



The calcium isotope systematics of Mars



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ABSTRACT

New Ca isotope data from a suite of Martian meteorites provide constraints on the Ca isotope composition of the Martian mantle and possible recycling of surface materials back into the mantle. A mean $\delta^{44/40}\text{Ca}$ of $1.04 \pm 0.09\%$ (2SD) is estimated for the Martian mantle which can also be taken as an approximation for Bulk Silicate Mars. This value is identical with the estimates for Bulk Silicate Earth, and the inner Solar System planets can therefore be considered homogeneous with respect to Ca isotopes. The Ca isotope composition of two Martian dunites varies by $\sim 0.3\%$ despite strong chemical and mineralogical similarities and this difference can be caused by the presence of carbonate, probably of pre-terrestrial origin, implying a protracted period of the existence of CaCO_3 -rich fluids and sufficient amounts of CO_2 on the surface of Mars. The variability of $\delta^{44/40}\text{Ca}$ within the groups of shergottites and nakhlites (clinopyroxene cumulates) cannot be related to partial melting and fractional crystallization in any simple way. However, there is no necessity of incorporating surface lithologies with isotopically light Ca into the mantle sources of Martian meteorites. These inferences are consistent with the absence of large scale crust–mantle recycling and thus of plate tectonics on Mars.

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1. Introduction

Mars and Earth are rock-dominated planets, having broadly similar bulk compositions, with Mars being enriched in volatile elements (e.g., S, Se, K, Pb) compared to Earth (e.g., Dreibus and Wänke, 1987; McLennan, 2003). As a consequence of its smaller size ($\sim 11\%$ of the terrestrial mass), Mars can lose most of its internally generated heat by conduction and appears not to show evidence for plate tectonic activity. Its major geologic activity ceased early in its history (Grott et al., 2013; Mezger et al., 2013) while Earth's has been continuing vigorously. The study of magmatic rocks from Mars and their chemical and isotope signatures can therefore provide important insights into early mantle differentiation processes of planetary bodies (e.g., Kleine et al., 2009).

Stable isotope variations of major elements (e.g., Mg, Si, Fe, Ca) in magmatic systems have long been below analytical resolution of mass spectrometry techniques to become useful geochemical tools and only more recently have high-precision studies found that the isotopes of major elements such as Mg, Si, Fe and Ca fractionate during high-temperature magmatic processes

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(e.g., Amini et al., 2009; Georg et al., 2007; Teng et al., 2010; Williams et al., 2004). These elements are among the most abundant in the mantles and/or cores of rocky planets, planetesimals and moons, and therefore play key roles in deciphering planetary rock cycles, core–mantle segregation, phase transitions and melting processes.

The early studies of mass-dependent Ca isotope fractionation focused on biological cycling (Skulan and DePaolo, 1999; Zhu and Macdougall, 1998) as well as high temperature condensation–evaporation processes in the early Solar System (e.g., Niederer and Papanastassiou, 1984; Russell et al., 1978), while more recent Ca isotope research focused on low-temperature geochemical and biogeochemical cycling, such as the oceanic Ca cycle (Farkaš et al., 2007), bio-mineralization (Böhm et al., 2006; Gussone et al., 2007), carbonate diagenesis (Fantle and DePaolo, 2007; Teichert et al., 2009) or forest ecosystems (Holmden and Bélanger, 2010). These observations demonstrate the potential utility of Ca isotopes as tracer for geological processes. Calcium has a high abundance, lithophile character and plays an essential role in a variety of geological and biological processes, including phenomena such as crystallization of major rock-forming minerals, metamorphism, hydrothermal processes, weathering, diagenesis, bio-mineralization, plant growth and the global carbon cycle. Calcium isotope fractionation during inorganic mineral precipitation is expected to be small ($< 2\%$), although systematic $\delta^{44/40}\text{Ca}$ variations in different

