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Martian magmatism from plume metasomatized mantle

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Direct analysis of the composition of Mars is possible through delivery of meteorites to Earth. Martian meteorites include ~165 to 2400 Ma shergottites, originating from depleted to enriched mantle sources, and ~1340 Ma nakhliites and chassignites, formed by low degree partial melting of a depleted mantle source. To date, no unified model has been proposed to explain the petrogenesis of these distinct rock types, despite their importance for understanding the formation and evolution of Mars. Here we report a coherent geochemical dataset for shergottites, nakhliites and chassignites revealing fundamental differences in sources. Shergottites have lower Nb/Y at a given Zr/Y than nakhliites or chassignites, a relationship nearly identical to terrestrial Hawaiian main shield and rejuvenated volcanism. Nakhlite and chassignite compositions are consistent with melting of hydrated and metasomatized depleted mantle lithosphere, whereas shergottite melts originate from deep mantle sources. Generation of martian magmas can be explained by temporally distinct melting episodes within and below dynamically supported and variably metasomatized lithosphere, by long-lived, static mantle plumes.

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Comparative planetology relies on assumptions that physical processes occurring for Earth can be used to compare with processes acting on other planetary bodies. This logic has been applied to Mars, where the broadly basaltic surface composition has been considered analogous to volcanism in terrestrial hotspot locations, including Hawaii. Large volcanic edifices on Mars, including Olympus Mons, Alba Patera, Elysium, Arisia, Pavonis, and Ascræus have been attributed to partial melting above mantle plumes. Mars does not appear to have had plate tectonics, implicating long-lived and static volcanism above mantle plumes, in contrast to age-progressive volcanism occurring in oceanic and continental settings on Earth. This difference, coupled with the distinct thickness and flexural rigidity of the elastic lithosphere on both planets, make assumptions of similar volcano-magmatic processes challenging. For example, observed pre-shield, shield, post-shield erosional, and rejuvenated stages of volcanism observed in Hawaii have not been recognized for Mars owing to the lack of plate motion.

Direct and precise geochemical observations for Mars are possible by analysis of meteorites recognized as having a martian heritage, from trapped Ar, Xe, and N$_2$ signatures identical to the martian atmosphere, and by their distinct oxygen isotope compositions. These meteorites, which represent near-surface extrusive or hypabyssal intrusive rocks within the martian crust, including shergottites, nakhlites and chassignites, and ancient (4100–4400 Ma) crustal rocks, are the ground truth for remote sensing and make assumptions of similar volcano-magmatic processes challenging. For example, observed pre-shield, shield, post-shield erosional, and rejuvenated stages of volcanism observed in Hawaii have not been recognized for Mars owing to the lack of plate motion.

The geochemical identity of shergottite source reservoirs is well expressed in $^{87}$Sr/$^{86}$Sr–$^{143}$Nd/$^{144}$Nd space, where samples are corrected for ingrowth from $^{87}$Rb and $^{147}$Sm decay since crystallization. Shergottites define long-term Rd and Nd-depleted, intermediate, and enriched groups and, collectively, span compositions a factor of four greater than found in terrestrial ocean island or mid-ocean ridge basalts. The 1270–1420 Ma average of 1340 ± 40 Ma nakhlites and chassignites are isotopically distinct from shergottites, with depleted Sr and Nd isotope compositions. Nakhlites (clinopyroxene-rich mafic rocks) and chassignites (dunites) are petrogenetically a low- to moderate partial melts from the same depleted mantle source. The relationship of nakhlites and chassignites to shergottites is poorly understood. Both deplet shergottites and nakhlites have $^{142}$Nd enrichments consistent with early-formed Sm/Nd-enriched mantle sources. But $^{182}$W and $^{142}$Nd data for nakhlites indicate a more complex origin than for shergottites that cannot be explained by early silicate differentiation alone. Instead, late incompatible-element source enrichment must have occurred between major silicate differentiation at 4504 Ma and crystallization of the nakhlites at ~1340 Ma.

In this study, we present a coherent geochemical dataset for 24 shergottites and 16 nakhlites that highlights fundamental differences in their incompatible trace-element compositions. These trace-element differences can be explained by melting of metasomatized mantle sources, likely the martian lithosphere, for nakhlites and chassignites, and deep mantle plume sources for shergottites. Combined with Sr-Nd isotope variations and geophysical evidence for high effective elastic thickness of the martian lithosphere (≥150 km), these data are consistent with generation of shergottites from mantle plume partial melts and nakhlites and chassignites from lower degree partial melting of hydrated mantle during loading of the martian lithosphere. These modes of formation for martian meteorites are analogous to Hawaiian main shield and rejuvenated volcanism, respectively. Instead of loading of moving oceanic lithosphere above a stationary hotspot, however, Mars manifests dynamic support of thick lithosphere by static mantle plumes, and the generation of large volcanic loads and the largest volcanoes in the Solar System.

