GEOLOGY

Two billion years of magmatism recorded from a single Mars meteorite ejection site

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The timing and nature of igneous activity recorded at a single Mars ejection site can be determined from the isotope analyses of Martian meteorites. Northwest Africa (NWA) 7635 has an Sm-Nd crystallization age of 2.403 ± 0.140 billion years, and isotope data indicate that it is derived from an incompatible trace element–depleted mantle source similar to that which produced a geochemically distinct group of 327- to 574-million-year-old "depleted" shergottites. Cosmogenic nuclide data demonstrate that NWA 7635 was ejected from Mars 1.1 million years ago (Ma), as were at least 10 other depleted shergottites. The shared ejection age is consistent with a common ejection site for these meteorites. The spatial association of 327- to 2403-Ma depleted shergottites indicates >2 billion years of magmatism from a long-lived and geochemically distinct volcanic center near the ejection site.

INTRODUCTION

Insights into the duration of igneous activity and the nature of magma sources in Mars are made from analyses of shergottite meteorites—mafic to ultramafic igneous rocks from Mars' crust composed mainly of pyroxene, plagioclase (commonly maskelynite), and, in many cases, olivine [for example, McSween and Treiman (*1*)]. Shergottites are also characterized by their trace element concentrations and the radiogenic isotope compositions of their mantle sources [for example, Borg and Draper (*2*)], which are distinct from those that produced the other Martian igneous rocks classified as nakhlites and chassignites (*3*). The shergottites were launched from Mars' crust by large bolide impacts (*4*, *5*); however, the unknown spatial associations of these meteorites before launch and a relatively narrow range of crystallization ages from 150 to 574 million years (My) (*6*–*8*) have limited our understanding of long-term igneous processes.

Geochemical data obtained from Northwest Africa (NWA) 7635, a 195.8-g partly fusion-crusted olivine-plagioclase-phyric rock that was found in Algeria in 2012, both extend the recognized period of shergottite magmatism and provide constraints on the prelaunch spatial association of a suite of geochemically related shergottite specimens. This specimen is porphyritic with phenocrysts (up to 200 μm) of plagioclase completely converted to maskelynite, Fe-rich olivine, augite, and low-Ti magnetite in a finer-grained matrix composed mainly of igneous-zoned, Fe-rich augite (see Fig. 1 and the Supplementary Materials). Accessory pyrrhotite and rare ilmenite are present, but no identifiable phosphate grains have been found. Although NWA 7635 does not contain pigeonite, we consider it to be a petrologic variant of a typical shergottite, in much the same way the petrologic variants of the type specimen Shergotty (*9*, *10*) have been included in the shergottite group. Shock features include the presence of maskelynite and glassy veins that crosscut the igneous texture, but there is no evidence for shock-induced reequilibration of igneous textures and compositional zoning. Furthermore, there is no evidence for terrestrial desert weathering products in the sample aliquot analyzed in this study. Isotope analyses of Sm-Nd, Lu-Hf, and Rb-Sr that constrain the age and mantle source compositions were conducted on a 2.2-g portion from the interior of NWA 7635 (table S1). Cosmogenic nuclide concentrations of ^{10}Be (half-life, 1.36 My) and ^{26}Al (half-life, 0.705 My) were measured to constrain the cosmic-ray exposure age, and ^{14}C (half-life, 5730 years) was measured to constrain the terrestrial age; the sum of exposure and terrestrial ages is the time since the launch from the surface of Mars (ejection age).