igneous rocks were reported (Amini et al., 2009) and are further supported by the observations of systematic Ca isotope fractionation between orthopyroxene and clinopyroxene in mantle xenoliths, the extent of which is suggested to be compositionally dependent (Feng et al., 2014). These observations indicate that resolvable Ca isotope fractionation may indeed occur during high-temperature igneous processes such as partial melting and fractional crystallization (e.g., Huang et al., 2010b, 2011). Recent data of Valdes et al. (2014) do not imply systematic differences in $\delta^{44/40}\text{Ca}$ among melts derived from different chemical reservoirs in the Earth's mantle (i.e., HIMU, DMM, EM). Notably, most basalts analyzed by Valdes et al. (2014) and Jacobson et al. (2015) have $\delta^{44/40}\text{Ca}$ values below that inferred for the Earth's upper mantle which is estimated to be $1.05 \pm 0.04\%$ (2σ ; Amini et al., 2009; Huang et al., 2010b). Other processes that may cause Ca isotope variability in igneous lithologies include fluid–rock interactions (John et al., 2012) as well as reprocessing of low-temperature mineralization products such as Ca-carbonates and Ca-sulfates in near-surface environments (e.g., Gussone et al., 2003; Huang et al., 2011; Marriott et al., 2004).

The Ca isotope variability in Martian meteorites is still poorly understood, but scant available data imply similar Ca isotope compositions to those of the Earth's mafic lithologies (Simon and DePaolo, 2010; Valdes et al., 2014). Here, we aim to contribute further to the understanding of geochemical history of Mars through the Ca isotope analyses of SNC (Shergotty–Nakhla–Chassigny) meteorites and Allan Hills (ALH) 84001 orthopyroxene, and to constrain the $\delta^{44/40}\text{Ca}$ of the Bulk Silicate Mars (BSM), compare it with that of the Earth, and evaluate the processes leading to Ca isotope variations among Martian samples.

2. Samples and methodology

Calcium isotope compositions were obtained for 23 Martian meteorites. Following petrologic classification for shergottites, four basaltic shergottites (Shergotty, Zagami, Los Angeles, Northwest Africa [NWA] 856), six olivine-phyric shergottites (Elephant Moraine [EETA] 79001 lithology A, Larkman Nunatak [LAR] 06319, Yamato [Y] 980459, NWA 1068, NWA 6162, Sayh al Uhaymir [SaU] 005), one olivine–orthopyroxene-phyric shergottite (Roberts Massif [RBT] 04262), two lherzolitic shergottites (ALH 77005, Y-000097), and one diabasic shergottite (NWA 5990) were analyzed. Six clinopyroxene-bearing nakhlites (Nakhla, Lafayette, Miller Range [MIL] 03346, Y-000593, NWA 817, NWA 5790), two dunitic chassignites (Chassigny, NWA 2737), and ALH 84001 were also measured for Ca isotope compositions. Fusion crusts were removed and only interior portions of the samples were processed.

Powdered whole-rock samples were dissolved in a mixture of ultrapure concentrated HNO_3 –HF (1/6 v/v) in Teflon® screw-top vials; dried residues were refluxed repeatedly with concentrated HNO_3 and equilibrated in 6M HCl. An aliquot corresponding to $\sim 1.8 \mu\text{g}$ Ca was taken from the stock solution, which was checked for the absence of precipitates in order to exclude laboratory-induced Ca isotope fractionation, and spiked with a mixed ^{42}Ca – ^{43}Ca tracer prior to ion-exchange separation. Calcium was purified using 100- μl columns packed with MCI-gel (Mitsubishi Chemicals) and 1.8N HCl following the method described in Teichert et al. (2009). Calcium isotope ratios were measured using a Triton T1 thermal ionization mass spectrometer, housed at the Universität Münster, following the protocols of Gussone et al. (2011). The Ca isotope data in this study is reported in per mil deviation from the NIST SRM 915a reference material (Eisenhauer et al., 2004) and calculated as $\delta^{44/40}\text{Ca}$ (‰) = $[(^{44}\text{Ca}/^{40}\text{Ca})_{\text{sample}} / (^{44}\text{Ca}/^{40}\text{Ca})_{\text{SRM915a}} - 1] \times 1000$. Three to four analyses of SRM 915a material per sample wheel were performed with unknown samples. The $\delta^{44/40}\text{Ca}$ of unknown samples were

normalized to the average SRM 915a value of the session. The reliability of the analytical technique was assessed through the analysis of reference rocks and replicate analyses of unknown samples (see Table 1). Replicate analyses of unknown samples reproduced generally within better than $\pm 0.10\%$ (2SD).

