



Lithium isotope constraints on crust–mantle interactions and surface processes on Mars

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Abstract

Lithium abundances and isotope compositions are reported for a suite of martian meteorites that span the range of petrological and geochemical types recognized to date for Mars. Samples include twenty-one bulk-rock enriched, intermediate and depleted shergottites, six nakhlites, two chassignites, the orthopyroxenite Allan Hills (ALH) 84001 and the polymict breccia Northwest Africa (NWA) 7034. Shergottites unaffected by terrestrial weathering exhibit a range in $\delta^7\text{Li}$ from 2.1 to 6.2‰, similar to that reported for pristine terrestrial peridotites and unaltered mid-ocean ridge and ocean island basalts. Two chassignites have $\delta^7\text{Li}$ values (4.0‰) intermediate to the shergottite range, and combined, these meteorites provide the most robust current constraints on $\delta^7\text{Li}$ of the martian mantle. The polymict breccia NWA 7034 has the lowest $\delta^7\text{Li}$ (−0.2‰) of all terrestrially unaltered martian meteorites measured to date and may represent an isotopically light surface end-member.

The new data for NWA 7034 imply that martian crustal surface materials had both a lighter Li isotope composition and elevated Li abundance compared with their associated mantle. These findings are supported by Li data for olivine-phyric shergottite NWA 1068, a black glass phase isolated from the Tissint meteorite fall, and some nakhlites, which all show evidence for assimilation of a low- $\delta^7\text{Li}$ crustal component. The range in $\delta^7\text{Li}$ for nakhlites (1.8 to 5.2‰), and co-variations with chlorine abundance, suggests crustal contamination by Cl-rich brines. The differences in Li isotope composition and abundance between the martian mantle and estimated crust are not as large as the fractionations observed for terrestrial continental crust and mantle, suggesting a difference in the styles of alteration and weathering between water-dominated processes on Earth versus possibly Cl–S-rich brines on Mars. Using high-MgO shergottites (>15 wt.% MgO) it is possible to estimate the $\delta^7\text{Li}$ of Bulk Silicate Mars (BSM) to be $4.2 \pm 0.9\text{‰}$ (2σ). This value is at the higher end of estimates for the Bulk Silicate Earth (BSE; $3.5 \pm 1.0\text{‰}$, 2σ), but overlaps within uncertainty.

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1. INTRODUCTION

Understanding of the formation and evolution of Mars has greatly expanded in recent years through remote sensing and robotic missions to the martian surface and by detailed investigations of the steadily increasing number of martian meteorites (~70 individual specimens as of April 2015). Although the great majority of newly discovered meteorites belong to the Shergotty–Nakhla–Chassigny (SNC) group, the diversity of recognized petrologic and geochemical types of martian rocks has been rapidly expanding. Examples of “non-SNC” martian meteorites are ALH 84001, a ~4.1 Ga orthopyroxenite, thought to represent ancient martian crust (e.g., [Lapen et al., 2010](#)), and the ~4.4 Ga polymict breccia NWA 7034 ([Agee et al., 2013](#); [Humayun et al., 2013](#)). Previous studies have demonstrated the origin of these meteorites from Mars (e.g., [Bogard and Johnson, 1983](#); [Franchi et al., 1999](#); [Nyquist et al., 2001](#)), and also revealed evidence for prolonged geologic activity on their parent body (e.g., [Borg et al., 2008](#); [Misawa et al., 2008](#); [Nyquist et al., 2009](#)).

While genetically linked to Mars, martian meteorites reveal complexities in both martian mantle composition, as well as evidence for interaction between mantle-derived melts and crust (e.g., [Blichert-Toft et al., 1999](#); [Borg et al., 2002](#); [Basu Sarbadhikari et al., 2009, 2011](#); [Filiberto et al., 2010](#); [Lapen et al., 2010](#); [Brandon et al., 2012](#)). Overall, Mars appears to have undergone a quite different geochemical differentiation history compared with Earth, with very early (~4.5 Ga) differentiation, followed by a period of magmatic quiescence with rare manifestations of volcanism and no strong evidence for plate tectonics ([Harper et al., 1995](#); [Halliday et al., 2001](#); [Breuer and Spohn, 2003](#); [Debaille et al., 2009](#); [Kleine et al., 2009](#); [Carr and Head, 2010](#)).

