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Multiple early-formed water reservoirs in the interior of Mars

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Supplementary Information

Accompanying manuscript 'Multiple early-formed water reservoirs in the interior of Mars'

Quantification and correction of instrumental (background) hydrogen

1) *The Open University*. Nominally dry San Carlos olivine crystals were mounted in indium along with the reference apatites⁴⁴. These crystals were measured in the same manner as reference apatites and allowed assessment of background H₂O in the analysis chamber of the NanoSIMS. Since the martian apatites are present in standard polished thin sections made with epoxy, nominally dry phases in those sections were also measured. In session 1 the background measured on San Carlos olivine ranged from 40 to 147 ppm H₂O whereas a single analysis of a nominally anhydrous pyroxene in NWA 7034 yielded 43 ppm H₂O. To ensure we did not underestimate the instrumental contribution to the measured H₂O content of unknown apatites, a background water content of 147 ± 10 ppm was used with an associated δD of -462 ± 422 ‰ (2 σ standard deviation). The contribution of background H₂O to the measured values of martian apatite in session 1 was minor being between 7 and 29 % of the measured value. In session 2 the background measured on San Carlos olivine ranges from 9 to 10 ppm H₂O whereas a single analysis of a nominally anhydrous pyroxene in NWA 7034 yielded 61 ppm H₂O. To ensure we did not underestimate the instrumental contribution to the measured H₂O content of unknown apatites, a background water content of 61 ± 1 ppm was used with an associated δD of 843 ± 368 ‰ (2 σ). Note that the δD associated with San Carlos H₂O was 1404 ± 477 (2 σ standard deviation, n=5). The contribution of background H₂O to the measured values of martian apatite in session 2 was between 3 and 25 % of the measured value.

2) *NASA JSC*. Nominally dry San Carlos olivine crystals were mounted in indium along with the reference apatites. The background measured on San Carlos olivine ranged from 8 to 11 ppm H₂O whereas four analyses of a nominally anhydrous phases (pyroxene and maskelynite) in ALH 84001 yielded between 24 and 41 ppm H₂O. To ensure we did not underestimate the instrumental contribution to the measured H₂O content of unknown apatites, the average background water content of 34 ppm H₂O was used with an associated δD of 889 ± 824 ‰ (2 σ standard deviation, n=4). Note that the δD associated with San Carlos H₂O was 426 ± 646 (2 σ standard deviation, n=4). The contribution of background H₂O to the measured values of martian apatite was minor being <2 % of the measured value.

Martian hydrogen

A compilation of literature data used in this study can be found in the accompanying Supplementary Table 2. It includes H isotope data previously published for NWA 7034 (and paired samples) and ALH 84001. We also compiled in-situ H isotope data for enriched and depleted shergottites, as well as other geochemical information relevant to the discussion portion of this work.

A number of different mineral and glass phases have been measured in the depleted shergottites and enriched shergottites for D/H and H₂O content (Supplementary Table 2). In the depleted shergottites apatites, merrillite, pyroxene, olivine, ringwoodite, maskelynite, feldspathic

glass, ground mass glass, mineral-hosted melt inclusion glass, and impact melt/shock melt glass have been analyzed. The mineral phases yield water contents between 230 and 9600 ppm H_2O ^{23,27,29}, and the maskelynite and glasses yield a range of 18 to 76200 ppm H_2O ^{6,17,18,23,27,51,52}. In the enriched shergottites apatite, merrillite, pyroxene, silica, kaersutitic amphibole, mineral-hosted melt inclusions, feldspathic glass, and impact glass have been analyzed. The minerals yield a range H_2O contents between 30 to ~10000 ppm H_2O ^{17,25,65}. The modeling detailed in the Methods and in Figure 3A utilized data from the full range of textural contexts and mineralogical settings observed in depleted shergottites.

