nd system. The shergottites have been linked to a single mantle differentiation event at 4504 Ma. Thus, the shergottite Pb isotopic model here reflects a two-stage history 1) pre-silicate differentiation (4504 Ma) and 2) post-silicate differentiation to the age of eruption (as determined by concordant radiogenic isochron ages). The μ-values ($^{238}U/^{204}Pb$) obtained for these two different stages of Pb growth are μ_1 of 1.8 and a range of μ_2 from 1.4 - 4.7, respectively. The μ_1-value of 1.8 is in broad agreement with enstatite and ordinary chondrites and that proposed for proto Earth, suggesting this is the initial μ-value for inner Solar System bodies. When plotted against other source radiogenic isotopic variables (Sr_i, $\gamma^{187}Os$, $\varepsilon^{143}Nd$, and $\varepsilon^{176}Hf$), the second stage mantle evolution range in observed mantle μ-values display excellent linear correlations (r^2 >0.85) and represent a spectrum of Martian mantle mixing-end members (depleted, intermediate, enriched).

1. Introduction

The Pb isotopic system, which contains the daughter products of three long-lived decay chains of ^{238}U, ^{235}U, and ^{232}Th, has been invaluable in constraining the evolution and differentiation history of the Earth's mantle, crust, core, the lunar mantle, and the formation of the Earth-Moon system (e.g., Stacey and Kramers, 1975, Zartman and Haines, 1988, Hart et al., 1992, Connelly and Bizzarro, 2016, Snape et al., 2016). For Mars, however, there has been significant difficulty in applying this isotopic system due to the fact that Mars has a mantle with low μ–values ($^{238}U/^{204}Pb$) that range from 1-5 (Nakamura et al., 1982, Chen and Wasserburg, 1986, Jagoutz, 1991, Borg et al., 2005, Gaffney et al., 2007, Bouvier et al., 2008, 2009, Bellucci et al., 2015a). Rocks derived from long-lived, low μ reservoirs that have even minor contamination from materials derived from higher μ reservoirs such as the Martian or Earth's crusts (μ–values of 14 and 8-10, respectively; Stacey and Kramers, 1975, Bellucci et al., 2015b) will then produce ambiguous, linear trends in Pb isotopic diagrams. These linear trends, if interpreted incorrectly could be used to define >4 Ga crystallization ages for relatively recent rocks (Gaffney et al., 2007, Bouvier et al., 2008, 2009, Bellucci et al., 2016). Therefore, in cases where mixing between unradiogenic and radiogenic reservoirs may have occurred, particularly at the scale of individual minerals in Martian meteorites (e.g., Bellucci et al., 2016), the best approach to obtain any reliable information is to try and constrain the mixing end-members present in a single sample. For Martian samples, these mixing end-members are: 1) initial Pb, present at the time of a rock's crystallization, 2) radiogenic Pb, from the decay of U or Th present in some minerals since the time of crystallization, and 3) any un-supported radiogenic Pb inherited either from residence and mixing with radiogenic reservoir(s) on the Martian surface or terrestrial contamination (e.g., Gaffney et al., 2007, Bellucci et al., 2016).

One approach to constrain these mixing end-members is to apply an *in situ* analytical technique such as Secondary Ion Mass Spectrometry (SIMS) to target individual minerals in a given rock. This technique has the distinct advantage of minimizing any crystal boundary/surface contamination by targeting the centers of crystals, while at the same time avoiding U-bearing inclusions. Although individual measurements may be relatively imprecise, this method can produce large, statistically significant data sets with invaluable spatial and mineralogical context. Assuming that a large, statistically identical group can represent each individual mixing end-member confidently, this approach has been able to identify the most unradiogenic Pb in several Martian meteorites, which was interpreted as an accurate representation of initial Pb values (Bellucci et al., 2015a, 2016). Initial Pb is preserved in minerals that have an extremely low U/Pb or Th/Pb and have no radiogenic Pb ingrowth. Therefore, initial Pb can be used to define time integrated chemical variables μ and κ (= $^{232}Th/^{238}U$) of a sample's source and define a Pb model age based on a model of Pb growth in the host planetary body. This approach has been used successfully to constrain the Pb evolution in the mantles of the Earth, the Moon, and Mars (Stacey and Kramers, 1975, Bellucci et al., 2015a, Connelly and Bizzarro, 2016, Snape et al., 2016). While these models of Pb growth are almost certainly not accurate representations of the complex processes involved in planetary evolution, they provide useful first order mathematical quantifications of invaluable geochemical variables (μ and κ) in different reservoirs on a planetary body.

While none of the known Martian meteorites are thought to come directly from the Martian mantle, several varieties are mafic- to ultramafic rocks that are mantle derivatives. These include the shergottites, nakhlites, and chassignites (collectively the SNCs), Allan Hills (ALH) 84001, and a unique type of augite-rich shergottite, Northwest Africa (NWA) 8195. The shergottites can be classified based on their bulk rock rare earth element (REE) patterns including enriched (flat-slightly depleted REE), intermediate (slightly depleted LREE), and depleted (strongly depleted LREE) (e.g., Borg et al., 1997, 2003, 2005, Borg and Draper 2003). Based on the combined isotopic systems of Lu-Hf, Sm-Nd and U-Pb, the differentiation history of the source reservoirs of ALH 84001 and the shergottites can be linked with a single mantle differentiation event (Lapen et al., 2010, Bellucci et al., 2015a, Borg et al., 2016, Kruijer et al., 2017). The most recent and comprehensive ^{146}Sm-^{142}Nd and ^{147}Sm-^{143}Nd isotopic study indicates this event likely occurred at 4504 $^{+5.4}/_{-5.7}$ Ma (Borg et al., 2016). In contrast, the ^{146}Sm-^{142}Nd and ^{182}Hf-^{182}W systems indicate that the mantle differentiation histories for the shergottites must be fundamentally different from that of the nakhlites and chassignites (Kleine et al., 2004, 2009, Foley et al., 2005, Nimmo and Kleine, 2007, Dauphas and Pourmand, 2011, Mezger et al., 2013). The difference in ^{142}Nd compositions between the meteorite groups has been attributed to a mantle overturn early in Martian history (Debaille et al., 2009) Alternatively, the difference in ε^{182}W between the shergottites and nakhlites/chassignites has been explained by the late addition(s) of material to the Martian mantle. There are currently two scenarios that can account for the late addition(s) to the Nakhla/Chassigny source, which are: 1) protracted accretion producing variable amounts of ^{182}W measured in the Martian meteorite groups ($\varepsilon^{182}W$ of -0.7 vs 3) or 2) rapid cooling of a planetary embryo and then a distinct later addition by a significant impactor melting a major portion of the mantle (e.g., Metzger et al., 2013, Borg et al., 2016). Regardless of the actual scenario of mantle accretion/differentiation that took place leading to the different $\varepsilon^{182}W$ compositions of the shergottites and the nakhlites/chassignites, two important conclusions can be made: 1) there were very likely late additions of primitive composition to the Martian mantle and 2) it is likely that core formation occurred rapidly, with the average estimate of age of core formation at 4559 ± 8 Ma (2σ, which is the average of all core-formation ages reported in Kleine et al., 2004, 2009, Foley et al., 2005, Nimmo and Kleine, 2007, Dauphas and Pourmand, 2011). The aim of this study is to obtain the initial Pb composition of at least one of each variety of shergottite, Nakhla, and Chassigny to better constrain the Pb isotopic growth in the Martian mantle. Importantly, the samples specifically targeted here have well-determined, concordant ages from several, non-Pb radiogenic, isotopic systems, avoiding the potential complications listed above. This approach will add new parameters for the differentiation history of the Martian mantle, investigate the effects of late accretion on Mars through time-integrated Pb modeling, and define mantle compositional mixing end-members in terms of μ- and κ-values. Subsequently, these models will be used to investigate two un-dated shergottites to test the applicability of common Pb chronology and source reservoir composition calculations on samples with unknown ages.