RESULTS

A ^{147}Sm-^{143}Nd isochron age of 2403 ± 140 million years ago (Ma) (2σ) was determined from seven mineral and leachate measurements (see Fig. 2, table S2, and the Supplementary Materials for details). This early Amazonian age is about 1.8 billion years older than that of any other recognized shergottite, whose ages fall into the middle-to-late Amazonian epoch in Mars' geologic history. The mantle source isotope compositions for NWA 7635 were calculated from initial Nd, Hf, and Sr isotope compositions of samples F1 and F5-R (table S3). The calculated initial $\varepsilon^{143}Nd_{(CHUR)}$, $\varepsilon^{176}Hf_{(CHUR)}$, and $^{87}Sr/^{86}Sr$ are +29.3 ± 3.1, +39.5 ± 7.8, and 0.699901 ± 0.000025, respectively (all

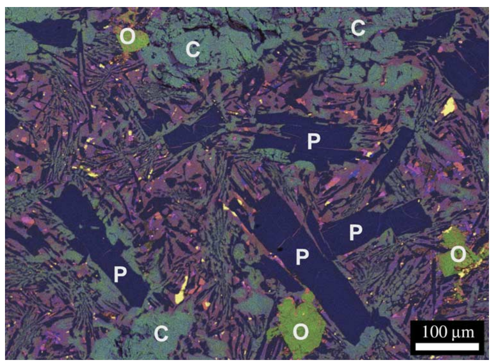

Fig. 1. False-color x-ray compositional map showing the mineralogy and mineral textures of NWA 7635. Mineral labels: O, olivine; P, plagioclase (maskelynite); C, clinopyroxene (augite). Chemical compositions: Fe (purple), Mg (green), Ca (blue), Ti (magenta), and S (yellow). Purple colors in the mesostasis represent Fe-rich augite.

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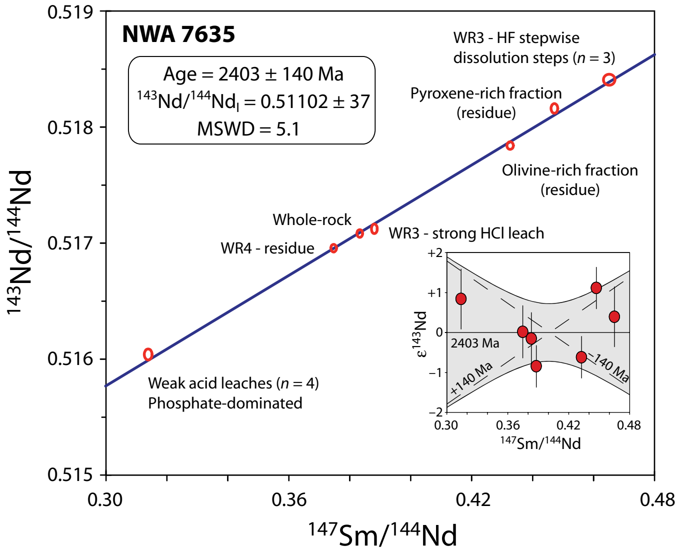

Fig. 2. Seven-point Sm-Nd isochron for NWA 7635 using an Isoplot model 1 solution (*40*). A weighted average of four separate dilute leaches is calculated as one phosphate-dominated leachate measurement, and a re-integration of three hydrogen fluoride (HF)–based sequential dissolution fractions is calculated as one measurement of whole-rock residue (see the Supplementary Materials for details). MSWD, mean square weighted deviation. The inset shows the analytical uncertainty and scatter in epsilon units of individual points that define the isochron.

uncertainties are at the 95% confidence level; see the Supplementary Materials). On the basis of these values, as well as (i) a two-stage mantle evolution model (*2*), (ii) a source formation age of 4504 Ma (*11*), (iii) a chondritic bulk Mars, and (iv) a Mars formation age of 4567 Ma, the $^{147}Sm/^{144}Nd$, $^{176}Lu/^{177}Hf$, and $^{87}Rb/^{86}Sr$ ratios of the hybridized source are $0.3035^{+0.0052}_{-0.0059}$, $0.0629^{+0.0035}_{-0.0040}$, and $0.0217^{+0.0017}_{-0.0019}$, respectively (Fig. 3). These ratios indicate that NWA 7635 is derived from the most incompatible trace element (ITE)–depleted source yet measured for any Martian rock.