Shock implantation of martian atmosphere

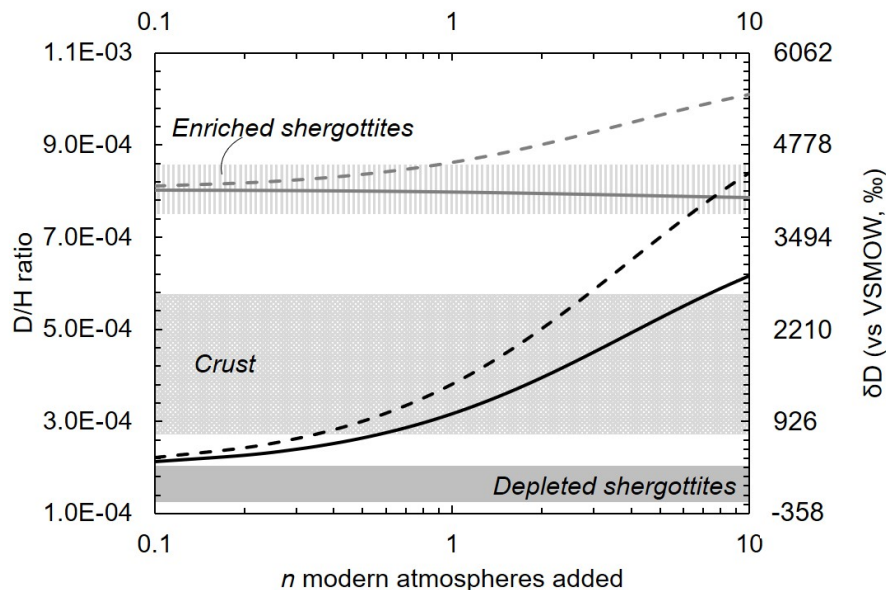
We have discussed in the main paper and the Methods how shock implantation is unlikely to have caused the higher D/H ratios observed in enriched shergottites compared to the depleted shergottites (e.g., Figure 3). Several of the basaltic martian meteorites that have been studied for H isotopes, have shock pressures associated with them^{63,64}. Extended Data Figure 1 shows the D/H ratio-shock pressure pairs for both enriched and depleted shergottites. Plotted are all the D/H data available for a given sample irrespective of textural constraints or mineral/glass phase type. The figure firstly highlights the lack of shock pressure estimates for several of the enriched shergottites for which there exist D/H data (GRV 020090 and LAR 06319). Secondly, the Extended Data Figure 1 shows that impact glasses lower the average D/H of each enriched shergottite, but the opposite is true for the depleted shergottites Yamato 980459 and Tissint. This seems to rule against enriched shergottites being more affected by shock implantation of hydrogen than the depleted shergottites. Thirdly, the range in D/H ratios (indicated by the error bars in Extended Data Figure 1) of Zagami and Shergotty make it difficult to discern any correlations in the data amongst enriched shergottites. On the other hand, there is a positive correlation within the depleted shergottite data, which may support our modelling (Figure 3) that the depleted shergottite D/H data can be explained by variable amounts of replacement of magmatic water D/H by the atmosphere (presumably by impacts and shock). It is important to bear in mind that in addition to martian meteorites being shocked, the enriched shergottites are nearly always more fractionated (lower MgO contents, more fractionated HSE contents) than depleted shergottites⁶⁶. This feature may be an artifact of sampling of meteorites but suggests that the enriched shergottites have experienced more magmatic processing than depleted shergottites. Such magmatic processing would not change the fact that to explain the majority of enriched shergottite data would require almost complete to complete replacement of their magmatic water D/H by atmospheric water. Whether or not such extensive magmatic processing is represented in the enriched shergottite D/H data is unclear at present.