2. Samples

The studied samples encompass four enriched shergottites (Larkman Nunatak (LAR) 12011, Ksar Ghilane (KG) 002, Roberts Massif (RBT) 04261 and Zagami), one intermediate shergottite (ALH 77005), two depleted shergottites (LAR 12095 and Tissint), the orthopyroxenite ALH 84001, Nahkla, and Chassigny. Sample descriptions for the previously reported enriched shergottite Pb data and ALH 84001 are available in Bellucci et al. (2015a) and the sample description and data for Chassigny are available in Bellucci et al. (2016). Sample descriptions for the samples analyzed in this study are presented below.

For this study one additional enriched shergottite - KG 002 (previously described by Llorca et al. 2013) has been analyzed. It is a coarse-grained basaltic shergottite with large grains of maskelynitized plagioclase that are 4 to 5 mm in size. KG 002 has a REE pattern that is slightly depleted in LREE and a positive Eu anomaly. The trace element pattern, major element concentrations, mineral chemistry and petrography are similar to the enriched shergottite Los Angeles. The cosmic ray exposure age of KG 002 is 3 Ma but no radiogenic isotopic isochrons are available for this sample to determine the age of crystallization. As a group, the enriched shergottites have a relatively restricted range in source reservoir compositions in ε^{176}Hf (-17 to -18), ε^{143}Nd (-7.2 to -6.7), and γ^{187}Os (5 to 14.7) (Table 1. Blichert-Toft et al., 1999, Borg et al., 2005, Debaille et al., 2008, Lapen et al., 2008, Shafer et al., 2010, Brandon et al., 2012, Righter et al., 2015).

The intermediate shergottite analyzed for this study, ALH 77005, was originally described by McSween et al. (1979). Allan Hills 77005 is a cumulate gabbroic rock, which has had all of its plagioclase converted into maskelynite, and has a slightly depleted LREE signature. Concordant Rb-Sr and Sm-Nd dates indicate an age of crystallization of 176 ± 6 Ma (Figure 1, Borg et al., 2002). Allan Hills 77005 has a source reservoir composition in ε^{176}Hf, ε^{143}Nd, and γ^{187}Os of 32.4, 11.1, and 2.1, respectively (Table 1. Bilchert-Toft et al., 1999, Borg et al., 2002, and Brandon et al., 2012).

The two depleted shergottites analyzed for this study were Tissint and LAR 12095. Tissint, described in detail by Balta et al. (2015), has a depleted REE pattern. Plagioclase has been converted to maskelynite. Tissint also has accessory pyrrhotite that is suitable for analysis. Additionally, Tissint contains no evidence for terrestrial alteration, consistent with its recent fall and extremely short residence time in an arid desert. Ages constrained from Rb-Sr and Sm-Nd isochrons are concordant and have an average age of 574 ± 20 Ma (Figure 1, Brennecka et al., 2014). Despite the lack of evidence for terrestrial alteration, Tissint contains multiple sources of Pb and distinct Pb isotopic compositions from multiple leaching steps (Moriwaki et al., 2017). These multiple compositions have been interpreted to be remnants of interactions with the Martian crust (Moriwaki et al., 2017) and thus, *in situ* techniques are likely to be extremely helpful to obtain the most accurate initial Pb composition possible. Larkman Nunatak 12095 is a depleted shergottite with an even more depleted LREE pattern than Tissint (Castle and Herd, 2015). There is no precise chronological information available for LAR 12095 but a model age, based on Lu-Hf and Sm-Nd isotopic systematics, is thought to be similar to that of the other depleted shergottites and ranges from 400-550 Ma (Righter et al., 2015). The source reservoir for the depleted shergottites has an inferred range of ε^{176}Hf and ε^{143}Nd of 50-58 and 39-42, respectively (Table 1. Grosshans et al., 2013, Brennecka et al., 2014, Righter et al., 2015).

Nakhla is a meteorite fall and terrestrial contamination is assumed to be negligible. The meteorite is a clinopyroxenite, mainly composed of clinopyroxene with minor olivine, plagioclase, mesostasis, K-feldspar, oxides, FeS, and chalcopyrite (e.g., Harvey and McSween, 1992). Previous studies using a variety of analytical techniques have obtained a similar crystallization age for Nakhla with an average of 1362 ± 54 Ma (Figure 1; Papanastassiou and Wasserburg, 1974, Gale et al., 1975, Nakumurua et al., 1982, Beard et al., 2013). Nakhla has a similar ε^{142}Nd signature to that of the depleted shergottites and Chassigny (Borg et al., 2006, Debaille et al., 2009). However, as stated above Nakhla and Chassigny are derived from a completely different source reservoir(s) than that of the shergottites (Debaille et al., 2009, Kleine et al., 2004, 2009, Foley et al., 2005, Nimmo and Kleine, 2007, Dauphas and Pourmand, 2011). Lastly, Nakhla and Chassigny have similar ages and source reservoir ε^{143}Nd and γ^{187}Os compositions of 16 and -5.5, respectively (Table 1. Brandon et al., 2000, Misawa et al., 2005, Debaille et al., 2009).

3. Analytical Methods

The Pb isotopic compositions of maskelynite, K-feldspar, and/or sulfide grains were determined using SIMS on polished epoxy-mounted samples or thin sections of each sample. Before analysis, each sample was cleaned in alternating 1-minute ultrasonic baths of water and ethanol. After thorough washing, a 30 nm coating of Au was applied to the surface. All measurements were conducted using a CAMECA IMS1280 instrument at the Swedish Museum of Natural History, Stockholm (NordSIMS facility) using previously described experimental protocols (Whitehouse et al., 2005, Bellucci et al., 2015a,b, 2016, Snape et al., 2016). An area of 35 × 35 μm was rastered for 70 s prior to Pb isotopic analysis to remove the gold coating and further minimize surface contamination. A 300 μm aperture was used to project a 12-15 nA O_2^- primary beam with a slightly elliptical 30 μm (long axis) spot on the surface of the sample. All analyses were conducted in multi-collector mode at a mass resolution of 4860 (M/ΔM), using an NMR field sensor in regulation mode to maintain the stability of the magnetic field. Lead isotopic ratios were measured in a multi-collector array of low noise (<0.03 cps) ion-counting electron multipliers for 160 cycles with a count time of 10 s, resulting in a total collection time of 1600 s. Isotopic ratios were calculated as integrated means for all analyses. The largest potential source of inaccuracy is in the relative gain differences between ion counters, which is accounted for by bracketing unknown measurements with BCR-2G (~11 μg/g Pb) and correcting isotopic measurements using the accepted values of this reference material (Woodhead and Hergt, 2000). External reproducibility for all measurements performed here in $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ is 0.3% and in $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$ = 0.9%, 0.7%, and 1.0%, respectively (all uncertainties 2σ). Lastly, for all of the Pb isotope modelling described below, the U decay constant recommendation of Steiger and Jäger (1977) and isotopic ratio of U ($^{238}U/^{235}U$ of 137.88) were used.

