



The internal structure and geodynamics of Mars inferred from a 4.2-Gyr zircon record

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Combining U–Pb ages with Lu–Hf data in zircon provides insights into the magmatic history of rocky planets. The Northwest Africa (NWA) 7034/7533 meteorites are samples of the southern highlands of Mars containing zircon with ages as old as 4476.3 ± 0.9 Ma, interpreted to reflect reworking of the primordial Martian crust by impacts. We extracted a statistically significant zircon population (n = 57) from NWA 7533 that defines a temporal record spanning 4.2 Gyr. Ancient zircons record ages from 4485.5 ± 2.2 Ma to 4331.0 ± 1.4 Ma, defining a bimodal distribution with groupings at 4474 ± 10 Ma and 4442 ± 17 Ma. We interpret these to represent intense bombardment episodes at the planet's surface, possibly triggered by the early migration of gas giant planets. The unradiogenic initial Hf-isotope composition of these zircons establishes that Mars's igneous activity prior to ~4.3 Ga was limited to impact-related reworking of a chemically enriched, primordial crust. A group of younger detrital zircons record ages from 1548.0 ± 8.8 Ma to 299.5 ± 0.6 Ma. The only plausible sources for these grains are the temporally associated Elysium and Tharsis volcanic provinces that are the expressions of deep-seated mantle plumes. The chondritic-like Hf-isotope compositions of these zircons require the existence of a primitive and convecting mantle reservoir, indicating that Mars has been in a stagnant-lid tectonic regime for most of its history. Our results imply that zircon is ubiquitous on the Martian surface, providing a faithful record of the planet's magmatic history.

Mars | meteorites | zircon | geodynamics

Given the basaltic compositions of the majority of rocky planets in the Solar System, zircon is not predicted to be a common component of these worlds (1). However, it is abundant in the polymict breccia meteorites (Northwest Africa [NWA] 7034/7533 and their pairs) that are samples of the Martian surface regolith and believed to originate from the southern highlands of Mars (2–7). These meteorites contain ancient crustal components that date back to the earliest history of the planet, including lithic fragments interpreted to be of igneous, sedimentary, and impact origin all preserved in a fine-grained matrix. Recent high-precision U–Pb ages of zircons from NWA 7034 define dates ranging from 4476.3 ± 0.9 Ma to 4429.7 ± 1.0 Ma (4), representing the oldest directly dated material from Mars. These meteorites are thus key samples that provide insights into the geologic history of Mars. We conducted a systematic search for zircon crystals in the NWA 7533 meteorite to extract a statistically significant number of grains for high-resolution isotopic and geochemical investigation. The inferred young <225-Ma lithification age (8) of the paired NWA 7034 meteorite implies that these breccias may contain a record that spans most of the planet's history. Our objective is to provide a comprehensive geochronological archive that allows for a more complete understanding of the differentiation history of Mars, including the

extraction timescales and reworking mechanism(s) of its primordial crust. In combination with the initial Hf isotope compositions of individual zircons, this record can be used to constrain the age, location, and time evolution of the major planetary geochemical reservoirs. This approach can ultimately provide insights into the elusive internal structure of Mars, including its geodynamic regime.

The U–Pb Geochronology of Ancient Martian Zircons

Fifty-three grains (51 zircons and 2 baddeleyites) large enough for high-resolution geochronology were recovered from a crushed 15-gram aliquot of NWA 7533. To complement the ages of zircons recovered from the bulk rock aliquot, we extracted 21 zircons from a 10-mg aliquot of an isolated crustal lithic clast of basaltic composition (clast C27; *SI Appendix, Supplementary Text*). Zircon crystals range in size from 30 μm to 80 μm, including rounded, anhedral, and subhedral to euhedral grains (*SI Appendix, Fig. S1*). These crystals represent the largest archive of material suitable for high-resolution geochronology currently available for Mars.

Forty-one grains (39 zircons and 2 baddeleyites) defining mostly concordant U–Pb ages within uncertainty (less than 5%

Significance

We discovered a zircon record in a Martian meteorite that spans 4.2 Gyr, nearly the entire geologic history of Mars. Ancient zircons define a bimodal distribution with groupings at 4474 ± 10 Ma and 4442 ± 17 Ma, reflecting intense bombardment episodes triggered by the migration of the gas giant planets. A group of younger detrital zircons record ages from 1548.0 ± 8.8 Ma to 299.5 ± 0.6 Ma. The only plausible sources for these grains are the Elysium and Tharsis volcanic provinces that are the expressions of deep-seated mantle plumes. The chondritic-like Hf-isotope compositions of these zircons require the existence of a primitive and convecting mantle reservoir. Thus, these grains provide a tangible record of the deep Martian interior.

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discordant) record $^{207}\text{Pb}/^{206}\text{Pb}$ dates ranging from 4485.5 ± 2.2 to 4331.0 ± 1.4 Ma (Fig. 1A). The rare earth element patterns of a subset of seven of these zircons with $^{207}\text{Pb}/^{206}\text{Pb}$ ages from 4476.6 ± 1.0 to 4438.2 ± 0.8 Ma are consistent with an igneous origin (SI Appendix, Fig. S2). The $^{207}\text{Pb}/^{206}\text{Pb}$ age distribution of the grains (Fig. 1C) defines two statistically distinct populations with mean ages of 4474 ± 10 Ma and 4442 ± 17 Ma. These data indicate that the bulk of the igneous activity associated with reworking of the primordial crust occurred in two punctuated episodes, followed by a rapid decline in magmatic activity after 4331.0 ± 1.4 Ma. Four zircons extracted from the basaltic clast C27 returned overlapping $^{207}\text{Pb}/^{206}\text{Pb}$ dates (Fig. 1B), consistent with an igneous origin for these grains. In particular, one zircon (C27-NS2b3) from C27 with nearly concordant U–Pb systematics defines a $^{207}\text{Pb}/^{206}\text{Pb}$ date of 4443.6 ± 1.2 Ma, which we interpret as the best estimate of the minimum crystallization age of this

basaltic clast. Thus, C27 is the oldest Martian basalt reported so far and falls within the age range of the 4442 ± 17 Ma zircon population.