Results

**Compositions of shergottites and nakhlites.** We present new data for 24 shergottite meteorites and compare these data with those obtained for 16 nakhlites and chassignites using identical analytical protocols that involved complete dissolution of samples (see Methods). Measurement under identical analytical conditions removes non-systematic error from analysis of individual meteorites in different laboratories. Shergottites range from picobasalt to basaltic compositions, with enriched shergottites having elevated total alkalis (Na$_2$O + K$_2$O) relative to intermediate or depleted shergottites (Fig. 2). Nakhlites and chassignites span a wide range of compositions from low-SiO$_2$ picobasalt to basaltic andesite. Shergottites range from incompatible trace-element-depleted to trace-element-enriched compositions that are distinct from nakhlites and chassignites and are well expressed when comparing incompatible trace-element ratios (Ce/Pb, Nb/Y, La/Yb, Ba/Nb, Zr/Ti, and Zr/Ti) vs. indices of magmatic fractionation (MgO; Fig. 3).

Depleted shergottites have lower absolute abundances of incompatible trace elements and rare earth elements (REEs) than intermediate or enriched shergottites and low CI-chondrite-normalized light REE/heavy REE (La/Yb$_n$ = 0.114 ± 0.044; 1 SD), (Fig. 4). Ratios of La/Yb for intermediate shergottites (La/Yb$_n$ =
Fig. 2 Total alkalis (Na$_2$O + K$_2$O) vs. silica diagram for martian meteorites and data for rocks from the Mars Exploration Rovers. Blue dots are Mars Exploration Rover data (MERs; ref. 13). Chassignite meteorites are star symbols with <41wt % SiO$_2$. Data sources are this study and literature = nakhlites and chassignites (Zr* (Zr/SiO$_2$) = 0.4 ± 0.1; Ta* (Ta/SiO$_2$) = 1.3 ± 0.3) vs. nakhlites and chassignites (Nb* (Nb/SiO$_2$) = 0.5 ± 0.1).

Distinct martian geochemical characteristics. Major-element and trace-element results for shergottites, nakhlites, and chassignites reinforce several previously identified characteristics of these rocks. Shergottite data highlights the incompatible-element-depleted, intermediate and -enriched compositions of samples11. Intermediate shergottites are the most mafic analyzed in this study, with enriched shergottites generally more silica rich. Nakhlite and chassignites have light REE enrichment relative to the heavy REE30. The data also reveal fundamental differences in the REE or HFSE inter-element ratios for the different geochemical types of shergottite, or between nakhlites and chassignites, from either hot or cold deserts.

Discussion

The available samples for study from Mars are meteorites, many of which are found and resided on Earth for significant periods of time (>100 years) prior to collection. The meteorites also have limited total mass making analysis of large (>30 g) well-homogenized aliquots, as is typically done for terrestrial igneous rocks, virtually impossible. Many of the martian meteorites that we studied show evidence for terrestrial alteration effects, including anomalously elevated large ion lithophile element (e.g., Cs, Ba, Sr) and U abundances. For example, the depleted shergottite DaG 476—a hot desert find—has Ba/Nb of ~1500, relative to Antarctic martian meteorite finds with Ba/Nb typically <30. Terrestrial alteration has had no effect on the majority of the REEs or high field strength elements (HFSEs) such as Nb, Ta, Hf, Zr, or Y. This is reflected in well-defined groupings for nakhlites and chassignites, and for incompatible element-enriched, intermediate, and -depleted shergottites for Nb/Y, La/Yb, and Zr/Nb (Fig. 3). For example, we find no systematic differences in the REE or HFSE inter-element ratios for the different geochemical types of shergottite, or between nakhlites and chassignites, from either hot or cold deserts.