DISCUSSION

Source Sm/Nd and Lu/Hf ratios for shergottites (Fig. 3A) [and, for orthopyroxenite Allan Hills 84001 (ALH 84001), see Lapen *et al.* (*12*)] show an array that can be interpreted as a three-component mixing relationship between ITE-depleted deep mantle, ITE-depleted shallow mantle, and ITE-enriched shallow upper mantle end-member compositions calculated by Debaille *et al.* (*13*). The source compositional range for shergottites can be explained by mixing these three distinct end-members that are hypothesized to have formed during differentiation of a Mars magma ocean (*2*, *13*). A plot of source Rb/Sr versus Sm/Nd ratios of shergottites (inset of Fig. 3A) does not show the three-component mixing relationships because the Rb/Sr and Sm/Nd ratios of the two ITE-depleted end-members are nearly identical. The distribution of shergottite data on the mixing diagrams indicates that there are three distinct clusters of shergottites: those that are ITE-enriched, ITE-depleted, and occupy a discrete intermediate position. Shergottites are thus classified into these three distinct isotopic groups designated enriched, depleted, and intermediate, based on these isotope systematics and source compositions (Fig. 3A), as well as trace element abundances (*6*, *14*, *15*). The source compositions of NWA 7635 suggest that it is derived from source mixtures that are similar to those that produced the other known depleted shergottites.

The mantle source connections between other shergottites and NWA 7635 are further evaluated with the short-lived ^{146}Sm-^{142}Nd isotope system, a monitor of mantle source reservoirs in Mars that formed in the first 100 to 200 My after planet formation (*3*). An average of measured $^{142}Nd/^{144}Nd$ ratios from each aliquot measured (see the Supplementary Materials) yields $\varepsilon^{142}Nd = 0.918 \pm 0.077$. When compared to other shergottites on a $\varepsilon^{142}Nd$ versus present-day source $\varepsilon^{143}Nd$ diagram (Fig. 3B), NWA 7635 is indistinguishable in its isotope characteristics from the linear source mixing trend defined by the other shergottite data. The slope of the data array defines an apparent ^{142}Nd-^{143}Nd age of 4504 ± 6 Ma, identical to that reported in the study by Borg *et al.* (*11*). Although the nakhlites and chassignites are evidently derived from mantle sources distinct from those of shergottites (*16*), the isotope data presented here do not indicate that NWA 7635 is derived from mantle sources that are different from those that produced the other depleted shergottites. NWA 7635 is derived from Mars mantle source mixtures that are the most ITE-depleted, yet it shares mantle source characteristics with other shergottites.

The mantle source similarities between NWA 7635 and other depleted shergottites permit the inference that all of them may be derived from the same magmatic center on Mars. Our ejection age of NWA 7635 is identical to that determined for at least 10 other ITE-depleted shergottites (*17*–*19*): the mean of these 11 ejection ages is 1.1 ± 0.2 My (Fig. 4). Cosmogenic nuclide studies indicate three separate ejection events for depleted shergottites overall: one around 1 My [the event accounting for most of the depleted shergottites (*n* = 11)], one around 3 My (an event that launched depleted shergottites NWA 5990, NWA 7032, and QUE 94201), and one distinctly old launch event around 18 My for Dhofar 019 (*17*, *18*, *20*, *21*). The meteorites having a 1.1-My ejection age consist of 11 depleted shergottites, including NWA 7635, but have no intermediate or enriched shergottites. The identical ejection ages and similar mantle source compositions for the group of 11 depleted shergottites strongly suggest that they were all launched from Mars by a single impact.