It has been proposed that the zircon ages from 4476.3 ± 0.9 Ma to 4429.7 ± 1.0 Ma reported by Bouvier et al. (4) reflect the secular cooling of the secondary crust following a cataclysmic giant impact event, perhaps related to the formation of the Martian crustal dichotomy (9). However, the punctuated nature of the zircon age distribution does not support this proposal but instead indicates that the main reworking of the primordial crust occurred in distinct pulses over a period of ~ 150 Myr. This age distribution is consistent with reworking of the primordial crust by impacts, which implies two main episodes of bombardment at ~ 4475 Ma and ~ 4440 Ma followed by a rapid decline in impact activity. We note that the abundance of highly siderophile elements and the osmium isotope composition of NWA 7034/7533

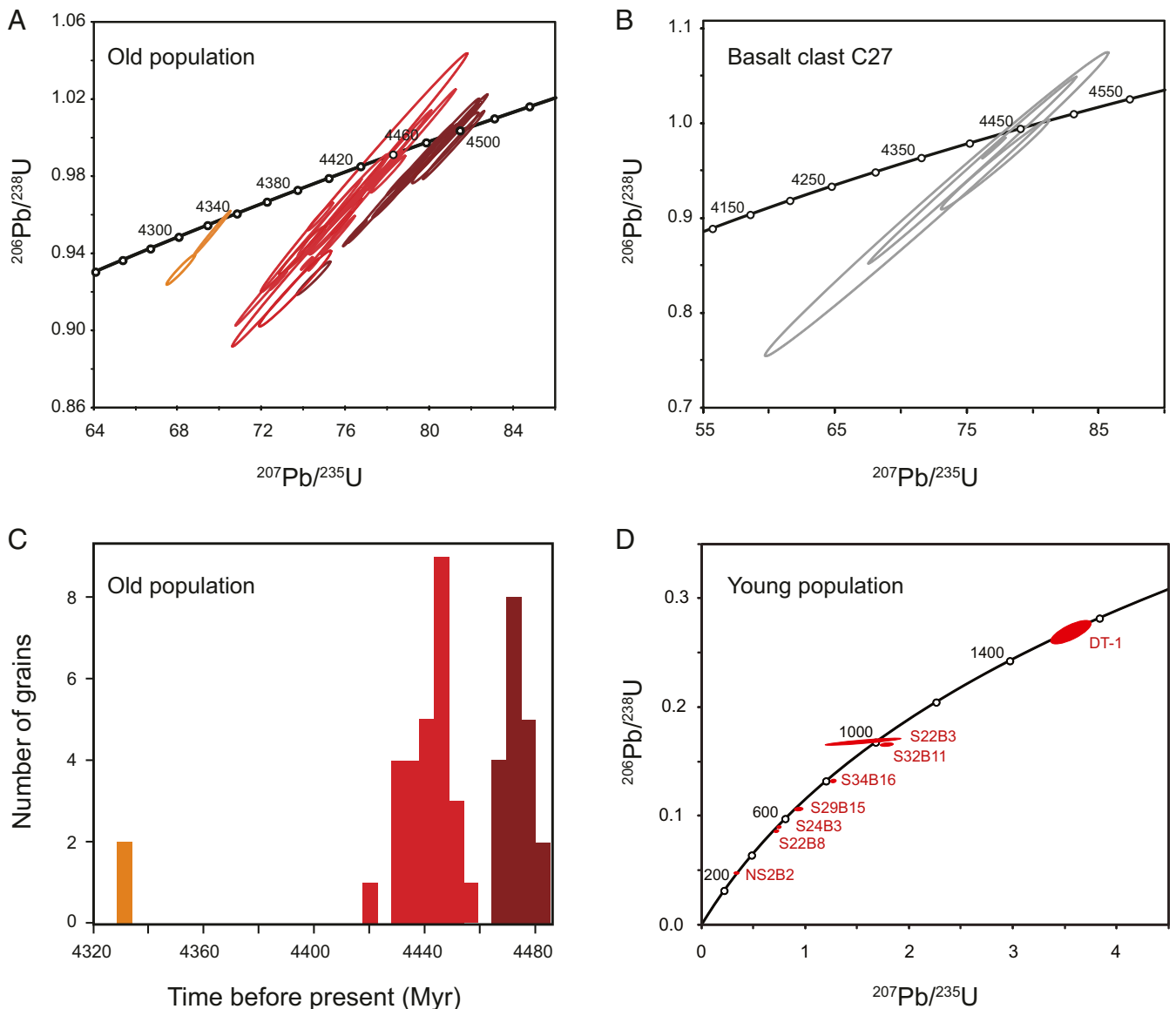


Fig. 1. (A) A U–Pb concordia diagram for 41 zircon and baddeleyite grains from the NWA 7533 meteorite. All depicted grains have U–Pb ages that are less than 5% discordant. (B) A U–Pb concordia diagram for four zircons extracted from clast C27. Labels on concordia curves represent time B.P. in millions of years. (C) Plot of the $^{207}\text{Pb}/^{206}\text{Pb}$ ages of the zircon and baddeleyite depicted in A in a histogram with bin sizes of 5 Myr together with NWA7034 zircons (4). (D) A U–Pb concordia diagram for the eight zircons belonging to the young detrital grain population (Table 1). Data-point error ellipses are 2σ in all concordia diagrams. U–Pb isotope data are reported in full in Dataset S1 and SI Appendix, Table S3. Note that the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the zircons described here (Dataset S1) are within a similar range of values to that reported in earlier studies (2, 16).

are consistent with early bombardment episodes (10). The oldest preserved Martian zircon (S34b5) with nearly concordant U–Pb systematics records a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 4485.5 ± 2.2 Ma. The lack of older zircons may indicate that the southern hemisphere of Mars did not endure significant bombardment episodes prior to this time, assuming that the zircon record is representative of global planetary processes.

Migration of the gas giant planets is thought to have initiated a short-lived influx of water-rich outer Solar System bodies to the inner Solar System, which resulted in the intense bombardment of the rocky planets ~ 700 Myr after Solar System formation (11). Revised timescales of giant planet migrations suggest that this event occurred much earlier, namely in the first 100 Myr of the history of the Solar System (12). The 32 ± 20 Myr time window of impact-related igneous activity recorded by the bimodal distribution of Martian zircon ages is similar to the short-lived ~ 30 -Myr influx of outer Solar System bodies predicted to occur as a consequence of the giant planet migration (11, 13). As such, our chronology of igneous activity on early Mars that we relate to impact activity aligns with the revised timescale and consequence of giant planet migration.