4. Results

Results from individual measurements of phases in the meteorites studied here are presented in Supplementary Table 1 and Supplementary Figure 1, while the x-y weighted averages, which represent a single statistical population, for $^{204}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ are presented in Table 1 and Figure 2. Maskelynite was the only phase analysed for all four enriched shergottites (Zagami, RBT 04262, LAR 12011, and KG 002), the intermediate shergottite (ALH 77005), one depleted shergottite (LAR 12095), and ALH 84001 (this study and Bellucci et al., 2015a). Both sulfides and maskelynite were analysed in Tissint, since the sulfides had higher Pb concentrations and less radiogenic Pb than the maskelynite, they are assumed to represent the initial Pb in Tissint (Supplementary Figure 1). Unfortunately, the other depleted shergottite (LAR 12095) yielded no usable sulfide analyses due to isotopically heterogeneous time resolved spectra or overlapping SIMS spots with grain boundaries. The plagioclase in Nakhla did not experience enough shock pressure to be converted into maskelynite and was analysed here. The phases used to determine the initial Pb in Chassigny were three analyses of K-feldspar and a sulfide grain (Bellucci et al., 2016). A statistically identical population of the least radiogenic Pb isotope compositions were used to determine an x-y weighted average and any analyses outside of that statistically identical population were rejected (Supplementary Table 1). Similar to analyses of ALH 84001 (Bellucci et al., 2015a), it was impossible to determine an x-y weighted mean for $^{204}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ for Nakhla and Chassigny because the spread in the data generated an MSWD and probability of fit which were too large for a statistically identical population in two dimensions. As such, a one-dimensional weighted average of $^{208}Pb/^{206}Pb$ compositions that correspond to the same analyses used in the calculation of the x-y weighted mean for $^{204}Pb/^{206}Pb$ vs. $^{207}Pb/^{206}Pb$ were used to determine the initial Pb $^{208}Pb/^{206}Pb$ composition for these two meteorites (Supplementary Figure 1). As reported with previous studies using this method (Bellucci et al., 2015a), the initial Pb measurements reported here are the least radiogenic Pb analysed for each respective meteorite, contain no measurable U, and are therefore assumed to represent initial Pb for these samples (e.g., Bellucci et al., 2015a, 2016).

5. Discussion

5.1 Shergottites

Five of the shergottites studied have concordant ages in multiple isotopic systems and encompass all major groupings (depleted-intermediate-enriched). To produce accurate Pb model ages in agreement with those ages, a two-stage model can be constructed using previously established mantle chronology (after Stacey and Kramers, 1975, Bellucci et al., 2015a). The Pb isotopic model used here starts at the time of Solar System formation at 4.567 Ga (Connelly et al., 2012) and begins with the Pb isotope composition of Canyon Diablo Troilite (CDT; Tatsumoto et al., 1973, Chen and Wasserburg, 1983). Since the estimate for the time of core formation on Mars is within error of that for Solar System formation (Kleine et al., 2004, 2009, Foley et al., 2005, Nimmo and Kleine, 2007, Dauphas and Pourmand, 2011) and the shergottite source reservoir experienced a mantle differentiation event at 4.504 $^{+5.4}/_{-5.7}$ Ga (Borg et al., 2016), this two stage model encompasses two segments of Martian mantle history: 1) post-core formation and pre-silicate differentiation at 4.567 - 4.504 Ga and 2) post-silicate differentiation to time of crystallization for each meteorite (defined as the average of all radiogenic isotope system ages for an individual meteorite, Figure 1, Table 1). The accuracy of the model presented here is based on minimizing average Δ_t where Δ_t =

crystallization age – Pb model age, and is presented in Figure 3. The age range and composition of shergottites for this study is expanded from that of Bellucci et al. (2015b) to include the depleted shergottite Tissint with a crystallization age of 574 Ma and the intermediate shergottite ALH 77005 with a crystallization age of 180 Ma (Figure 1). Over the five compositionally unique samples and ca. 600 Ma of crystallization history represented here, the average Δ_t is minimized with a μ_1 (post-core formation, pre-silicate differentiation) of 1.8 (Figure 3). After the silicate differentiation event at 4.504 Ga, to achieve the correct Pb model ages, the source reservoirs require a μ_2 ranging from 1.4 – 4.7 (Table 1, Figure 3).

Two of the shergottites analyzed here do not have external age constraints (KG 002 and LAR 12095). Using the model obtained from all other shergottites, to achieve the initial Pb measured in KG 002, a model age of 360 Ma and a mantle μ_2-value of 3.1 for both are required (Table 1). This model age is the oldest for the enriched shergottites yet studied, and the source mantle μ-value is the lowest yet determined for an enriched shergottite. Due to the extremely low abundances of Pb and appropriately sized maskelynite, LAR 12095 has the biggest uncertainties associated with the estimation of initial Pb (Table 1, Figure 2). The initial Pb composition for LAR 12095 lies in a field that is more radiogenic in $^{207}Pb/^{206}Pb$ than all of the models presented for this study. As such, a Pb-Pb model age for LAR 12095 would be a ‘future age’ and thus cannot be explicitly calculated for LAR 12095. Since there are no external age constraints for LAR 12095, a source μ-value cannot be explicitly calculated as opposed to the rest of the meteorites in this study. However, the source mantle μ-value of 1.5 can be estimated using only $^{204}Pb/^{206}Pb$ for LAR 12095 and an age of 500 Ma, which is in broad agreement with its Lu-Hf and Sm-Nd systematics (Righter et al., 2015).

5.2 Nakhla and Chassigny

The shergottite model presented above cannot be used to calculate initial Pb model ages that are in agreement with the external age constraints of Nakhla and Chassigny. Therefore, the mantle from which these two meteorites originate must have a differentiation history that is fundamentally different to that of the shergottites. For the following discussion, it is assumed that these meteorites are derived from the same mantle source region (e.g., McCubbin et al., 2013). To construct the Pb isotopic model for the source region for these meteorites, the primordial Pb isotope composition was used (Canyon Diablo Troilite at 4.567 Ga) and since core differentiation was virtually simultaneous with accretion, it is ignored here. However, any secondary mantle differentiation event(s) lack other external age estimates, such as the 4.504 Ga age derived from the coupled Sm-Nd system determined for the shergottite source region (e.g., Borg et al., 2016). A simple approach is taken here and assumes a similar two-stage model to the shergottites. All of the potentially important events that reflect changes in μ_1 (pre- silicate differentiation) and μ_2 (post- silicate differentiation) have been plotted in Figure 4. For a differentiation event occurring at 4.3 Ga or older, there exist no μ_1-values that can be used to achieve the initial Pb compositions measured in Nakhla and Chassigny. Similarly, after 3.8 Ga, the generated curves do not have μ_1-values that can be used to achieve the initial Pb compositions measured in these meteorites (shaded regions in Figure 4). A median estimate between 4.3 and 3.8 Ga for the time of differentiation is at 4.1 Ga. This number has been chosen as an intermediate value between the boundary conditions. Choosing this value results in a pre-differentiation μ_1 of 0.75 and corresponding post differentiation μ_2 of 2.8 for Chassigny and 2.5 for Nakhla. This μ_1-value and timing of differentiation is different from that of the shergottite source region of 1.8 (Figure 3). Since μ_1 is not consistent between meteorite groups, it explicitly implies that the early mantle differentiation history cannot be similar between both groups.

Since there are no external time constraints that can be used for comparison, these values for the differentiation time and subsequent μ-values are speculative. However, some general statements can be made about the differentiation history for Chassigny and Nakhla. The isotopic composition needed at 4.1 Ga to produce the isotopic compositions of Nakhla and Chassigny is almost identical to that at 4.504 Ga needed to produce the isotopic compositions of the shergottites (Table 1, Figure 5). If the event at 4.504 Ga does represent the last stages of Martian accretion (e.g., Borg et al., 2016) and added primitive material to the Martian mantle, it would have mixed with any evolving Pb, thereby interfering with both the time of differentiation and μ_1-value calculations here (Figure 5). Similarly, if material were added to the source region of the nakhlites and chassignites, any closed box modelling of all other isotopic systems would be explicitly affected (e.g., Debaille et al., 2009). Any late additions of primitive material of CDT-like composition would have mixed with the evolving Pb and retarded the Pb growth, thus mathematically necessitating a decreased μ_1 value and a later time of differentiation. This is illustrated in Figure 5, whereby the growth trajectory of early Pb and mixing of early Pb with a primitive reservoir (i.e., CDT) are geometrically similar but proceed in opposite directions. Therefore, if there were late additions of primitive material, it would have had the effect of retarding Pb evolution and decreasing the overall μ in the source region through the addition of primordial Pb. This mixing phenomenon in Pb isotopes for early planetary evolution has also been recently considered to explain variations in the initial phases of Pb growth in the Earth-Moon system (Connelly and Bizzarro, 2016).