Hydrogen isotope mixing models

In addition to the modeling discussed in the Methods section, we performed mass balance-constrained isotopic mixing models (Supplementary Figure 1). The figure shows the results of hypothetical mixing between martian mantle sources and martian atmosphere. The calculations use the estimate of water in the martian mantle (3.84×10^{19} kg H_2O) and assume that water is equally distributed between the enriched and depleted shergottite sources (1.92×10^{19} kg H_2O).

each). In the model, the D/H of the shergottite source regions are assumed to be 1.99×10^{-4} (⁶) and 8.03×10^{-4} (see Methods) for the depleted and enriched shergottite sources, respectively. We used the mass of water in the modern-day atmosphere (4.91×10^{19} kg H₂O) and mixed multiples of this mass with the water in each of the depleted and enriched shergottite sources. The atmospheric D/H was also varied from 7.79×10^{-4} and 1.09×10^{-3} (e.g., ²). Supplementary Figure 1 shows that even if the entire mass of water in the modern-day atmosphere (i.e., $n = 1$) was mixed with the depleted shergottite source it does not explain the high D/H of the proposed enriched shergottite source, nor does it explain all of the H-isotope variation observed in the crust. If the D/H signature of the martian mantle is ubiquitously low (i.e., Y-98 – like) and the high D/H of the enriched shergottite source is explained by mixing of atmospheric water to the source (via an unknown mechanism) then this requires an extraordinary amount of water (Supplementary Figure 1). In fact, it would require a mass of water 1.3 times greater than the total mass of water calculated to reside in the mantle, which seems highly unlikely. More probable is the observation that if the mantle contains two geochemically distinct sources with two distinct D/H ratios then the D/H of the crust, which represents an average geochemical signature of the mantle, would also represent an average and would lie between the two, which is the case (Supplementary Figure 1).

Supplementary Figure 1. Mass-balance constrained isotopic mixing model showing the results of the hypothetical mixing of water directly from the atmosphere into the martian mantle. Atmospheric water is mixed with H₂O in each of the depleted (gray lines) and enriched shergottite (black lines) mantle reservoirs. The atmospheric D/H²⁻⁴ was varied from 7.79×10^{-4} and 1.09×10^{-3} solid and dashed lines, respectively. We used the mass of water in the modern-day atmosphere (4.91×10^{19} kg H₂O) and mixed multiples of this mass with the water in each of the mantle sources.