Formation Timescale and Reworking of the Primordial Martian Crust

Twenty-one zircons defining $^{207}\text{Pb}/^{206}\text{Pb}$ ages ranging from 4485.5 ± 2.2 Ma to 4331.0 ± 1.4 Ma were large enough for concomitant U–Pb and $^{176}\text{Lu}/^{177}\text{Hf}$ analyses (*SI Appendix, Table S1*). We show in Fig. 2A that the zircons predominantly record unradiogenic initial ϵ_{Hf} values (the ϵ_{Hf} value is the deviation of the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of a sample from the Chondritic Uniform Reservoir [CHUR] in parts per 10⁴) ranging from -0.6 ± 0.7 to -3.9 ± 0.5 , which indicates derivation from an enriched crust. Hf isotope data were also acquired for the zircon defining a $^{207}\text{Pb}/^{206}\text{Pb}$ date of 4443.7 ± 1.2 Ma that was extracted from the C27 basaltic clast (NS2b3), which provides petrological context. The grain records an initial ϵ_{Hf} value of -2.0 ± 0.4 , consistent with the clast being the product of remelting of an older, crustal reservoir. Our more comprehensive Hf dataset is consistent with an earlier report (4), but the identification of more enriched initial Hf isotope signatures for the same time periods requires an earlier crust extraction event and/or a source reservoir with a lower $^{176}\text{Lu}/^{177}\text{Hf}$ ratio. Moreover, the greater range of initial Hf isotope compositions for a given age may indicate a protracted episode of crust extraction and/or heterogeneity in the $^{176}\text{Lu}/^{177}\text{Hf}$ value of the primordial crust.

The four zircons with the most enriched initial Hf isotope compositions, which have $^{207}\text{Pb}/^{206}\text{Pb}$ ages ranging from 4401.3 ± 0.7 Ma to 4474.0 ± 1.0 Ma, require a source reservoir with a $^{176}\text{Lu}/^{177}\text{Hf}$ value of 0.008, assuming an extraction age of 4560 Ma (*SI Appendix, Fig. S3*). On Earth, such low $^{176}\text{Lu}/^{177}\text{Hf}$ values are typically associated with evolved felsic lithologies (14), rock types not predicted to be generated during the extraction of the primordial Martian crust (15). Moreover, the basaltic composition of clast C27 containing ~ 4440 -Ma igneous zircons cannot be produced by reworking of a more evolved protolith and, instead, implies a mafic composition for the source reservoir. A possibility is that the $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of the primordial crust is primarily controlled by fractional crystallization of zircon and/or baddeleyite such that the $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of the source bears no compositional information. This is supported by the observation that basaltic magmas produced by melting of the primordial crust such as clast C27 may ultimately have crystallized zircons. This is in line with the large variability in the $^{176}\text{Lu}/^{177}\text{Hf}$ ratios observed for individual basaltic clasts from NWA 7034/7533, which range from 0.011 to 0.050 [(2) and clast C27; *SI Appendix, Table S2*]. We show in Fig. 2A that the zircon data are consistent with the reworking of a single crustal reservoir extracted by 4547 Ma and characterized by domains with variable $^{176}\text{Lu}/^{177}\text{Hf}$ ratios ranging from 0.004 to 0.014. These data reemphasize the early

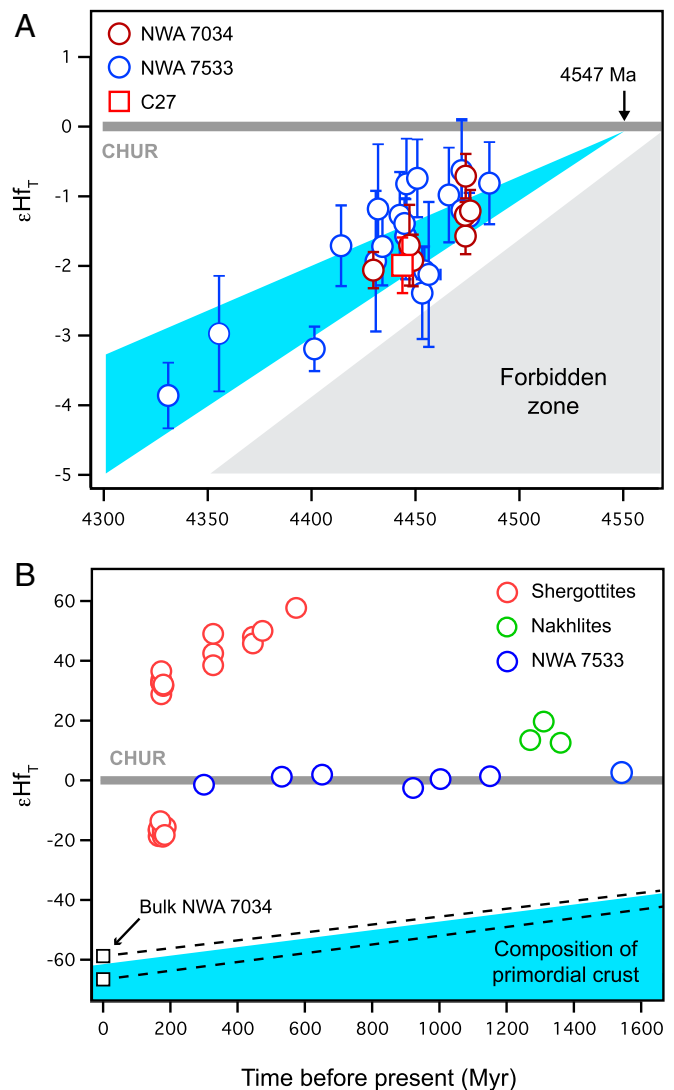


Fig. 2. Hf isotope evolution diagrams. (A) The initial ϵ_{Hf} values for ancient individual zircons extracted from the bulk rock NWA 7533 as well as one zircon extracted from the C27 basaltic clast together with previously published data from NWA 7034 (4). The blue zone represents the time evolution of a crustal reservoir extracted at 4547 Ma and characterized by $^{176}\text{Lu}/^{177}\text{Hf}$ values ranging from 0.004 to 0.014. The upper boundary of the forbidden region represents a reservoir with a $^{176}\text{Lu}/^{177}\text{Hf} = 0$ and a formation age defined by the age of the Solar System at 4567.3 ± 0.16 Ma (38). Uncertainty on the ϵ_{Hf} values reflects the internal precision (2σ) of the individual measurements. Uncertainty on the $^{207}\text{Pb}/^{206}\text{Pb}$ ages (2σ) is smaller than symbols. (B) The initial ϵ_{Hf} values for the young zircon population (Table 1) plotted together with Martian meteorites of comparable ages (21–24) as well as two bulk aliquots of NWA 7034 (39) and their back-projected time evolution as stippled lines.