5.3 Martian mantle differentiation history

In addition to constraining the μ-value of various Martian source reservoirs through time, initial Pb compositions can also be used to determine the time integrated κ ratio of a planetary body. In $^{208}Pb/^{206}Pb$ vs. $^{204}Pb/^{206}Pb$, initial Pb compositions of all samples measured here form a linear trend (Figures 2, 6). Using a Pb growth model beginning with assumed primordial CDT composition and the time of Solar System formation at 4.567 Ga, similar to the Pb growth models proposed earlier, most of the initial Pb compositions can be modelled with a κ-value of 3.6 (Figure 6), indicating that the Th/U value has not significantly fractionated during mantle differentiation events on Mars. Two meteorites lie outside of uncertainty of the modelled κ-value (Chassigny and the depleted shergottite LAR 12095) and may have been derived from mantle reservoirs with a slightly decreased Th/U. In addition, a κ-value of 3.6 is similar to that determined for the Earth, the Moon, and ordinary chondrites (Galer and O'Nions, 1985, Rocholl and Jochum, 1993, Snape et al., 2016).

For the first time, accurate Pb model ages with a corresponding source reservoir μ-value have been determined for all varieties of the shergottites, as well as Nakhla and Chassigny. Based on the models proposed here, a comparison between the source reservoir compositions for all other long-lived radiogenic isotope systems can now be inferred. When compared to the calculated mantle source μ-values of 1.4-4.7 here, the source variables in $^{87}Sr/^{86}Sr_i$, $\gamma^{187}Os$, $\varepsilon^{176}Hf$, and $\varepsilon^{143}Nd$ (given in Table 1) give strong linear correlations (r^2 of 0.86, 0.95, 0.85, and 0.98 respectively, Figure 7). While the other source variables do not represent parent-daughter ratios like the μ-values calculated here, they represent the time-integrated behavior of these radiogenic pairs. These linear correlations indicate that the major differentiation events of the Martian mantle affected all parent-daughter ratios of the shergottites and ALH 84001 at the same time, best determined for the time of the Martian silicate differentiation event at 4.504 Ga (Borg et al., 2016). It can be inferred that the mantle differentiation event that affected the parent-daughter ratios of radiogenic isotopic systems in the source reservoir of Nakhla and Chassigny must have behaved in a similar way.

5.4 Mars, other inner Solar System bodies, and implications for planetary differentiation

The original (post core formation, pre silicate differentiation) mantle source reservoir for Mars inferred from the shergottites had a μ-value of 1.8. Since it is likely that the source region of Nakhla/Chassigny has experienced late addition/mixing and cannot record a pristine evolutionary history, the μ-values for these meteorites are not taken into account in the following discussion. A Martian initial μ-value of 1.8 is not significantly elevated over ordinary and enstatite chondritic composition of ~1 (e.g., Tera, 1983, Göpel et al., 1994). Additionally, the most recent estimates for the ordinary chondrite materials that accreted to form the Earth indicate that these materials also had an initial μ-value of 1.8 (Connelly and Bizzarro, 2016). Given the identical stable Cr isotopic compositions of ordinary, enstatite chondrites, the Moon, and the Earth (e.g., Trinquier et al., 2009, Mougel et al., 2018), this μ-value (1.8) seems likely to represent the primordial μ-value of inner Solar System bodies.

If Mars accreted with a μ-value of 1.8, like that proposed for the Earth and ordinary chondrites (e.g., Connelly and Bizzarro, 2016), and core formation occurred contemporaneously with planetary formation, it is very likely that core formation did not significantly affect the U/Pb value of silicate Mars (Martian mantle μ-values of 1.4-4.7). This is in broad agreement with the low concentrations of Pb measured in iron meteorites (e.g., Tatsumoto et al., 1973) and similar observations for the very early Earth (e.g., Connelly and Bizzarro, 2016). Thus, the increase in μ-value for the intermediate and enriched shergottites must have occurred during the mantle differentiation event at 4.504 Ga. It has been observed that the precipitation and fractionation of sulfides is able to elevate the μ-value in an enriched residual source reservoir by a factor of around 4 (Gaffney et al., 2007), which is in very good agreement with the present model for the intermediate-enriched shergottite source reservoirs with μ-values of 3.1-4.7. This differentiation event at 4.504 Ga involving sulfides is also recorded in the complementary depleted shergottite reservoir with a μ-value of 1.4-1.5.

6. Conclusions

In combination with previous studies, the initial Pb isotopic compositions of mantle-derived Martian meteorites including four enriched, one intermediate, and two depleted shergottites, Chassigny, and Nakhla have been measured in multiple analyses of maskelynite, plagioclase, K-feldspar and/or sulfide grains using SIMS. These data have been used to construct models of Pb isotopic evolution in both the shergottite source mantle reservoir(s) and the Nakhla/Chassignite source mantle reservoir(s), which, based on other isotopic systems, must have fundamentally distinct differentiation histories. These two separate models generate initial Pb model ages that are in complete agreement with the age constraints provided by all other radiogenic isotopic systems and provide an internally consistent chronology for the crystallization of Martian meteorites over 4 Ga of Martian history. However, the model for the differentiation history of the source reservoir of Nakhla/Chassigny is complicated by the evidence of likely late accretion.

The models constructed here have yielded μ-values that have excellent linear correlations with other radiogenic isotopic source reservoir compositions ($^{87}Sr/^{86}Sr_i$, $\gamma^{187}Os$, $\varepsilon^{143}Nd$, and $\varepsilon^{176}Hf$), indicating a relatively simple differentiation history of the Martian mantle sampled by the shergottites. The model for the shergottites proposed here indicates that Mars accreted with an initial μ-value of 1.8, which is in agreement with recent estimates for the early Earth and ordinary chondrites. Post accretion, the core formation had little to no affect on the bulk U/Pb value of Mars. At 4.504 Ga, the mantle experienced a differentiation event, which resulted in the formation of a depleted (μ-value of 1.4-1.5), intermediate (μ-value of 3.5) and enriched sources (μ-values of 3.1-

4.7). Despite the fractionation events occuring in the U/Pb system, κ remained constant throughout Martian history with a value of 3.6, which is also in agreement with the Earth, the Moon, and chondrites.

Acknowledgements

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Figures

Figure 1. Weighted averages for the ages of the meteorites studied here. All age constraints are from isotopic systems in the legend on the figure. References for each meteorite as follows: RBT 04262: Lapen et al. (2008) and Shih et al. (2009), Zagami: Borg et al. (2005); LAR 12011: Shafer et al. (2010); ALH 77005: Borg et al. (2002); Tissint: Brennecka et al. (2014); Chassigny: Misawa et al. (2006); Nakhla: Cohen et al., (2017), Gale et al. (1975), Nakumurua et al. (1982), Papanastassiou and Wasserburg (1974).

Figure 2. Initial Pb compositions for ten Martian meteorites investigated. Each symbol is representative of an x-y weighted average of several maskelynite, plagioclase, K-feldspar, or sulfide analyses from each meteorite (See Supplementary Figure 1 and Bellucci et al., 2015a). Included in this diagram are lines corresponding to shergottite model time (S.m.t., after Figure 3) that correspond to all μ-values at a given time at time at 4090 Ma, 500 Ma, and 0 Ma (S.m.t: solid lines). Similarly, the dashed line illustrates a 1400 Ma age determined using the Chassigny and Nakhla model (Chassigny and Nakhla model time: C.N.m.t.) described in Figure 4.