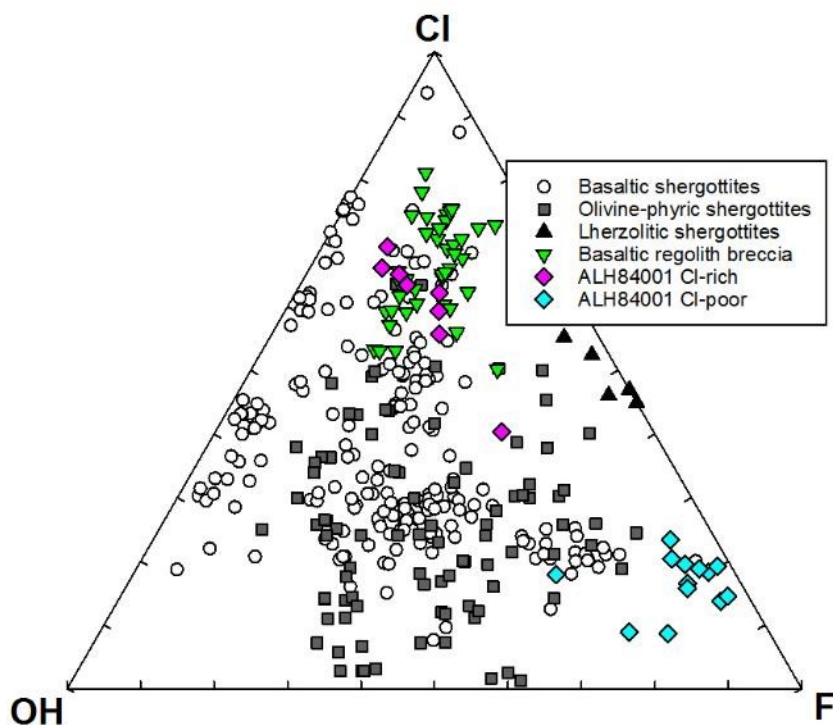


Apatites in samples of the martian crust

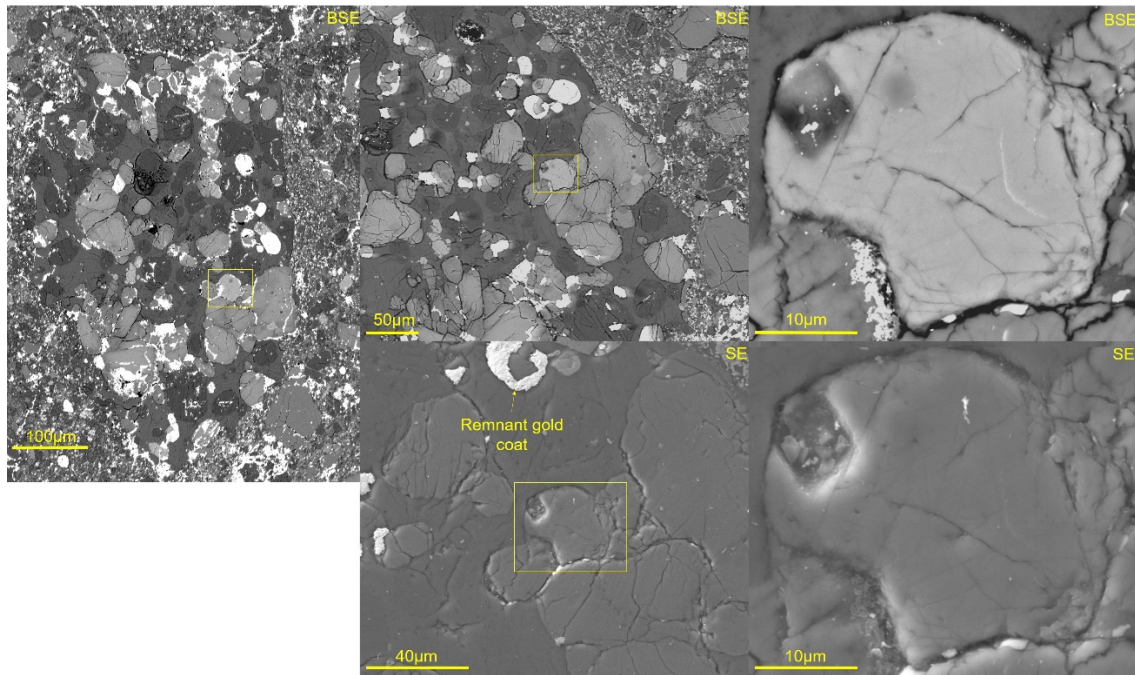
The chemistry of apatites in samples of the martian crust are provided in Supplementary Table 1 and shown in Supplementary Figure 2. Back-scattered electron (BSE) and secondary electron (SE) images of the phosphates analyzed by NanoSIMS from NWA 7034 and ALH 84001 are shown in Supplementary Figures 3 to 9, with the apatites highlighted by yellow boxes (NWA 7034) or labelled (ALH 84001).

Apatite in thin sections of ALH 84001 occur in two different chemical (Supplementary Figure 2) and textural settings (Supplementary Figure 9), indicating that there are two generations of apatite in ALH 84001 with Cl contents between 1.2 ± 0.3 wt.% and 4.1 ± 0.6 wt.% (uncertainty represents 1 standard deviation of the mean). The chemical composition of the Cl-rich apatites we measured are similar to the range of Cl (3.4-4.4 wt.%) and F (0.9-1.9 wt.%) contents reported in previous studies^{17,25,67}. The Cl-poor apatite found (Supplementary Figure 9a-c) is chemically distinct and has not been reported previously, to the best of our knowledge.