solidification history of the planet and support thermal models predicting magma ocean crystallization within 10 Myr of Solar System formation (15). If zircons in the NWA 7533 breccia provide a representative record of the early magmatic activity of the planet, our comprehensive Hf isotope dataset suggests that the bulk of the igneous activity on Mars prior to ~ 4.3 Ga was associated with reworking of the primordial crust within a 150-Myr window. As important, this record does not provide evidence for the generation of any mantle-derived, juvenile crust in the first 250 Myr of the planet’s history after magma ocean solidification and extraction of the primordial crust.

Identification of a Long-Lived Primitive Reservoir in the Deep Martian Interior

Eight zircons extracted from the bulk rock aliquot record U–Pb crystallization ages from 1548.0 ± 8.8 Ma to 299.5 ± 0.6 Ma (Fig. 1D and Table 1), significantly younger than the main population depicted in Fig. 1A. These grains are characterized by rounded shapes (SI Appendix, Fig. S4) indicative of various degrees of abrasion analogous to detrital zircons in terrestrial systems, implying that they experienced significant transport prior to their incorporation in the meteorite breccia. Collectively, these observations suggest that the young grains are unrelated to the ancient zircon population.

Young, U-rich, metamict zircons (or zircon domains) have been reported in the NWA 7034/7533 meteorites, defining typically discordant U–Pb ages clustering around ~ 1.5 Ga (3, 5, 16). This brief epoch is interpreted to reflect a transient thermal event experienced by the protolith material to the meteorite breccia such that the ages recorded by these metamict zircons reflect variable resetting of the U–Pb systematics of the ancient zircon population. Metamict zircons similar to those described in earlier studies were identified here (SI Appendix, Fig. S5), but these were not analyzed. The young zircons we describe have younger and highly variable ages as well as, on average, lower U content (SI Appendix, Fig. S6) relative to previously described metamict grains (3, 5, 16), resulting in limited radiation damage and a higher degree of concordance (Fig. 1D). Critically, the Laue diffraction patterns obtained for one of our young zircons (DT-1) indicate a crystalline structure (SI Appendix, Fig. S7), establishing that the grain is not metamict. The remaining young zircons, which have not been characterized by Laue diffraction, have Th/U ratios that are typical of igneous zircons (SI Appendix, Fig. S8), similar to DT-1. Moreover, based on noble gas systematics (8), the age span defined by most of our young zircons falls within a period when the host meteorite breccia did not experience significant thermal events. Thus, we conclude that the young, detrital zircon population identified here is unrelated to the metamict zircon population described in earlier work and that their ages reflect the primary magmatic crystallization of the zircon (SI Appendix, Supplementary Text).

The preponderance of U–Pb ages clustering at ~ 1.5 Ga for apatites distributed throughout the breccia has been used to suggest that this age represents a transient and pervasive thermal pulse corresponding to the solidification of the breccia (3). This interpretation, however, cannot be reconciled with the U–Pb crystallization ages of the young zircons reported here that span from 1548.0 ± 8.8 Ma to 299.5 ± 0.6 Ma. Thus, although the ~ 1.5 -Ga event may reflect a thermal pulse that affected a

significant fraction of the material protolith to the breccia, final assembly must have occurred after 299.5 ± 0.6 Ma. We note that a young solidification age based on noble gas systematics of less than 225 Ma has been proposed for the NWA 7034 meteorite (8), in agreement with our results and interpretation.

Although the ages we report for the young zircons are similar to some shergottite meteorites (17–19), it is unlikely that these rocks were the source of the young zircon population given that igneous zircons have not been reported in shergottites (20). Moreover, six zircons record ages (1548.0 ± 8.8 Ma and from 1003.0 ± 13.6 Ma to 650.9 ± 1.5 Ma) that are not temporally associated with known Martian meteorites (17–19). We show in Fig. 2B the initial Hf isotope composition of seven zircons with ages ranging from 1548.0 ± 9.0 Ma to 299.5 ± 0.6 Ma. In contrast to known meteorites with comparable ages that are characterized by highly enriched or depleted initial Hf isotope compositions (21–24), the young zircon population displays a narrow range of initial ϵ_{Hf} values varying from -2.53 ± 1.04 to $+2.27 \pm 1.50$, corresponding to a weighted mean of 0.30 ± 0.65 . It is possible that the chondritic-like initial ϵ_{Hf} signal observed in these zircons reflects fortuitous mixing of ancient mantle and/or crustal Martian reservoirs. However, the Lu/Hf ratios of reservoirs formed in the planet's first billion years of evolution such as the primordial crust and the mantle sources of shergottites as well as that of the ALH84001 meteorite will result in source reservoirs with highly radiogenic or unradiogenic Hf isotope compositions at the time of formation of the young zircons (SI Appendix, Fig. S9A). Similarly, the mantle sources of ~ 1.4 -Ga nakhlites and the ~ 2.4 -Ga shergottite NWA 7635 have superchondritic Lu/Hf ratios resulting in highly radiogenic compositions by ~ 1.5 Ga (SI Appendix, Fig. S9B). As nakhlites have near-chondritic Lu/Hf ratios, remelting of a nakhlite-like crust may result in a reservoir that evolves parallel to CHUR but with compositions typically more radiogenic than that observed for the young zircons (i.e., $>+10$ epsilon units at ~ 300 Ma). However, nakhlites are depleted in Zr (25) such that zircon crystallization from the remelting of this rock type is considered unlikely (1). Furthermore, it would still require mixing of a remolten nakhlite-like crust with an enriched endmember such as the primordial crust or, alternatively, the mantle source of enriched shergottites in variable proportions with time to result in a chondritic-like initial ϵ_{Hf} signal over ~ 1.3 Gyr. Although fortuitous mixing of inferred mantle and crustal reservoirs based on existing knowledge of Martian meteorites can admittedly not be completely ruled out, we consider this possibility exceedingly unlikely. Rather, the persistence of a chondritic-like Hf isotope signal recorded by zircons over ~ 1.3 Gyr suggests the presence a source reservoir on

