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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. 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 the 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$_i$, γ^{187}Os, ε^{143}Nd, and ε^{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 comprises 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 to 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

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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 ($= {}^{232}\mathrm{Th}/{}^{238}\mathrm{U}$) 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 $^{146}\mathrm{Sm}$–$^{142}\mathrm{Nd}$ and $^{147}\mathrm{Sm}$–$^{143}\mathrm{Nd}$ isotopic study indicates this event likely occurred at 4504 $^{+5.4}/_{-5.7}$ Ma (Borg et al., 2016). In contrast, the $^{146}\mathrm{Sm}$–$^{142}\mathrm{Nd}$ and $^{182}\mathrm{Hf}$–$^{182}\mathrm{W}$ 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 $^{142}\mathrm{Nd}$ compositions between the meteorite groups has been attributed to a mantle overturn early in Martian history (Debaille et al., 2009). Alternatively, the difference in $\varepsilon^{182}\mathrm{W}$ 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 $^{182}\mathrm{W}$ in the Martian meteorite groups ($\varepsilon^{182}\mathrm{W}$ of -0.7 vs 3) or 2) rapid cooling of a planetary embryo and then a distinct later addition by a significant impactor, which melted a portion of the mantle (e.g., Mezger et al., 2013; Borg et al., 2016). Regardless of the actual scenario of mantle accretion/differentiation that took place leading to the different $\varepsilon^{182}\mathrm{W}$ 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 an age of core formation of 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 undated 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, Nakhla, and Chassigny. Sample descriptions and Pb data for the previously reported enriched shergottites 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 $\varepsilon^{176}\mathrm{Hf}$ (-17 to -18), $\varepsilon^{143}\mathrm{Nd}$ (-7.2 to -6.7), and $\gamma^{187}\mathrm{Os}$ (5 to 14.7) (Table 1, Blichert-Toft et al., 1999; Borg et al., 2005; Debaille et al., 2009; 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 (Fig. 1, Borg et al., 2002). Allan Hills 77005 has a source reservoir composition in $\varepsilon^{176}\mathrm{Hf}$, $\varepsilon^{143}\mathrm{Nd}$, and $\gamma^{187}\mathrm{Os}$ of 32.4, 11.1, and 2.1, respectively (Table 1, Blichert-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 (Fig. 1, Brennecka et al., 2014). Despite the lack of ev-