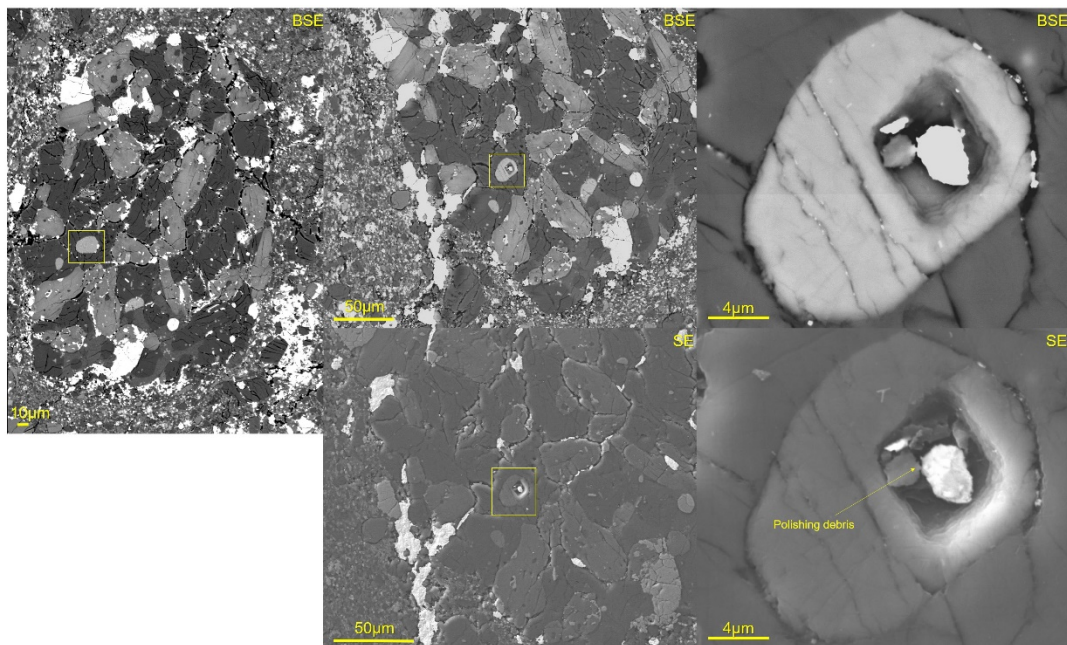
Supplementary Figure 2. Ternary plot of apatite X-site occupancy (mol.%) from martian meteorites. Data sources: ALH 84001 (this study), basaltic regolith breccia NWA 7034 and shergottites^{9,47,68}.