The mode effect—where non-representative volumes of rock are chosen, resulting in greater variability in chemical measurements—is a significant issue if not recognized in meteorites owing to the small sample sizes typically studied by investigators (generally <5 g). To examine this effect, we analyzed separate aliquots of material from shergottites NWA 7042, NWA 5298, NWA 7257, NWA 3171, DaG 476, and Tissint, and for nakhlites NWA 998, Nakhl, and MIL 090136. We find that while variations in absolute abundances of elements for separate aliquots can be large, up to 20% in some cases, the relative abundances and inter-element ratio variations are more limited (typically <10%). Occasionally, there are large variations in major-element abundances; for example, 50% variation for K$_2$O in NWA 7042, and extreme heterogeneity between separate aliquots (e.g., NWA 998). Despite these variations, the inter-element ratios of key elements (e.g., Nb, Zr, Ta, Hf, Y) and the REE patterns of samples are unaffected, allowing assessment of the magmatic processes acting in Mars.

A remarkable aspect of shergottite, naklrite, and chassignite compositions is their similarity to geochemical differences observed between Hawaii main shield-stage and rejuvenated-stage volcanic rocks. Hawaiian shield-stage lavas form from the highest degrees of partial melting, above the plume conduit25. Rejuvenated-stage lavas occur after the main stages of volcanism and erupted peripheral to the Hawaiian plume center26–30. These rejuvenated alkalic basaltic lavas are incompatible-element-enriched low-degree partial melts, yet have Sr and Nd isotopic compositions requiring long-term depleted mantle sources relative to the shield source. These characteristics are like those for nakhlites and chassignites (Fig. 4). Such characteristics are difficult to explain by crustal contamination of parental magmas, since martian regolith (represented by NWA 7034/7533 and its pairs) is similar to terrestrial crust in having lower Nb/Y than nakhlites and chassignites. The variations in Nb/Y and Zr/Y for nakhlites are therefore common to the sense of fractionation for Hawaiian rejuvenated lavas and cannot be produced by crustal contamination.

A hallmark of Hawaiian rejuvenated-stage volcanism is that it begins after a volcanically quiescent period, requiring a mechanism to engender further melting. Several models have been proposed28, with the most popular invoking the depleted source as an intrinsic part of the Hawaiian plume that has been pervasively metasomatized by infinitesimally low-degree melts26–30. Maximum extents of rejuvenated melting occur during decompression of the mantle by lithospheric flexure, reaching a maximum ~200 km downstream from the plume30. For Mars, joint analysis of gravity and topography has been used to estimate effective elastic thickness of the lithosphere, typically interpreted
as the depth of the 650 °C isotherm, or the point at which the material is too weak to support geological stresses over >10^8 years. It has been shown that thickness of the martian lithosphere increases with age and decreases with radiogenic power from K, Th, and U decay. In detail, the region with the most massive magmatism—Tharsis—appears to be dynamically supported, suggesting the presence of a mantle plume, and consistent with relatively young (<100 Ma) volcanism in this region. It has also been proposed that subsurface variations in load, including the presence of a depleted mantle composition, might exist underneath nearly all large martian volcanoes.

We interpret shergottites to be analogous to shield-stage or pre-shield-stage and post-shield-stage, whereas nakhlites and chassignites are analogous to rejuvenated-stage igneous rocks. In the absence of plate tectonics, stationary plume-generated melting would be expected to strongly deplete portions of the martian lithosphere and mantle, as has been suggested from gravity and topography. During plume impingement and maturation, eruption of large volumes of basaltic magmas would occur leading to loading of the lithosphere, a flexural bulge and a flexural moat around the volcanic load. Flexural moats are observed around nearly all the Tharsis volcanoes from gravity data and are similar to, although significantly larger than, flexural bulges around Hawaiian-Emperor chain volcanoes. To generate partial melts responsible for nakhlites and chassignites by lithospheric flexure, metasomatism of portions of depleted mantle would be required. Evidence for a water-bearing lithosphere is provided from its rheology, and from addition of fluids into nakhlite and chassignite compositions.

Niobium/Y-Zr/Y systematics of nakhlites and chassignites support a model of partial melting of depleted mantle metasomatized by fluids. The relationships of high Nb/Y of Hawaiian rejuvenated and main shield lavas and nakhlites and chassignites and shergottites must reflect fundamental differences in Nb, Y, and Zr behavior during partial melting. Phases that have affinity for Nb, but less so for Zr or Y, include amphibole, rutile, ilmenite, and mica, of which mica and amphibole have been observed in nakhlite and chassignite melt inclusions. Complete exhaustion of such phases during melting would explain the high Nb/Y of both nakhlite and chassignite compositions.

The similarity between martian meteorites and terrestrial basaltic analogs implies important planetary comparisons.