Table 1. U–Pb age data and ^{176}Lu – ^{176}Hf systematics of the NWA 7533 young zircon population

Sample	Age (Ma)*	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$	$^{178}\text{Hf}/^{177}\text{Hf}$	$^{180}\text{Hf}/^{177}\text{Hf}$	ϵ_{Hf_T}
NS2B2	299.5 ± 0.6	0.000556	0.282560 ± 13	1.46718 ± 2	1.88666 ± 2	-1.41 ± 0.46
S22B8	531.1 ± 0.6	0.001681	0.282502 ± 15	1.46726 ± 6	1.88715 ± 32	1.24 ± 0.53
S29B15	650.9 ± 1.5	0.001510	0.282447 ± 25	1.46736 ± 7	1.88661 ± 37	1.93 ± 0.89
S34B16	921.5 ± 21.5	0.000670	0.282142 ± 12	1.46715 ± 3	1.88669 ± 9	-2.53 ± 1.04
S22B3	1003.0 ± 13.6	0.000990	0.282181 ± 24	1.46721 ± 4	1.88669 ± 12	0.44 ± 1.04
S32B11	1153.0 ± 43.6	0.000505	0.282111 ± 15	1.46715 ± 7	1.88668 ± 15	1.64 ± 2.13
DT-1	1548.0 ± 8.8	0.001173	0.281898 ± 38	1.46711 ± 12	1.88663 ± 21	2.27 ± 1.50
S24B3	533.3 ± 1.3	—	—	—	—	—

*We report the $^{238}\text{U}/^{206}\text{Pb}$ ages for grains younger than 800 Ma and the $^{207}\text{Pb}/^{206}\text{Pb}$ ages for grains older than 800 Ma (note that the $^{238}\text{U}/^{206}\text{Pb}$ age was used for grain S22B3 given the large uncertainty of the $^{207}\text{Pb}/^{206}\text{Pb}$ age). Using this approach, the weighted mean of the ϵ_{Hf_T} corresponds to 0.30 ± 0.65 . Using only the $^{207}\text{Pb}/^{206}\text{Pb}$ ages to calculate the initial Hf isotope composition returns a weighted mean of 1.14 ± 1.12 for the ϵ_{Hf_T} values, which overlaps with our preferred approach. Age uncertainties are 2σ . Uncertainties on the Hf isotope ratios reflect the 2SE internal precision in last decimal places. U–Pb data are reported in full in Dataset S1 and SI Appendix, Table S3. —, no data available.

Mars that has not experienced significant Lu/Hf fractionation relative to CHUR. The Hf isotope compositions recorded by the young zircon population confirm that their U–Pb ages reflect primary magmatic ages as opposed to resetting ages of a ~ 4.45 -Ga zircon population, which would result in highly unradiogenic ϵHf_T values ranging from approximately -60 to -100 ϵ -units at the time of isotopic resetting (*SI Appendix, Fig. S10*). We infer that the persistence of a CHUR-like Hf-isotope signal for a significant part of the recent history of Mars must reflect the existence of a yet unrecognized primitive mantle reservoir not sampled by existing Martian meteorites.

The similarity in the initial Hf isotope compositions of the young zircon population, corresponding to a weighted mean of 0.30 ± 0.65 , suggests a common mantle source for these grains that has been sampled by pervasive, deep-seated magmatic activity from 1548.0 ± 8.8 Ma to 299.5 ± 0.6 Ma. This time interval also provides constraints on the plausible volcanic sources that produced these zircons. Our current understanding of the ages of the volcanic surfaces of Mars suggests that magmatic activity in the southern highlands, the inferred source region of the NWA 7034/7533 meteorites, is believed to have ceased by 1 Ga at the latest (26). In contrast, the bulk of the volcanic activity on Mars in the time period defined by the young zircons is restricted to the Tharsis and Elysium provinces. Thus, the only plausible volcanic sources for the young zircon population are the Tharsis and Elysium provinces, requiring significant dispersal of the zircon grains, consistent with their typically rounded and abraded nature. We note that the dispersion of dust particles of comparable size to that of the zircons (<100 μm) is thought to have been efficient in the post-Noachian epoch, primarily driven by aeolian processes (27). Importantly, the Tharsis region appears to be dynamically supported (28), which suggests the presence of a mantle plume (29), consistent with the long-lived magmatic history and relatively young volcanism in this region (26). Therefore, the primitive initial Hf isotope composition of the young zircon population most likely reflects that of the deep Martian mantle. The minor variability in the initial Hf isotope compositions defined by the young zircons could reflect small-scale residual heterogeneity of the deep mantle or, more likely, contamination of the primitive composition by minor assimilation of the highly anomalous lithospheric mantle and crustal reservoirs during magma ascent before eruption.

Our results and interpretation suggest that plume-related volcanic activity on Mars resulted in the production and subsequent large-scale dispersal of zircon minerals on the planet's surface. Theoretical considerations indicate that highly explosive mafic volcanism prevailed on Mars for most of its geologic history (30), including in the Tharsis region (31), causing the global dispersal of fine-grained volcanic ashes. To assess the formation of zircon as a product of plume-related volcanism on Mars, we modeled the chemical evolution of a melt generated by partial melting of a primitive mantle composition at a depth corresponding to the base of the Martian lithospheric mantle (*SI Appendix, Supplementary Text*). Our results show that zircon saturation will occur after intensive fractional crystallization (*SI Appendix, Fig. S11*) when about 3% of the original melt is left. This melt will likely exist as small interstitial pockets in mafic rocks. Thus, zircon formation is compatible with the chemical evolution of melts derived from the primitive mantle that experienced a protracted cooling history. Episodic explosive volcanism such as that inferred for the Tharsis region provides a mechanism for efficient dispersal of zircon on the Martian surface. Alternatively, aeolian erosion of subvolcanic complexes is also a plausible means of excavating zircons and subsequently distributing them over the Martian surface.