The igneous crystallization ages of depleted shergottites that have 1-My ejection ages range between 348 Ma and 2.4 billion years ago (Ga) (*6*, *7*, *22*–*27*), which spans close to half of Mars' history. This long span of crystallization ages for these depleted shergottites suggests that there was at least 2 billion years of magmatic activity near the proposed ejection site on Mars. A crater-counting chronology, based on recently acquired high-resolution images, indicates that calderas on major volcanoes from the Elysium and Tharsis regions on Mars have undergone repeated activation and resurfacing (*28*–*30*). Both the Elysium and Tharsis volcanoes evidently formed before 3.6 Ga, followed by episodes of subsequent volcanic eruptions (lava flows). Crater-counting ages of some of those volcanoes indicate activity spanning more than 3 billion years (that is, Alba Mons, Biblis Tholus, Jovis Tholus, Uranius Mons, and Hecates Tholus), suggesting a long history of active volcanism from spatially restricted sites on Mars (*30*, *31*). The long activity of Martian volcanic centers from sample and crater chronologies confirms the very long-lived mantle plume dynamics in Mars (*32*, *33*). Shergottites and ALH 84001 (*12*) share mantle radiogenic isotopic characteristics, implying that they are part of the same overall mantle-melting environment, in contrast to that producing the nakhlites and chassignites (*16*, *34*). Mantle convection that evidently drove this long-lasting Martian magmatism was ineffective in mixing early formed and distinct mantle reservoirs, largely because of a lack of toroidal flow and relatively stable convection cell boundaries in the mantle (*32*).