Figure 3. A two-stage Pb isotopic model for the shergottites studied here with concordant ages in other isotopic systems (Figure 1). The model assumes a silicate differentiation event at 4.504 Ga (Borg et al., 2016), minimizes the average Δ_t (difference between initial Pb model age-concordant age), and determines μ-values after core formation and

pre 4.504 Ga (μ_1) and post 4.504 Ga (μ_2). Gray bands represent 2σ uncertainty estimates on the average Δ_t of Pb model ages.

Figure 4. A two-stage Pb isotope model for the Nakhla and Chassigny. Since there is no information on the differentiation history of the Martian mantle that led to these mantle reservoirs, various arbitrary timing for multiple differentiation events are used. Boundary conditions exist where average Δ_t=0 cannot have occurred before 4.3 and after 3.8 Ga (grey shaded regions). The dashed line at μ_1 of 0.75 corresponds to our estimate of the median mathematical solution at 4.1 Ga.

Figure 5. Pb growth from (primordial) CDT to 4.504 Ga (black curve) and mixing line between evolved Pb and CDT composition (red dashed curve). The trajectory of the Pb growth from 4.567 Ga to 4.504 Ga and mixing in Pb-Pb diagrams are linear, but opposite. Therefore, any additions of primitive Pb composition would have apparently retarded any Pb growth but kept it on the same geometrical trajectory. This retardation would dictate mathematical requirements of a lower μ_1 and a later time of differentiation presented, which was calculated in Figure 4.

Figure 6. A time integrated κ ($^{232}Th/^{238}U$) value from 4.567 Ga to present of 3.6 is calculated in $^{204}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ for all investigated samples. The linearity seen between samples in this figure indicates that there has been limited fractionation between U and Th in the Martian mantle, as represented by the range of sample material analyzed here, through geologic time.

Figure 7. Mantle source μ-values vs. other the source values for other long-lived radiogenic parameters including $^{87}Sr/^{86}Sr_{i}$, $\gamma^{188}Os$, $\varepsilon^{176}Hf$, and $\varepsilon^{143}Nd$. These parameters reflect the time-integrated behavior of the parent/daughter ratios throughout Martian history, similar to the μ-values calculated here. The Sr_i value for ALH84001 is plotted but was excluded from the linear regression due to its possible mixing with an elevated Rb/Sr source during its formation or analysis (Beard et al., 2013). Excellent linear correlations indicate relatively simple parent-daughter fractionations during mantle differentiation events. References for each value are presented in Table 1.

Figure 1

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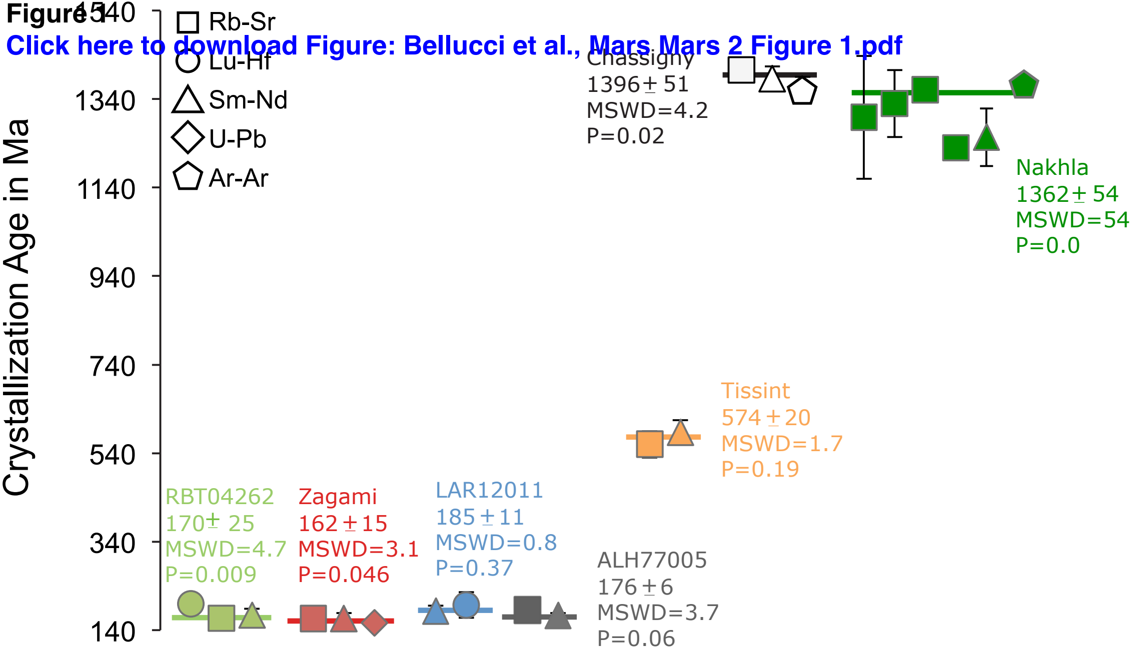

Figure 2

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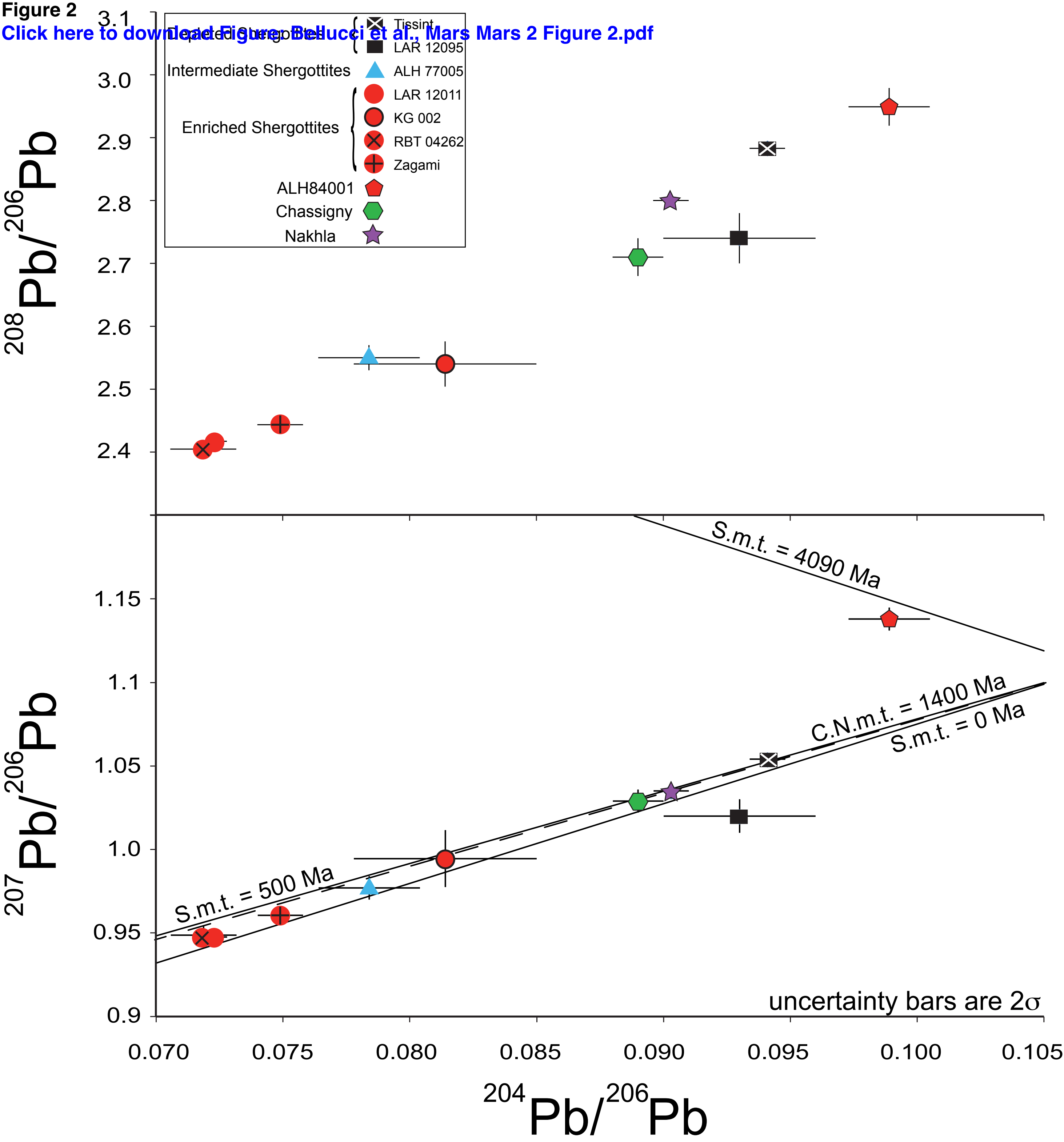