Implication for Planetary Evolution and the Geodynamics of Mars

Based on remote observation and modeling (26), it is argued that Mars is a single-plate planet in which heat is generated by radioactive decay and transported to the surface by conduction through a lithospheric plate overlying a convecting mantle. In this stagnant-lid tectonic regime, there is no recycling of surface material to the planetary interior. Thus, this geodynamic framework predicts the existence of three main geochemical reservoirs on Mars, namely an enriched crust, a complementary chemically depleted lithospheric mantle, and, lastly, a primitive, CHUR-like, convecting asthenospheric mantle. The bulk of the existing knowledge of the Martian interior comes from Martian meteorites, which include ~ 165 – 2400 Ma shergottites originating from depleted and enriched mantle sources as well as ~ 1340 -Ma nakhlites and chassignites formed by low-degree partial melting of a depleted mantle source (26). The discovery of a primitive Hf isotope signal in the young zircon population, that we relate to plume magmatism, suggests the existence of a deep-seated, isotopically homogenous and presumably convecting mantle reservoir. As such, the isotopically anomalous shergottites, nakhlites, and chassignites must reflect melting of a reservoir isolated from convective stirring, namely the lithospheric mantle (Fig. 3).

The Hf isotope dataset for >4.3 -Ga zircons firmly establishes that magma ocean crystallization occurred within 20 Myr of Solar System formation. However, this estimate is significantly older than that of up to 100 Myr after Solar System formation based on the Sm–Nd systematics of shergottite meteorites (32, 33). These protracted silicate differentiation timescales must reflect a temporally distinct, younger mantle fractionation event following planetary differentiation. The most prominent surface feature of Mars is its crustal dichotomy, expressed by a difference in the crustal thickness between the southern and northern hemispheres. This feature is commonly attributed to a giant impact after extraction of the primordial crust, resulting in significant remelting of the mantle and the production of a younger crust in the northern lowlands (34). Given that shergottites are understood to originate from the northern lowlands (19), the

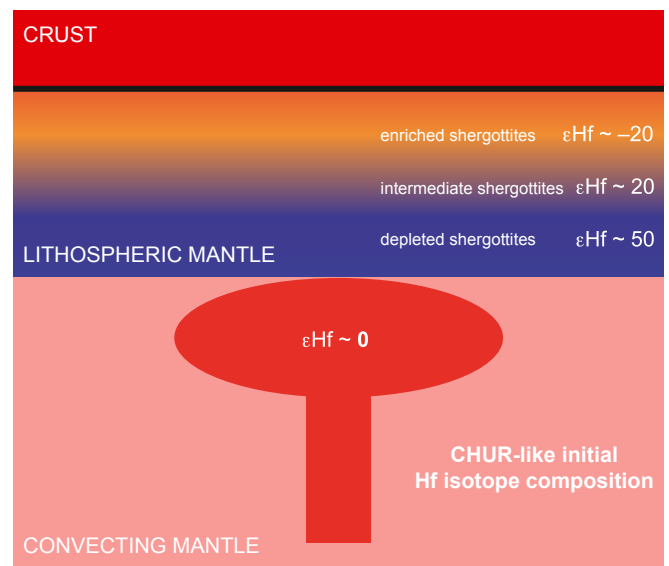


Fig. 3. Schematic representation of Mars's main geochemical reservoirs at the time of formation of the <600 -Ma shergottite lavas. The young zircons with chondritic-like initial Hf isotope compositions ($\epsilon\text{Hf}_T \sim 0$) are inferred to have been ultimately derived from plume-related magmatism sampling the convecting mantle. Note that the location of the source reservoir of enriched and intermediate shergottites is uncertain and could be located in the lithospheric mantle, crust, or both (2, 39).

formation timescale of their source region must reflect the last fractionation event experienced by the underlying mantle. If the origin of the Martian crustal dichotomy is related to a giant impact, the formation timescale of the shergottites' mantle source provides a minimum age estimate for the impact event.

The preservation of ancient, isotopically heterogeneous mantle reservoirs has been used to argue for inefficient mixing of the Martian mantle, possibly due to a sluggish convective regime (35). However, this is at odds with numerical simulations and thermal models that predict the establishment of an efficient convective regime shortly after magma ocean crystallization, including the existence of long-lived, deep-seated mantle plumes (29, 36). The identification of a pervasive primitive reservoir documented by <1.5-Ga zircons provides a tangible record of the deep Martian interior, which permits a better understanding of the internal structure and geodynamic regime of Mars. Our data support the existence of a stagnant lid consisting of a crust and complementary depleted lithospheric mantle, which overlies a primitive and, hence, nondifferentiated convecting deep mantle reservoir. The homogenous Hf isotope composition of the deep mantle inferred by our data implies efficient mixing of this reservoir. This requires onset of solid-state convection prior to complete magma ocean crystallization, which allowed efficient mixing of compositional heterogeneities inherited from magma ocean crystallization (36). Thus, our data imply that initiation of solid-state convection on Mars occurred within 10 Myr of Solar System formation. In contrast to Earth, which may have transitioned from a stagnant to a mobile lid regime early in its evolution (37), our data and interpretation support the view that Mars has been in a stagnant-lid tectonic regime for most of its geologic history, with limited or no recycling of surface material to the deep mantle.

Finally, whereas zircon is not an abundant component of mafic rocks on Earth, our study implies that it is likely ubiquitous on the surface of Mars, including its global dust reservoir. Moreover, the 4.2-Gyr age spread defined by the grains investigated here establishes that Martian zircons provide an unsurpassed record of the planet's magmatic history. In the context of future robotic exploration of Mars, including the aim of returning samples to Earth, our data make clear that a return mission targeted at acquiring zircon-bearing samples will be of high scientific value toward understanding the geologic history of Mars.