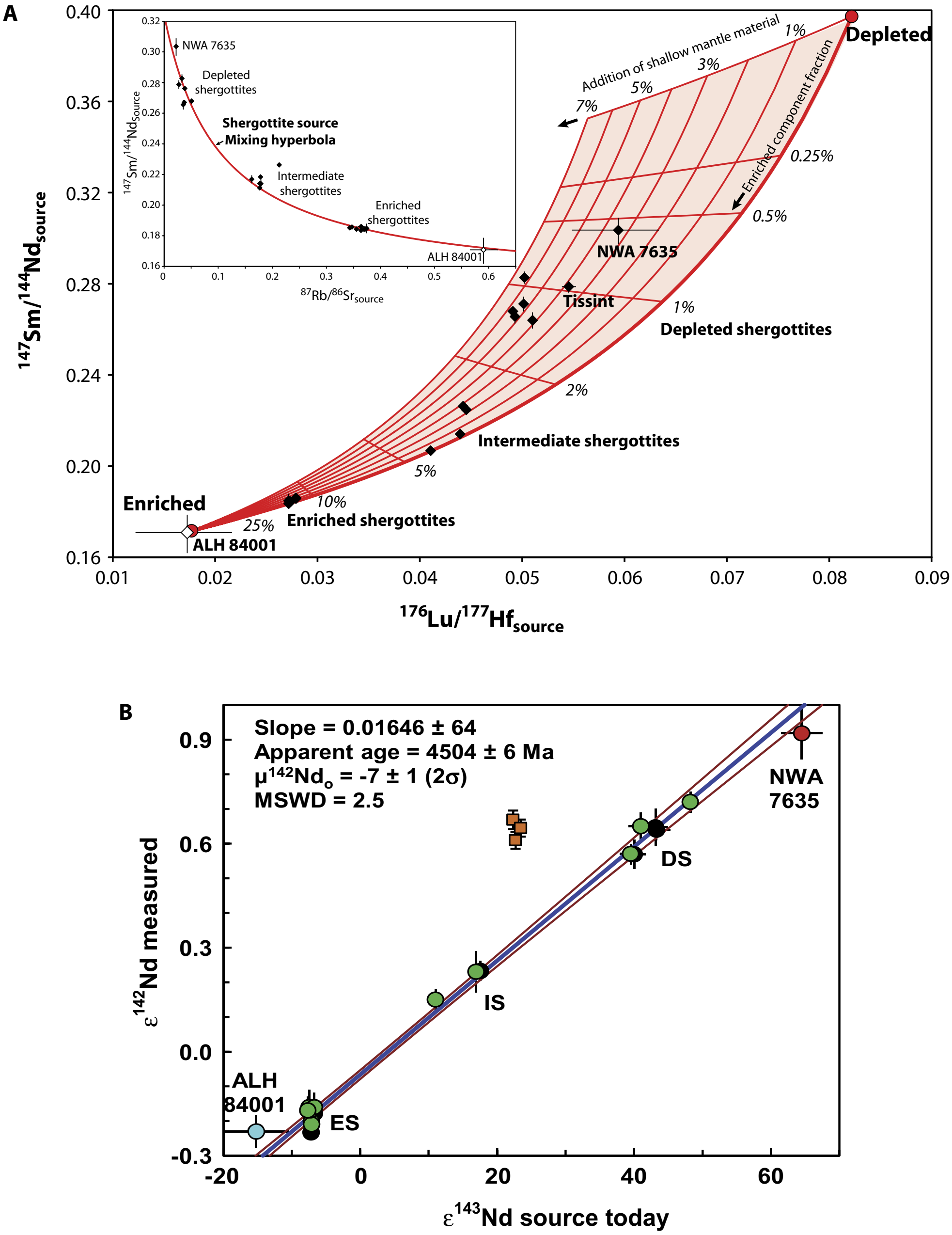

Fig. 3. (**A**) Source mixing array for shergottite Lu-Hf and Sm-Nd source compositions calculated using equations of Nyquist *et al.* (*8*) and mantle end-member compositions of Debaille *et al.* (*13*). Inset shows a best-fit mixing hyperbola for source Rb/Sr and Sm/Nd compositions of shergottites. Mixing depleted deep mantle (high Lu/Hf, high Sm/Nd, and low Rb/Sr) with 0 to 7% depleted shallower mantle material (low Lu/Hf, high Sm/Nd, and low Rb/Sr) and adding 0.5 to 12% enriched mantle material (low Lu/Hf, low Sm/Nd, and high Rb/Sr) can account for the compositions of depleted, intermediate, and enriched shergottites. NWA 7635 extends the observed range in depleted source compositions for all three isotopic systems. The source composition of ALH 84001 is not used in the regression or modeling but falls within error of the enriched end-member composition in Lu/Hf-Sm/Nd source space and on the mixing hyperbola for Rb/Sr-Sm/Nd source mixtures. Data sources are listed in table S3; ALH 84001 data are obtained from Lapen *et al.* (*12*) and Beard *et al.* (*36*). (**B**) Best-fit shergottite mixing line for long- and short-lived Sm-Nd isotope systems with 2σ error envelope. All data, except ALH 84001 and nakhlites (orange), are used in the regression. Average terrestrial standards define zero value for μ^{142}Nd ($\mu = 100 \times \varepsilon$). DS, depleted shergottites; IS, intermediate shergottites; ES, enriched shergottites. Data sources: black (*3*), green (*11*), orange (*16*), and blue (*12*).

MATERIALS AND METHODS

A total of 2.2 g of interior material was used for isotope analyses. Petrographic analyses and major and trace element concentration measurements of constituent phases were made from a representative polished thick section of the type material. Before disaggregation for mineral picking, the rock fragments were washed in an ultrasonic bath with ultrapure H_2O for 5 min to remove any surficial contamination. The fractions analyzed for Lu-Hf, Sm-Nd, and Rb-Sr isotopes were spiked with ^{176}Lu-^{178}Hf, ^{149}Sm-^{150}Nd, and ^{87}Rb-^{84}Sr isotope tracers before column chemistry following procedures outlined in the studies