3. Results

The stable Ca isotope compositions of Martian meteorites are listed in Table 1 along with CaO contents and plotted in Fig. 1. Age-corrected Ca isotope compositions (from ^{40}K decay to ^{40}Ca) differ less than 0.01‰ from the uncorrected values and make these corrections negligible (see Kreissig and Elliott, 2005, and Caro et al., 2010, for the effects of radiogenic ^{40}Ca ingrowth). This minor correction is in large part due to young magmatic ages of most meteorites from this study combined with low K/Ca < 0.03, with the exception of chassignites having K/Ca of 0.06–0.07. The overall $\delta^{44/40}\text{Ca}$ range is ca. 0.4‰ (from 0.71 to 1.14‰) and does not correlate with CaO contents or petrography in a simple way, perhaps with the exception of slightly larger $\delta^{44/40}\text{Ca}$ variation with increasing modal pyroxene (mostly clinopyroxene; orthopyroxene is dominant in ALH 8400 and is a minor phase in EETA 79001A and LAR 06319; Fig. 2a). Basaltic shergottites span the range in $\delta^{44/40}\text{Ca}$ with Shergotty showing the heaviest and Zagami the lightest Ca isotope composition of the whole Martian suite. The results for Zagami differ from those given by Farkaš et al. (2009) and Simon and DePaolo (2010) outside the analytical uncertainty (Fig. 1) but this may reflect lithological heterogeneity of Zagami (McCoy et al., 1999), also noted for recent Li data obtained from the same aliquot (Magna et al., 2015). The rather narrow range of $\delta^{44/40}\text{Ca}$ of $0.91 \pm 0.03\%$ (2SD) for the enriched (based on chondrite-normalized La_N/Sm_N ; Anders and Grevesse, 1989) olivine(–orthopyroxene)-phyric shergottites (LAR 06319, NWA 1068, RBT 04262) closely resembles that of basaltic shergottites ($0.94 \pm 0.35\%$, 2SD) indicating that incompatible element enrichment/depletion (Fig. 2b) is not paralleled by differences in Ca isotope compositions. These findings are underscored by intermediate and depleted shergottites having a mean $\delta^{44/40}\text{Ca}$ of $1.03 \pm 0.09\%$ (2SD) and $0.93 \pm 0.24\%$, respectively. Nakhlites show a mean $\delta^{44/40}\text{Ca}$ of $0.88 \pm 0.19\%$ (2SD), mimicking the $\delta^{44/40}\text{Ca}$ range found for shergottites, but at significantly higher CaO contents due to large amounts of modal clinopyroxene. Two dunites (Chassigny, NWA 2737) reveal a distinct $\delta^{44/40}\text{Ca}$ that differs by ca. 0.3‰ despite broadly similar petrography and chemistry, with the exception of the presence of carbonate ($\sim 1\%$) in NWA 2737 compared with only traces of carbonate in Chassigny. The orthopyroxenite ALH 84001 has a $\delta^{44/40}\text{Ca}$ of 1.06‰, indistinguishable from that reported by Simon and DePaolo (2010) within the uncertainty.

4. Discussion

4.1. Calcium isotope composition of Mars and significance for the inner Solar System planets

In order to derive an estimate for the $\delta^{44/40}\text{Ca}$ of BSM, several factors must be considered:

(i) The ~ 2.4 wt.% CaO in BSM (McSween, 2003) is significantly less than ~ 3.6 wt.% CaO in Bulk Silicate Earth (McDonough and Sun, 1995). From the average mineral assemblage of the Earth's upper mantle (Salters and Stracke, 2004) and considering high-temperature Ca isotope fractionation for the orthopyroxene–clinopyroxene pair of $\Delta^{44/40}\text{Ca}_{\text{opx-cpx}} = \sim 0.4\text{--}0.8\%$ in mantle peridotites (e.g., Amini et al., 2009; Feng et al., 2014), Huang et al. (2010b) calculated $\delta^{44/40}\text{Ca}_{\text{BSE}} = 1.05 \pm 0.04\%$ (2SD). Due to its low CaO content, olivine can be considered a subordinate Ca-phase (De Hoog et al., 2010) despite high modal abundance in

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