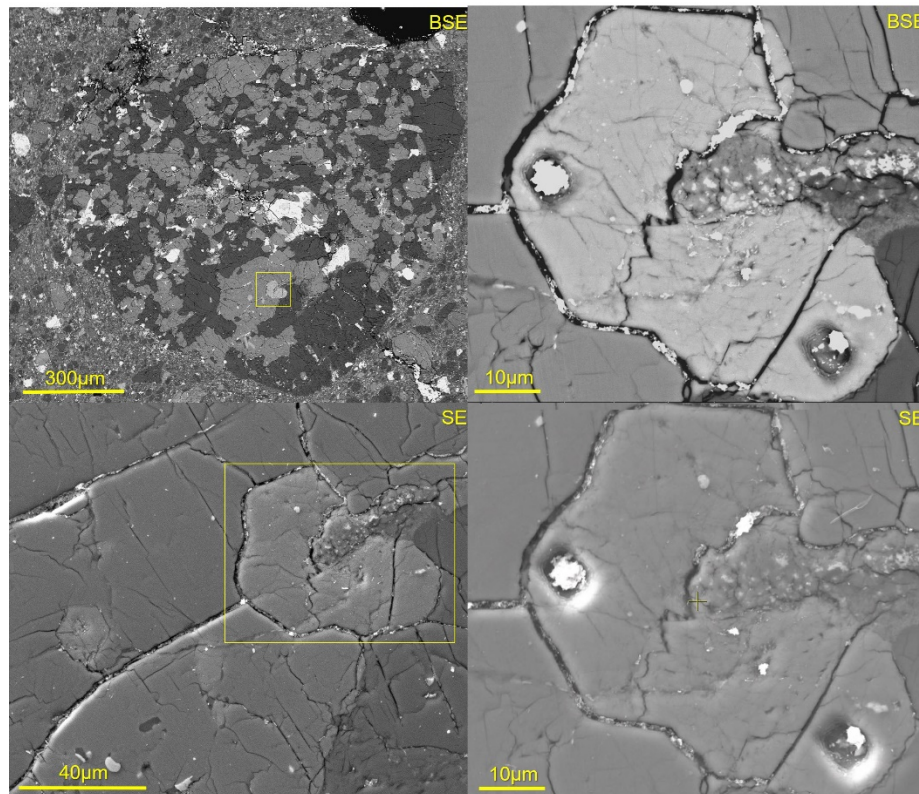
Supplementary Figure 3. Backscattered electron (BSE) and secondary electron (SE) images of apatite in basalt clast #76 (NWA 7034 2,3).



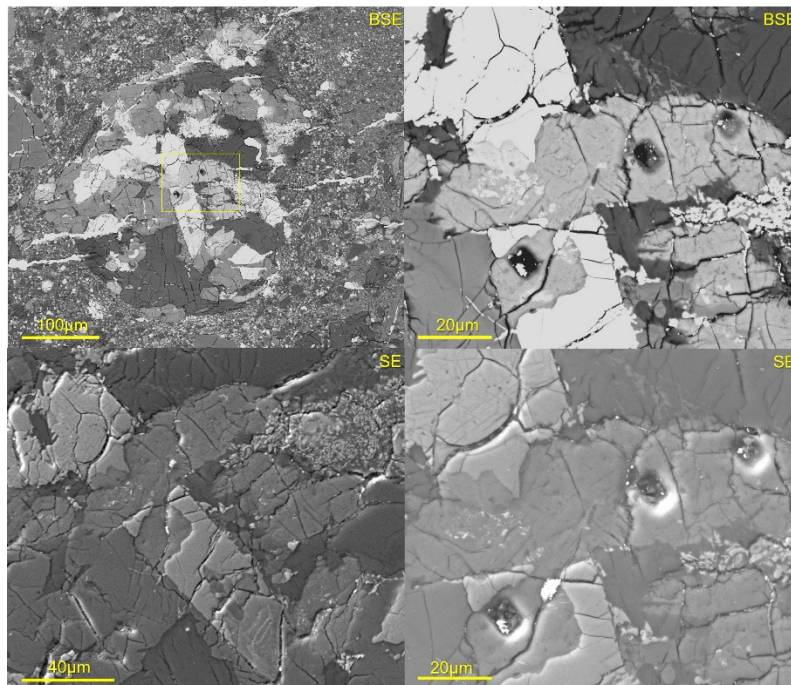
Supplementary Figure 4. BSE and SE images of apatite in basalt clast #75 (NWA 7034 2,3)