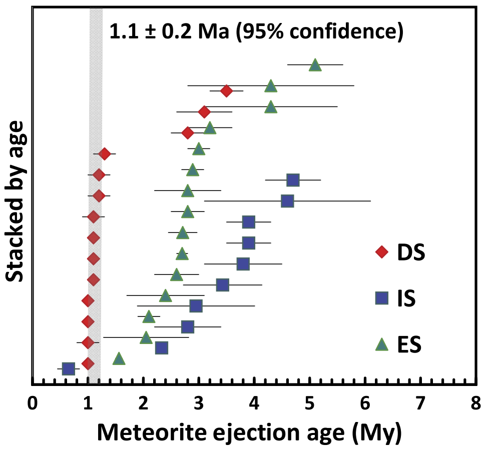

Fig. 4. Summary of Mars ejection ages for depleted, intermediate, and enriched shergottites. Data (with modified classification terminology) from Fig. 14 of Herzog and Caffee (*41*), with the addition of data from Wieler *et al.* (*17*) and this work. The group of 11 depleted shergottites with 1-My ejection ages (including NWA 7635) defines an average age of 1.1 ± 0.2 My (95% confidence) shown as the vertical gray box. These data show that only depleted shergottites were ejected at 1.1 Ma.

by Lapen *et al.* (*35*) and Beard *et al.* (*36*). Analyses of $^{147}Sm/^{144}Nd$, $^{142}Nd/^{144}Nd$, $^{143}Nd/^{144}Nd$, $^{176}Lu/^{177}Hf$, and $^{176}Hf/^{177}Hf$ isotope ratios were performed on a Nu Instruments Nu Plasma II multicollector inductively coupled plasma mass spectrometer (ICP-MS) at the University of Houston, following spike subtraction and instrumental mass fractionation corrections of Lapen *et al.* (*35*). The $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ isotope ratios were analyzed using a Micromass Sector 54 thermal ionization mass spectrometer at the University of Wisconsin–Madison, following spike subtraction and instrumental mass fractionation corrections described by Beard *et al.* (*36*).

Cosmogenic nuclide concentrations of ^{10}Be and ^{26}Al were measured by accelerator mass spectrometry at Purdue University (*37*), and concentration of ^{14}C was measured at the University of Arizona (*38*). The measured activities were 9.7- ± 0.1-dpm ^{10}Be/kg, 70- ± 5-dpm ^{26}Al/kg, and 46- ± 1-dpm ^{14}C/kg. The cosmic-ray exposure age of 1.0 ± 0.1 My was based on ^{10}Be and ^{26}Al concentrations, the chemical composition of the measured sample, and model production rates (*39*). This age agreed with the noble gas exposure age of 1.4 (±0.4) My (*17*). The terrestrial age was 2.3 ± 1.3 ky based on ^{14}C concentration, assuming a saturated activity of 61 dpm/kg for shergottites. The Mars ejection age for NWA 7635 was 1.0 ± 0.1 My. Full details of the analytical procedures are reported in the Supplementary Materials.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/2/e1600922/DC1
Materials and Methods
fig. S1. Images of the outer and inner portions of NWA 7635.
fig. S2. Plots of chondrite-normalized trace element compositions of shergottites and NWA 7635.
fig. S3. Measured $\mu^{142}Nd$ values for fractions of NWA 7635, Himalayan garnet schist 1, and Himalayan garnet schist 2 versus ^{142}Ce interference on ^{142}Nd, ^{144}Sm interference on ^{144}Nd, and the spike-to-sample ratio.
table S1. List of samples and data sources for source composition calculations.
table S2. ^{147}Sm-^{143}Nd isotopic analyses of NWA 7635.
table S3. Descriptions and weights of NWA 7635 samples analyzed for radiogenic and cosmogenic isotopes.
table S4. Laser ablation ICP-MS compositions of primary mineral phases in NWA 7635.
table S5. ^{146}Sm-^{142}Nd isotopic analyses of NWA 7635.
table S6. Lu-Hf isotopic analyses of NWA 7635.
table S7. Rb-Sr isotopic analyses of NWA 7635 maskelynite.
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