Materials and Methods

Around 15 g of the NWA 7533 meteorite were gently crushed using an agate mortar and pestle to a granularity inferior to 150 μm . Subsequently, the sample was subjected to magnetic separation using a Frantz isodynamic separator at progressively higher magnetic fields until the most magnetic mineral phases were removed and the resultant nonmagnetic fraction further purified with heavy liquids. A total of 57 grains, 55 zircons and 2 baddeleyites, ranging in size from 30 to 80 μm were recovered from this fraction. To complement the ages of zircons recovered from the bulk rock aliquot, we extracted zircons from a 10-mg aliquot of an isolated crustal lithic clast of basaltic composition (clast C27). A total of 21 zircons ranging in size from 15 to 70 μm were identified, from which the four largest were selected for isotopic investigation. We conducted concomitant high-precision U–Pb chronology and Hf isotope measurements of the zircons using solution-based methods, following protocols outlined by Bouvier et al. (4). In brief, zircon grains were cleaned in Pyrex beakers in an ultrasonic bath

with alternating steps of warm 3.5-M HNO_3 , H_2O , and acetone. The individual crystals were dissolved in separate Teflon capsules in an HF– HNO_3 (3:1) mixture, together with the mixed ^{202}Pb – ^{205}Pb – ^{233}U – ^{235}U EARTHTIME U–Pb tracer. After purification, the Pb and U isotopic ratios of the sample + tracer mixture were measured using the Triton Thermo-Fisher thermal ionization mass spectrometer at the Centre for Star and Planet Formation, University of Copenhagen. The Hf isotope composition and Lu/Hf ratios of individual zircons were determined from the same sample digestion as that used for U–Pb age determination. Following collection of the high-field-strength element and rare earth element (REE) washes from the U–Pb purification, ~5% of the solution was aliquoted for Lu/Hf ratio determination. Hafnium was purified from the high-field-strength element and REE washes and analyzed using a Neptune Plus Thermo-Fisher multiple-collection inductively coupled plasma source mass spectrometer (MC-ICPMS) at the Centre for Star and Planet Formation, University of Copenhagen. We conducted REE concentration determination for some of the larger zircons, where sufficient material was available. Sample aliquots of the individual zircons were analyzed using the high-resolution inductively coupled plasma mass spectrometer Thermo Scientific Element XR at Laboratoire Géosciences Océan (Université de Brest).

A polished section of the basalt clast C27 was characterized for petrology by scanning electron microprobe (SEM) at the Institut de Physique du Globe de Paris (IPGP). Following SEM characterization, a 1.5-mg aliquot of clast C27 was digested using HF– HNO_3 acid mixtures. The major and trace element composition of the clast was analyzed using the Agilent 7900 quadrupole inductively coupled plasma (Q-ICP-MS) at IPGP. Backscattered electron imaging, X-ray element mapping, and quantitative mineral analyses were conducted for clast C27 by field-emission (FE) electron probe microanalysis (EPMA) using the FE-EPMA JEOL JXA-8530F at the Department of Earth and Planetary Science, University of Tokyo.

One zircon from the crushed NWA 7533 aliquot, dubbed DT-1, was recognized to host a number of inclusions. To preserve the inclusions for future work, the DT-1 zircon was strategically polished and only investigated using *in situ* techniques. To demonstrate the crystallinity of the DT-1 zircon, we conducted a combined X-ray microfluorescence and Laue microdiffraction experiment of the grain before polishing and acquisition of the U–Pb and Lu–Hf data. The X-ray experiment was carried out on beamline 34-ID-E of the Advanced Photon Source at Argonne National Laboratory. The U–Pb systematics of this zircon was investigated using the CAMECA 1280 ion microprobe equipped with a high-brightness Oregon Physics Hyperion-II radio-frequency plasma oxygen ion source and housed by the Centre for Microscopy, Characterization and Analysis at the University of Western Australia. The Lu–Hf systematics of DT-1 was studied at the Geochronology and Tracers Facility, British Geological Survey, using a Thermo-Fischer Neptune Plus MC-ICP-MS coupled to an NWR193UC 193-nm excimer laser ablation system equipped with a TV2 low-volume ablation cell. A full description of the samples reported in this study and procedures used for data acquisition is presented in *SI Appendix*.

Data Availability. All study data are included in the article, [Dataset S1](#), and *SI Appendix*.

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1. E. B. Watson, M. Harrison, Zircon saturation revisited: Temperature and composition effects in a variety of crustal magma types. *Earth Planet. Sci. Lett.* **64**, 295–304 (1983).
2. M. Humayun et al., Origin and age of the earliest Martian crust from meteorite NWA 7533. *Nature* **503**, 513–516 (2013).
3. F. M. McCubbin et al., Geologic history of Martian regolith breccia Northwest Africa 7034: Evidence for hydrothermal activity and lithologic diversity in the Martian crust. *J. Geophys. Res. Planets* **121**, 2120–2149 (2016).
4. L. C. Bouvier et al., Evidence for extremely rapid magma ocean crystallization and crust formation on Mars. *Nature* **558**, 586–589 (2018).
5. S. Hu et al., Ancient geologic events on Mars revealed by zircons and apatites from the Martian regolith breccia NWA 7034. *Meteorit. Planet. Sci.* **54**, 850–879 (2019).

6. A. R. Santos et al., Petrology of igneous clasts in Northwest Africa 7034: Implications for the petrologic diversity of the Martian crust. *Geochim. Cosmochim. Acta* **157**, 56–85 (2015).
7. R. H. Hewins et al., Regolith breccia Northwest Africa 7533: Mineralogy and petrology with implications for early Mars. *Meteorit. Planet. Sci.* **52**, 89–124 (2017).
8. W. S. Cassata et al., Chronology of Martian breccia NWA 7034 and the formation of the Martian crustal dichotomy. *Sci. Adv.* **4**, eaap8306 (2018).
9. D. E. Moser et al., Decline of giant impacts on Mars by 4.48 billion years ago and an early opportunity for habitability. *Nat. Geosci.* **12**, 522–527 (2019).
10. S. Goderis, A. D. Brandon, A. D. B. Mayer, M. Humayun, Ancient impactor components preserved and reworked in Martian regolith breccia Northwest Africa 7034. *Geochim. Cosmochim. Acta* **191**, 203–215 (2016).