Fig. 3 MgO vs. Ce/Pb, Nb/Y, La/Yb, Ba/Nb, Zr/Ti, and Zr/Nb for shergottites, nakhlites, and chassignites. Chassignite meteorites are star symbols with >30 wt % MgO. Data are from this study and analytical uncertainties are smaller than symbols.
detail, however, differences in isotopic compositions would suggest that the homogenization of mantle isotopic compositions by convective mixing has not been as effective for Mars as for Earth. The variation in Sr-Nd isotope systematics for martian meteorites, and the ~4500 Ma large-scale differentiation ages from these isotope systems, indicate limited mantle stirring since planetary differentiation. This tectonic difference also explains the limited long-term time-integrated variation between Hawaiian main shield and rejuvenated lavas compared to the large difference in isotopic depletion for nakhlites and chassignites relative to intermediate or enriched shergottites.

Our interpretation of nakhlites and chassignites as forming during loading of the martian lithosphere provides predictive power. Martian rejuvenated volcanism should occur where lithosphere thickened and stabilized and where flexural uplift engendered partial melting. Sources of nakhlites and chassignites should be peripheral to plume volcanism at ~1300 to 1400 Ma and perhaps over longer periods of time for martian igneous rocks not currently sampled in the terrestrial meteorite collection. Additionally, shergottite crystallization ages (165–2400 Ma) generally preclude a direct link between nakhlites and chassignites. Nakhlites and chassignites come from a source that had prior melt depletion, and the previously extracted melts were likely similar to shergottites to explain mirrored elemental abundance patterns. Observations of 2400 to ~160 Ma shergottite magmatism on Mars supports continued and persistent plume magmatism for at least two billion years. This link may be further strengthened by the observation that NWA 6963—a shergottite—has trace-element abundances like nakhlites, suggesting some geochemical affinities between magma types. We interpret the current suite of martian meteorites to represent at least two phases of plume-related magmatism. The distinctive nature of martian meteorites to remotely sensed martian surface samples, in particular the higher alkali contents of some Gusev and Gale crater samples, possibly implies that alkali volcanism on Mars is driven by low-degree partial melting from metasomatization of martian lithosphere in response to mantle plume impingement, offering a mechanism for explaining the apparent differences observed between meteorites and mission data for Mars.

Methods
Sample preparation and analytical methods. New data were obtained for 24 shergottite meteorites, spanning the known range of incompatible element.
depletion and enrichment and showing a range of MgO contents, from 6.4 to 29 wt %. These data are compared with those obtained for 16 nakhlites and chassignites using identical protocols (Supplementary Data 1) and that were previously reported by Udry and Day20. For the desert finds, a Wells low-loss diamond wire saw was used to access material away from the fusion crust surface. For all materials, weathering or fusion crust surfaces were removed by crushing sample fragments with limited force, or by sawing, with sawn surfaces being thoroughly sanded with corundum powder, prior to generating the fine ground sample powders that were prepared using a clean alumina mortar and pestle.

Analytical procedures were undertaken at the Scripps Isotope Geochemistry Laboratory (SIGL). The standard technique used for all samples was digestion of 30 mg of sample powder in Teflon-distilled 27.5 M HF (4 mL) and 15.7 M HNO3 (1 mL) for >72 h on a hotplate at 150 °C, along with total procedural blanks and terrestrial basalt and anesite standards (BHVO-2, BCR-2, BIR-1a, AGV-2). The 50 mg powder aliquot was taken from a larger homogenized sample powder >0.5 g (up to 2 g) in all cases. Acid attack led to complete dissolution of rock samples, generating clear solutions, with no remaining solid material. Samples were sequentially dried and taken up in concentrated HNO3 to destroy rutile or ilmenite. Rutile has high affinity for Nb and, along with ilmenite, amphibole, and mica, have been recognized in terrestrial metasomatized lithosphere (MARID—mica–amphibole–rutile–ilmenite–diopsid67). To date, there is no evidence for such occurrences in the martian mantle, but the presence of amphibole and micas in some martian meteorites suggests that hydrated mineral associations are possible in the martian mantle62. Modeled melting of a depleted mantle with 1% rutile and 1% amphibole will result in rapid and complete exhaustion of exotropic phases, and high resultant Nb/Y for a given Zr/Y value at between 0.1 and 1% partial melting of the martian-depleted mantle or the terrestrial-depleted mantle.


data availability

The data that support the findings of this study are available within the paper and within the Supplementary Data file.