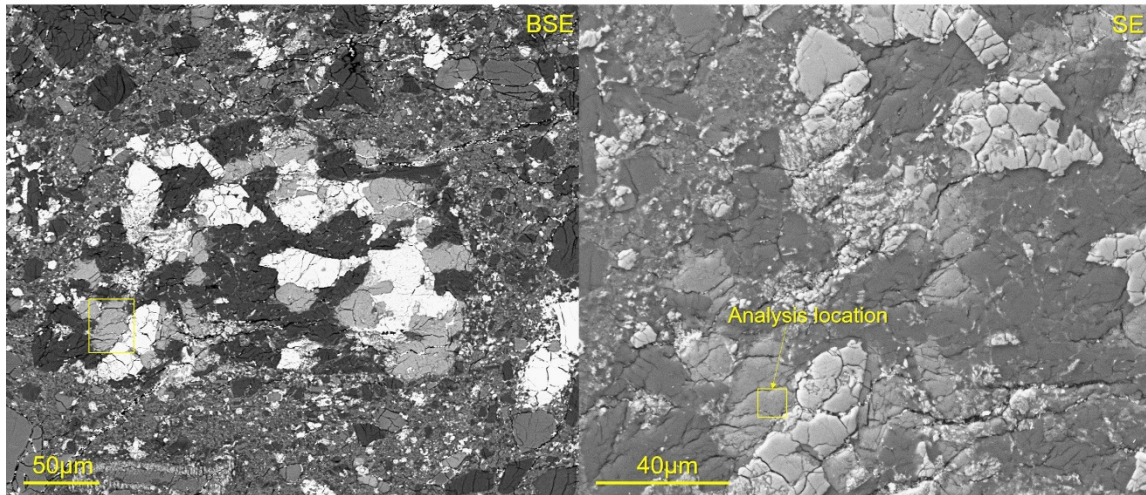
Supplementary Figure 5. BSE and SE images of apatite in granulitic basaltic clast #3 (NWA 7034 1B,2)



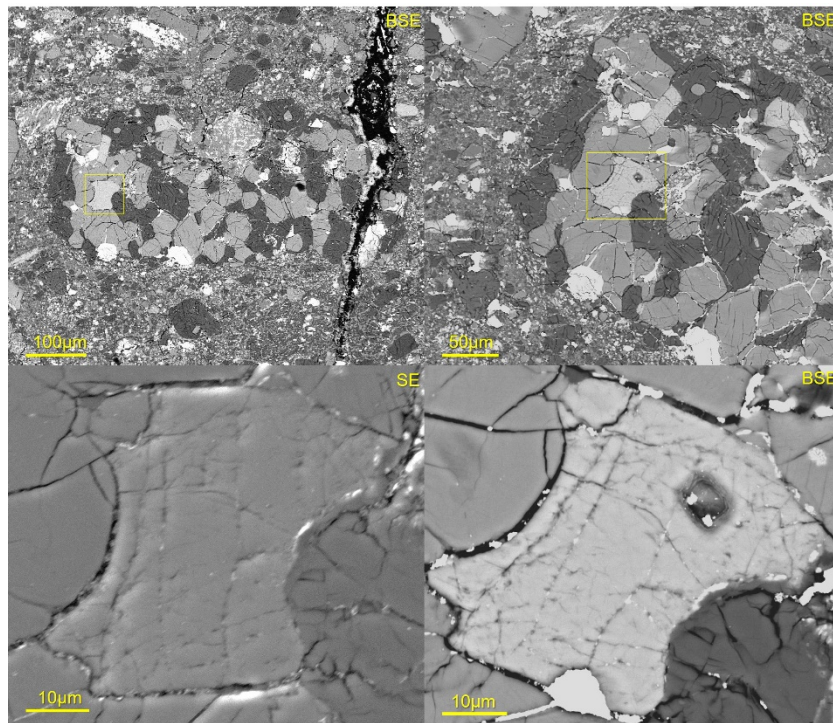
Supplementary Figure 6. BSE and SE images of apatite in FTP clast #2 (NWA 7034 1B,2)