Lithium isotopes and abundances are a useful tool for reconstructing the chemical differentiation of Mars. The currently available Li isotope data for bulk analyses of martian meteorites appear to reflect magmatic fractionation ([Bridges et al., 2005](#); [Magna et al., 2006](#); [Reynolds et al., 2006](#); [Seitz et al., 2006](#); [Filiberto et al., 2012](#)). In contrast, intra-mineral variations in Li abundances and isotope compositions in shergottites and nakhlites have been interpreted in the context of the presence of magmatic water and subsequent degassing ([Lentz et al., 2001](#); [McSween et al., 2001](#); [Beck et al., 2004](#); [Herd et al., 2005](#)), or have been related to kinetic isotope fractionation by diffusion ([Beck et al., 2006b](#); [Chaklader et al., 2006](#); [Treiman et al., 2006](#)). Lithium isotope fractionation at low temperatures may also represent a diagnostic tool for detecting alteration, hydrothermal exchange and weathering in the martian surface environment. For example, while Li isotope variations for some terrestrial igneous systems have been ascribed to magmatic differentiation processes (e.g., [Elliott et al., 2006](#); [Tomascak et al., 2008](#)), numerous studies have recognized that secondary hydrothermal processes can lead to large Li isotope fractionation in originally magmatic rocks (e.g., [Chan et al., 1992, 2002](#); [Pistiner and Henderson, 2003](#); [Huh et al., 2004](#); [Wunder et al., 2006](#); [Vigier et al., 2008](#); [Millot et al., 2010b](#)).

In this study, new whole-rock Li abundances and isotope data were obtained for a total of 31 martian meteorites, as well as for the Tissint black glass and leachates of nakhlite NWA 817. This comprehensive Li abundance and isotope data set allows elucidation of crust–mantle processes and estimates of martian mantle composition at greater resolution than has previously been possible. Ultimately, these data also constrain the Li isotope composition of the martian mantle and support a consistency in the Li isotope composition of the inner Solar System planets (i.e., Earth, Moon, Mars, howardite–eucrite–diogenite parent body(ies)).

2. SAMPLES AND METHODS

Lithium abundances and isotope compositions were obtained for 21 martian shergottites. Using petrological classification, these samples include five basaltic (Shergotty, Zagami, Los Angeles, NWA 856, NWA 4864), ten olivine-phyric (Tissint, Elephant Moraine [EETA] 79001 lithology A, Larkman Nunatak [LAR] 06319, Yamato [Y] 980459, NWA 1068, NWA 4925, NWA 6162, Sayh al Uhaymir [SaU] 005, SaU 051, SaU 094), two olivine–orthopyroxene-phyric (Roberts Massif [RBT] 04262, Dar al Gani [DaG] 476), three lherzolic (ALH 77005, Y-000097, NWA 1950), and one diabasic shergottite (NWA 5990). New Li abundance and isotope data are further reported for six clinopyroxene-bearing nakhlites (Nakhla, Lafayette, Miler Range [MIL] 03346, Y-000593, NWA 817, NWA 5790), two dunitic chassignites (Chassigny, NWA 2737), NWA 7034, and ALH 84001. Between ~0.6 and ~1.7 g were allocated from various sources for this study with a few smaller aliquots available for Chassigny, Lafayette, NWA 5790, NWA 7034 and Tissint (~100–250 mg); in the case of large aliquots, homogenized powders were prepared from ca. 40–60% of the allocated amounts, whereas all material was homogenized to a fine powder in the case of the lower sample masses. Fusion crusts were removed from samples and only interior portions of the meteorites were processed. A sub-aliquot of the recent Tissint fall was isolated containing a visually estimated 40–50% of black glass. The black glass has been suggested to represent a surface component on Mars ([Chennaoui Aoudjehane et al., 2012](#)). Additionally, to investigate potential pre-terrestrial alteration processes, a two-step ultrasonic leaching procedure was applied to an aliquot of NWA 817, which contains a large proportion of mesostasis (>15%) and evidence for pervasive pre-terrestrial aqueous alteration (see [Gillet et al., 2002](#)), by leaching for 2 × 10 min in de-ionized water and then for 10 min with 1 M HCl.

The analytical procedures for the digestion of bulk samples and the separation and purification of Li using a two-step cation-exchange chromatography are identical to those reported previously ([Magna et al., 2004, 2006](#)). Lithium concentrations and isotope compositions in all samples, with the exception of Tissint and NWA 7034, were measured using a *Neptune* multiple-collector inductively-coupled-plasma mass spectrometer (MC-ICPMS; Thermo Scientific, Bremen, Germany), housed at the Open

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