11. R. Gomes, H. F. Levison, K. Tsiganis, A. Morbidelli, Origin of the cataclysmic Late Heavy Bombardment period of the terrestrial planets. *Nature* **435**, 466–469 (2005).
12. D. Nesvorný, D. Vokrouhlický, W. F. Bottke, H. F. Levison, Evidence for very early migration of the Solar System planets from the Patroclus–Menoetius binary Jupiter Trojan. *Nat. Astron.* **2**, 878–882 (2018).
13. S. J. Mojzsis, R. Brasser, N. M. Kelly, O. Abramov, S. C. Werner, Onset of giant planet migration before 4480 million years ago. *Astrophys. J.* **881**, 44 (2019).
14. R. L. Rudnick, S. Gao, Treatise on geochemistry in *The Crust*, R. L. Rudnick, Ed. (Elsevier, Amsterdam, 2003), Vol. 3, pp. 1–64.
15. L. T. Elkins-Tanton, P. C. Hess, E. M. Parmentier, Possible formation of ancient crust on Mars through magma ocean processes. *J. Geophys. Res. Planets* **110**, E12501 (2005).
16. A. Nemchin *et al.*, Record of the ancient Martian hydrosphere and atmosphere preserved in zircon from a Martian meteorite. *Nat. Geosci.* **7**, 638–642 (2014).
17. L. E. Nyquist *et al.*, “Ages and geologic histories of Martian meteorites” in *Chronology and Evolution of Mars*, R. Kallenbach, J. Geiss, W. K. Hartmann, Eds. (Springer, 2001), vol. 96, pp. 105–164.
18. G. A. Brennecke, L. E. Borg, M. Wadhwa, Insights into the Martian mantle: The age and isotopics of the meteorite fall Tissint. *Meteorit. Planet. Sci.* **49**, 412–418 (2014).
19. T. J. Lapen *et al.*, Two billion years of magmatism recorded from a single Mars meteorite ejection site. *Sci. Adv.* **3**, e1600922 (2017).
20. A. N. Krot, K. Keil, E. R. D. Scott, C. A. Goodrich, M. K. Weisberg, “Classification of meteorites” in *Treatise on Geochemistry*, D. H. Heinrich, K. T. Karl, Eds. (Pergamon, Oxford, 2007), pp. 1–52.
21. J. Blichert-Toft, J. D. Gleason, P. Télouk, The Lu–Hf isotope geochemistry of shergottites and the evolution of the Martian mantle–crust system. *Earth Planet. Sci. Lett.* **173**, 25–39 (1999).
22. V. Debaille, Q. Z. Yin, A. D. Brandon, B. Jacobsen, Martian mantle mineralogy investigated by the ^{176}Lu – ^{176}Hf and ^{147}Sm – ^{143}Nd systematics of shergottites. *Earth Planet. Sci. Lett.* **269**, 186–199 (2008).
23. V. Debaille, A. D. Brandon, C. O’Neill, Q. Z. Yin, B. Jacobsen, Early Martian mantle overturn inferred from isotopic composition of nakhlite meteorites. *Nat. Geosci.* **2**, 548–552 (2009).
24. J. T. Shafer *et al.*, Trace element systematics and ^{147}Sm – ^{143}Nd and ^{176}Lu – ^{176}Hf ages of Larkman Nunatak 06319: Closed-system fractional crystallization of an enriched shergottite magma. *Geochim. Cosmochim. Acta* **74**, 7307–7328 (2010).
25. J. M. D. Day *et al.*, Martian magmatism from plume metasomatized mantle. *Nat. Commun.* **9**, 4799 (2018).
26. M. Grott *et al.*, Long-term evolution of the Martian crust–mantle system. *Space Sci. Rev.* **174**, 49–111 (2013).
27. L. Ojha, K. Lewis, S. Karunatillake, M. Schmidt, The Medusae Fossae Formation as the single largest source of dust on Mars. *Nat. Commun.* **9**, 2867 (2018).
28. D. McKenzie, D. Barnett, D.-N. Yuan, The relationship between Martian gravity and topography. *Earth Planet. Sci. Lett.* **195**, 1–16 (2002).
29. K. W. Kiefer, Melting in the Martian mantle: Shergottite formation and implication for present-day mantle convection on Mars. *Meteorit. Planet. Sci.* **38**, 1815–1832 (2003).
30. L. Wilson, J. W. Head, Mars: Review and analysis of volcanic eruption theory and relationships to observed landforms. *Rev. Geophys.* **32**, 221–263 (1994).
31. B. M. Hynek, R. J. Phillips, R. E. Arvidson, Explosive volcanism in the Tharsis region: Global evidence in the Martian geologic record. *J. Geophys. Res. Planets* **108**, 5111 (2003).
32. L. E. Borg, G. A. Brennecke, S. J. K. Symes, Accretion timescale and impact history of Mars deduced from the isotopic systematics of Martian meteorites. *Geochim. Cosmochim. Acta* **175**, 150–167 (2016).
33. V. Debaille, A. D. Brandon, Q. Z. Yin, B. Jacobsen, Coupled ^{142}Nd – ^{143}Nd evidence for a protracted magma ocean in Mars. *Nature* **450**, 525–528 (2007).
34. F. Nimmo, S. D. Hart, D. G. Korycansky, C. B. Agnor, Implications of an impact origin for the Martian hemispheric dichotomy. *Nature* **453**, 1220–1223 (2008).
35. S. B. Jacobsen, G. Yu, Extinct isotope heterogeneities in the mantles of Earth and Mars: Implications for mantle stirring rates. *Meteorit. Planet. Sci.* **50**, 555–567 (2015).
36. M. Maurice *et al.*, Onset of solid-state mantle convection and mixing during magma ocean solidification. *J. Geophys. Res. Planets* **122**, 577–598 (2017).
37. M. Brown, T. Johnson, N. J. Gardiner, Plate tectonics in the Archean Earth. *Annu. Rev. Earth Planet. Sci.* **48**, 291–320 (2020).
38. J. N. Connelly *et al.*, The absolute chronology and thermal processing of solids in the solar protoplanetary disk. *Science* **338**, 651–655 (2012).
39. R. M. G. Armytage, V. Debaille, A. D. Brandon, C. B. Agee, A complex history of silicate differentiation of Mars from Nd and Hf isotopes in crustal breccia NWA 7034. *Earth Planet. Sci. Lett.* **502**, 274–283 (2018).