Figure 3

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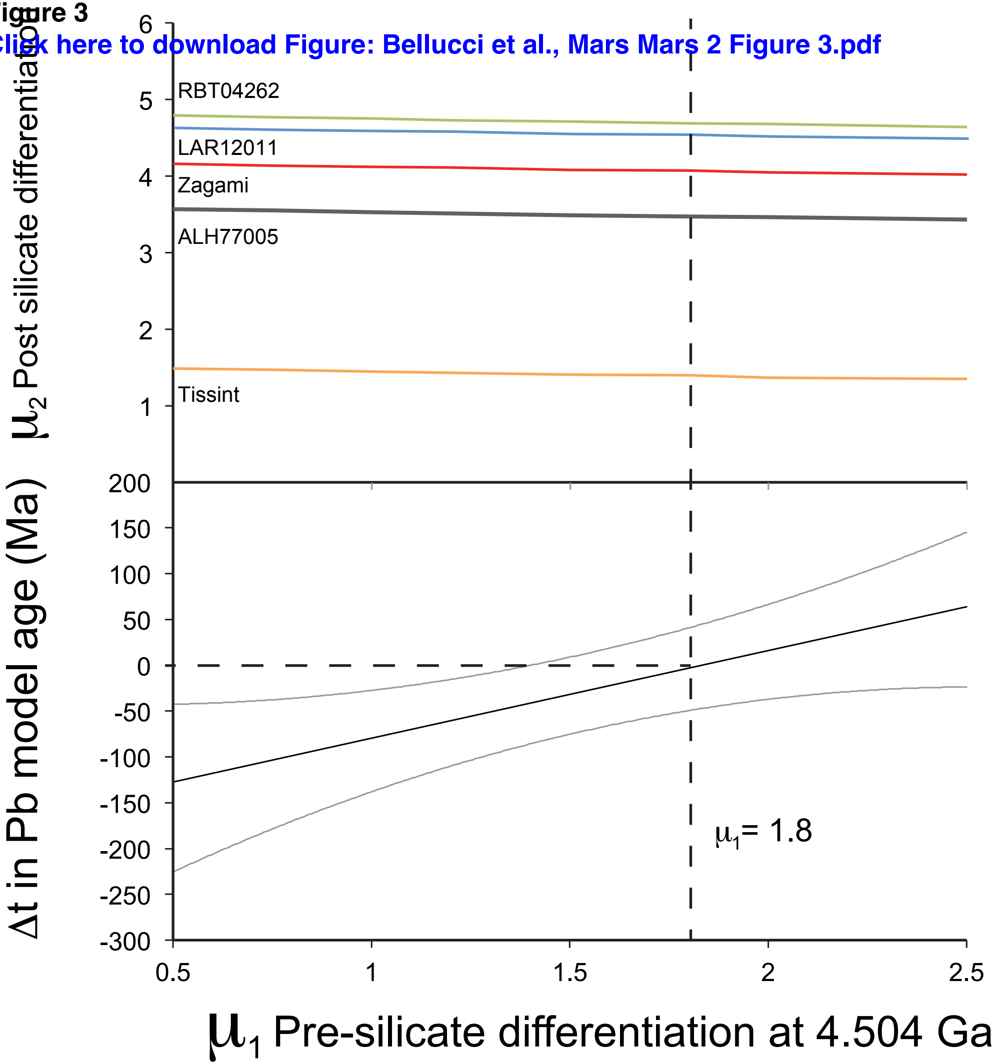

Figure 4

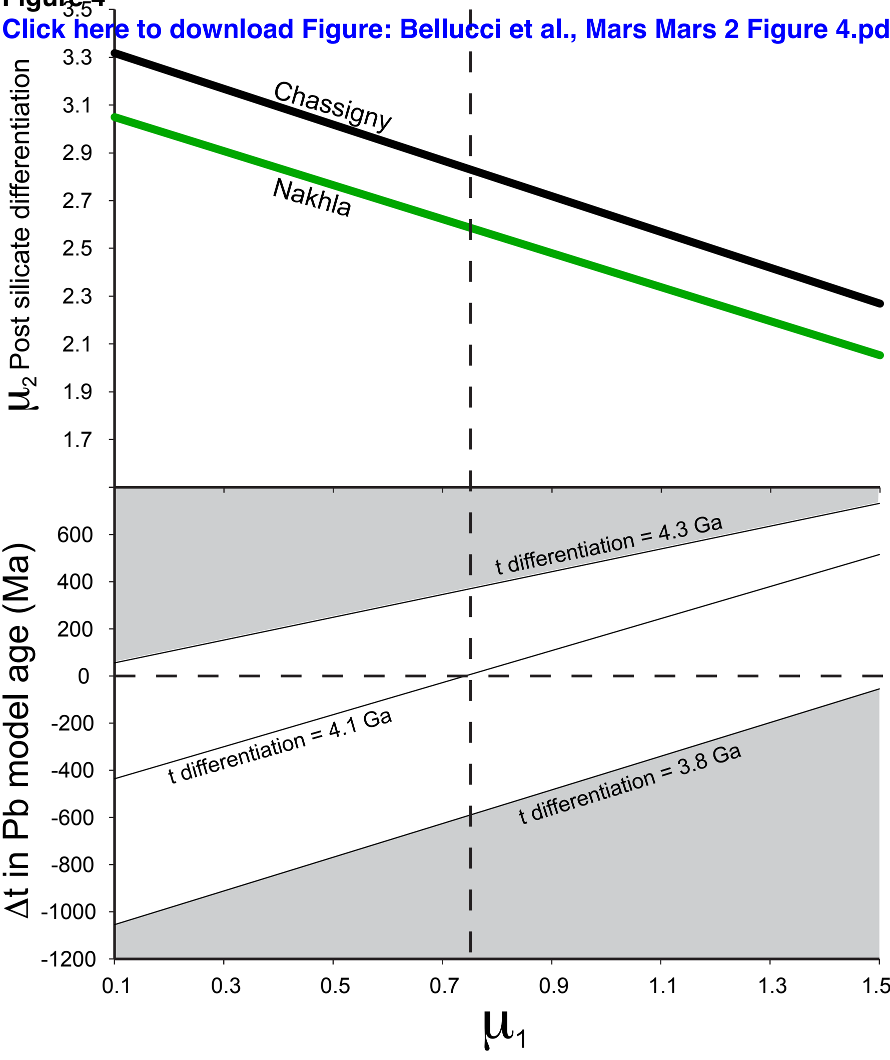
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
μ_2 Post silicate differentiation
Chassigny
Nakhla
600
400
200
0
-200
-400
-600
-800
-1000
-1200
Δt in Pb model age (Ma)
t differentiation = 4.3 Ga
t differentiation = 4.1 Ga
t differentiation = 3.8 Ga
0.1
0.3
0.5
0.7
0.9
1.1
1.3
1.5
μ_1