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High field strength elements and barium. The elements Ti, Zr, Y, and Nb are all high field strength elements (charge/radius ratio) that are not usually transported in aqueous fluids or strongly affected by metamorphic processes. These properties, and their systematic variation in melt compositions, are important tracers of source variations in volcanic rocks68. In plots of these elements vs. MgO, there is clear distinction in the shergottite geochemical groups (enriched, intermediate, depleted) for La/Yb, Nb/Y, and Zr/Nb (Fig. 3). While Ba is similarly incompatible to Nb and La, it can be strongly modified by terrestrial alteration, most notably in depleted shergottites (e.g., Da47). The similarity in Ce+/Zr+ would implicate melts with enriched shergottite-like characteristics as being similar to those that were lost from the source of nakhlites and chassignites.

Crystallization ages. Crystallization ages for shergottites were taken from the literature (Supplementary Data 1) and RB-Sr and Sm-Nd isotope crystallization ages were computed to plot the Sr-Nd isotope diagram (Fig. 1). Nakhlites and chassignites have been dated between 1270 and 1420 Ma, with an estimated mean age of 1340 ± 40 Ma on the basis of 40 individual age determinations (see ref. 20, and data in refs. 40,41,45,47,49,78).

Data sources for Figs. 1, 5. Age-correlated Sr and Nd isotope data for shergottites, nakhlites, and chassignites in Fig. 1 were obtained from refs. 13,53,56,40–30 and references therein. Terrestrial ocean island basalt and mid-ocean ridge basalt Sr-Nd isotopic data for Fig. 1 were obtained from refs. 25–39,95,51–99 and references therein. Since these data are from a range of laboratory sources, correction for non-systematic laboratory errors is not possible. Data for Fig. 5 are from refs. 25–39,95,51–99 and from refs. 60 for MORB and ref. 61 for the continental crust composition.

Construction of the melt model. A partial melt model was constructed to evaluate the nature of the sources of rejuvenated lavas and nakhlites and chassignites vs. the sources of Hawaiian main shield-stage lavas and shergottites. Neither depleted (olivine (OI), orthopyroxene (Opx), spinel (Sp), or garnet (Gt)) nor fertile mantle compositions (olivine, orthopyroxene, clinopyroxene (cpx), spinel, or garnet) can produce the trends in Fig. 5, using the partition coefficients summarized in http://earthref.org/KDD/ and in refs. 42–44 (OI/Opx/Opx/Cpx/Spinell/Alm/Amp/Phlog/Rutile/Zircon = [Nb] 0.0005/0.0013/0.00067/0.001/0.8/0.2/0.088/50/0; [Zr] 0.00031/0.013/0.11/0.14/0.6/0.2/17/4/100; [Y] 0.0057/0.07/0.4/3/0.051/0.4/0.018/0.76/0.7). Using a primitive mantle composition65 and a fertile mantle source assemblage (60% OI, 17–20% Opx, 15% Cpx, 5–8% Cr or Sp) with modal melting proportions of phases can reproduce the Hawaiian shield-stage lavas between 3 and 10% partial melting. At low degrees of partial melting (~0.1%), such a source would also lead to a composition like Hawaiian rejuvenated lavas, but it would not be able to reproduce the Sr-Nd isotope compositions that required a long-term depleted mantle source.

Despite the ability of a primitive mantle composition partial melt model to generate melts similar to Hawaiian rejuvenated lavas, such a source is implausible given the unradiogenic Sr and radiogenic Nd isotope signatures of these lavas, and the depleted source compositions required an even more depleted source, evident from the highly unradiogenic Sr and radiogenic Nd compositions of these samples.

For shergottites, we can generate the range of Nb/Y and Zr/Y observed in the depleted, intermediate, and enriched shergottites by exhausting garnet (depleted shergottites) and retaining progressive amounts of garnet in the residue (intermediate and enriched shergottites), consistent with prior studies14. The range found for the enriched shergottites is consistent with the composition of Hawaiian rejuvenated lavas.

Despite the ability of a primitive mantle composition partial melt model
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Author contributions

J.M.D.D. designed the project and wrote the paper. J.M.D.D., K.T.T., A.U., F.M., and Y.L. obtained samples. J.M.D.D., K.T.T., and A.U. performed analyses. J.M.D.D., K.T.T., A.U., F.M., Y.L., and C.R.N. all participated in the interpretation of the data and provided input on the manuscript.

Additional information

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