Figure 5

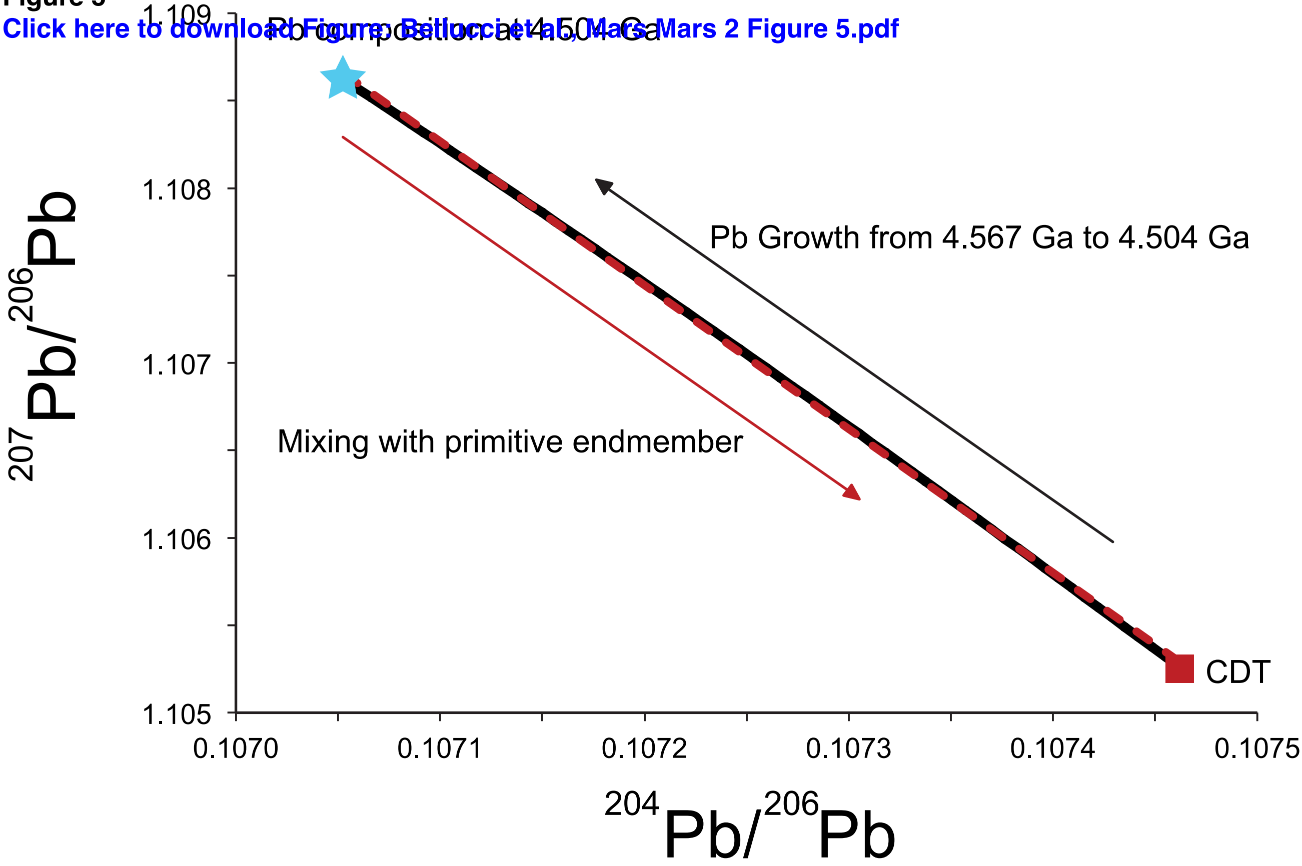
Pb composition at 4.504 Ga
Pb Growth from 4.567 Ga to 4.504 Ga
Mixing with primitive endmember
CDT
1.109
1.108
1.107
1.106
1.105
0.1070
0.1071
0.1072
0.1073
0.1074
0.1075
$^{207}Pb/^{206}Pb$
$^{204}Pb/^{206}Pb$

Figure 6
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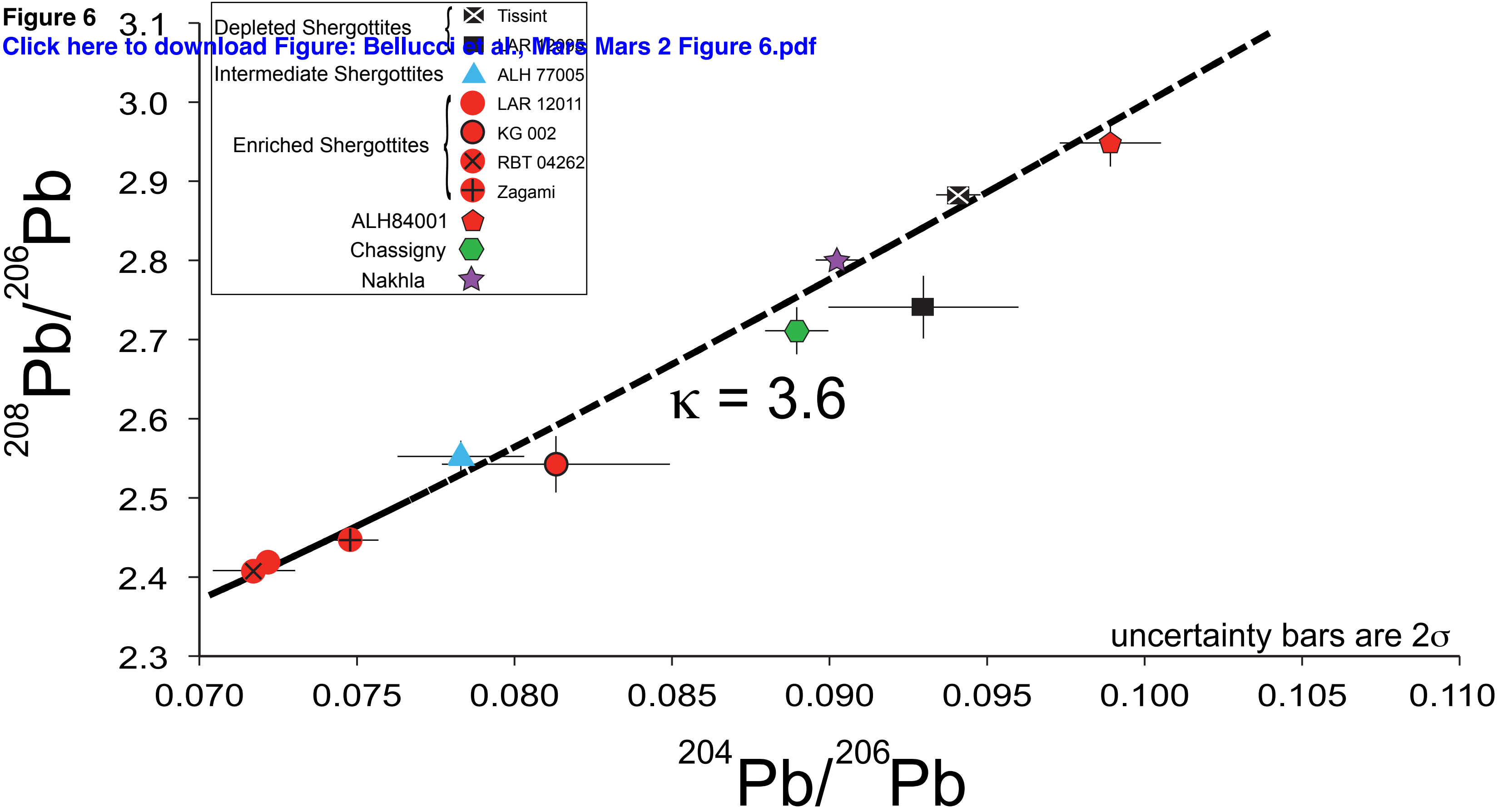

Figure 7

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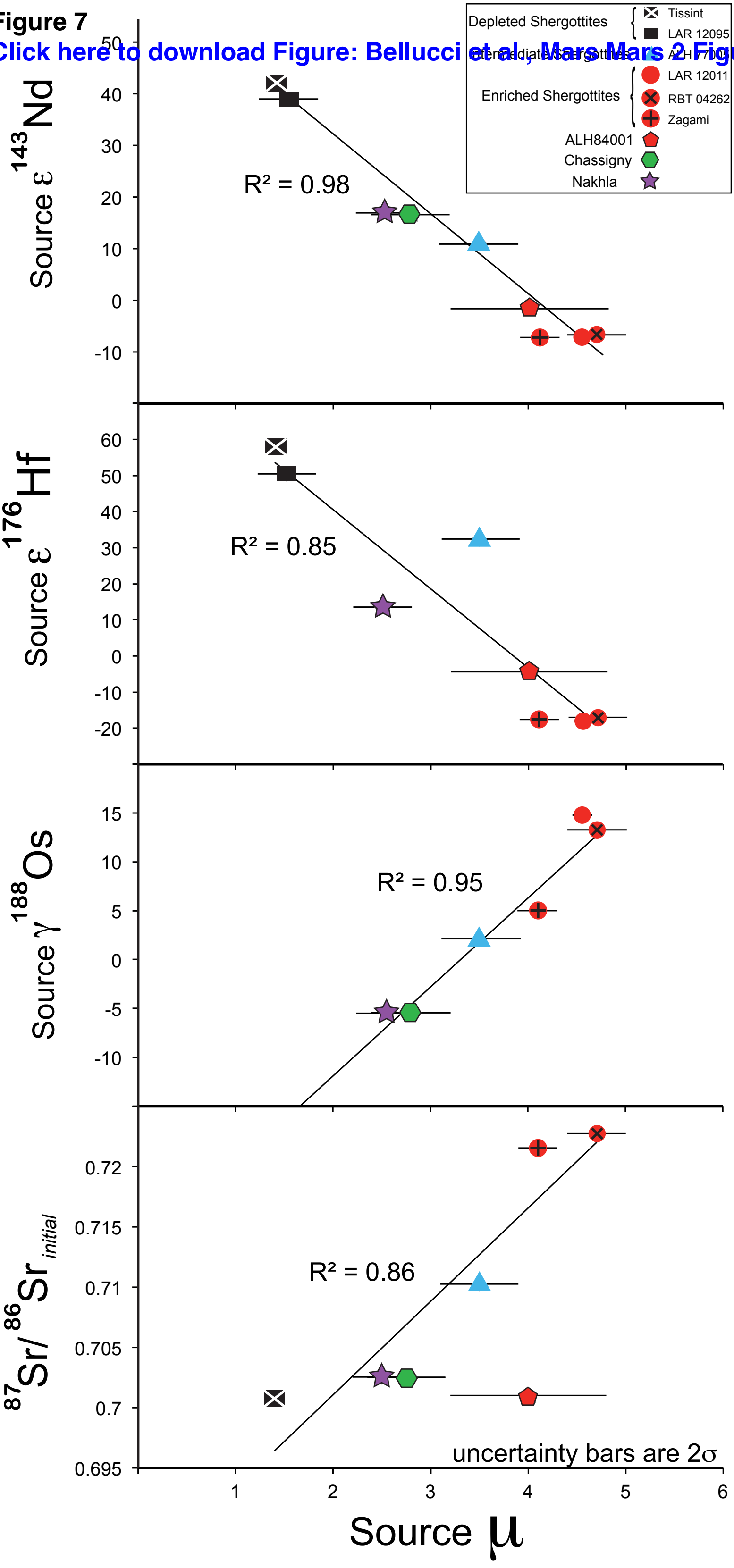

Table 1

Click here to download Table: Bellucci et al., 2017 Mars 2 Table 1.xlsx

Table 1. Initial Pb isotopic compositions, model ages, and source compositions

Sample	Type	$^{204}Pb/^{206}Pb$	2	$^{207}Pb/^{206}Pb$	2	$^{208}Pb/^{206}Pb$	2	n	Crystallization Age[1] in Ma	Pb Model Age in Ma	2	t*	1	2	2	^{176}Hf Source	^{143}Nd Source	^{187}Os Source
RBT 04261[2]	Enriched	0.0719	0.0013	0.949	0.006	2.405	0.011	14	170	240	180	-70	1.8	4.7	0.3	-17[k]	-6.7[L]	13.2[c]
LAR 12011[2]	Enriched	0.0723	0.0005	0.948	0.002	2.417	0.006	37	185	150	76	35	1.8	4.6	0.1	-18[J]	-7.2[J]	14.7[c]
Zagami[2]	Enriched	0.0749	0.0009	0.961	0.004	2.443	0.007	20	165	170	158	-5	1.8	4.1	0.2	-17.6[a]	-7.2[d]	5[c]
KG 002	Enriched	0.0814	0.0036	0.995	0.017	2.540	0.036	20	NA	360	802	NA	1.8	3.1	0.8	NA	NA	NA
ALH 77055	Intermediate	0.0784	0.0020	0.977	0.007	2.550	0.020	10	176	180	302	-4	1.8	3.5	0.4	32.4[a]	11.1[b]	2.1[c]
LAR 12095	Depleted	0.093	0.003	1.02	0.01	2.74	0.04	18	NA	NA	NA	NA	1.8	1.5	0.3	50.4[I]	39[I]	NA
Tissint	Depleted	0.0941	0.0007	1.054	0.003	2.883	0.008	5	574	570	213	4	1.8	1.4	0.1	58[h]	42[g]	NA
ALH 84001[2]		0.0989	0.0016	1.138	0.007	2.949	0.030	18	4090[k,2]	3850	170	240	1.8	4.0	0.8	-4.37[f]	-1.6[f]	NA
Compsition of the Shergottite/ALH84001 source Mantle		0.107		1.11		3.16												
Chassigny[3]		0.0890	0.0010	1.029	0.007	2.710	0.030	4	1396	1400	256	-4	0.75	2.8	0.4	NA	16.6[m]	-5.46[e]
Nakhla		0.0903	0.0007	1.035	0.003	2.800	0.010	13	1362	1380	214	-18	0.75	2.5	0.3	13.5[n]	16.9[n]	-5.5[e]
Nakhla/Chassigny Source at 4.1 Ga		0.106		1.11		3.14												

a) Blichert-Toft et al., 1999 b) Borg et al., 2002, c) Brandon et al., 2012, d) Borg et al., 2005, e) Brandon et al., 2000, f) Lapen et al., 2010, g) Brennecka et al., 2014, H) Grosshans et al., 2013, I) Righter et al., 2015, J) Shafer et al., 2010, k) Lapen et al., 2008, L) Shih et al., 2009, M) Misawa et al., 2005, N) Debaille et al., 2009, O)Beard et al., 2013,P) Gale e

*Where t = Crystallization age-Pb model age

1) See Figure 1

2) Pb isotope values from Bellucci et al., 2015a

3) Pb isotope values from Bellucci et al., 2016