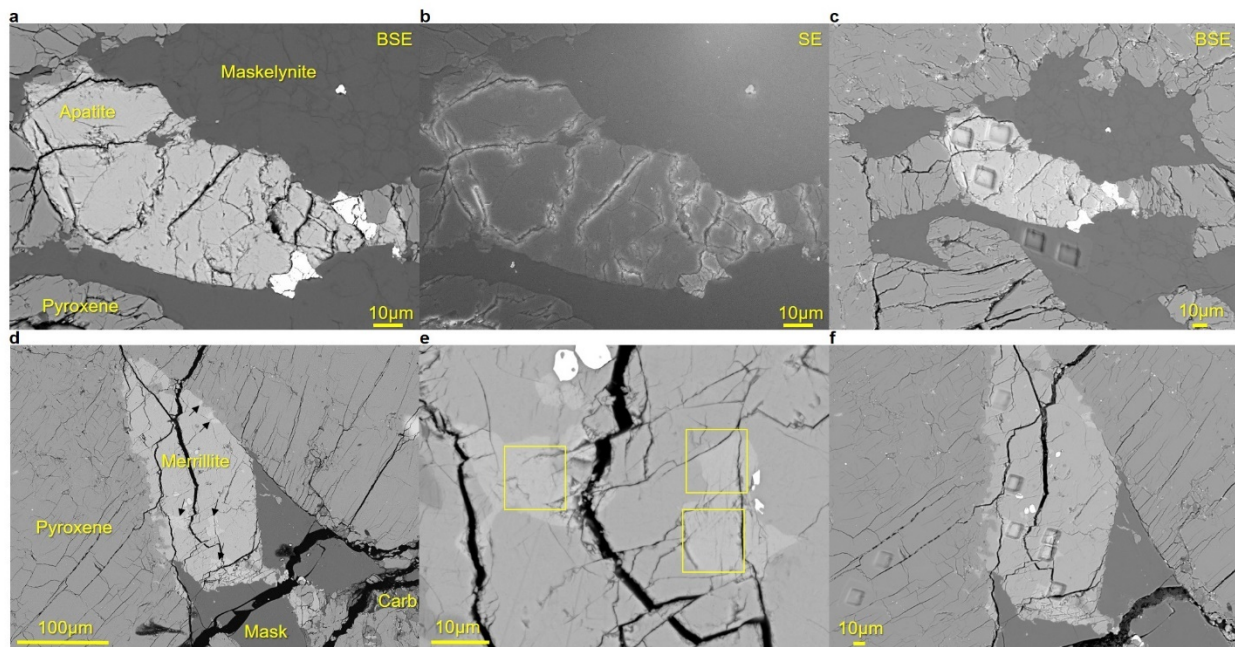
Supplementary Figure 7. BSE and SE images of apatite in FTP clast #64 (NWA 7034 1B,2)



Supplementary Figure 8. BSE and SE images of apatite in basalt clast #5 (NWA 7034 1B,2)



Supplementary Figure 9. Apatite grains in ALH 84001. Panels a-c show BSE and SE images of F-rich apatite in ALH 84001,205, and panels d-f show BSE images of Cl-rich apatite in ALH 84001,7. In panel-a black arrows indicate apatite and in panel-e yellow boxes indicate areas analyzed. Mask = maskelynite, Carb = carbonate.



The timing of fluid alteration in ALH 84001 and NWA 7034

We have already discussed the ages of ALH 84001 and NWA 7034 in the main manuscript. Allan Hills 84001 experienced hydrothermal alteration with crustal fluids at about 3.9 billion years ago¹². It is possible that Cl-rich apatite in ALH84001 record such fluid alteration. Northwest Africa (NWA) 7034 and its pairings represent a regolith breccia of basaltic bulk composition¹³, this sample contains lithic clasts up to ~4.4 Ga^{14,69}. However, the lithification of the basaltic breccia NWA 7034 is recorded in the disturbance of ages in apatite¹⁴. Thus, U-Pb ages of apatite throughout NWA 7034 and its pairings were reset at 1.5 Ga, including those in lithic clasts and the matrix, which is evidence this thermal annealing likely took place in the presence of crustal fluids, given the Cl-rich nature of all the apatites¹⁴. Together, these meteorites provide means of assessing the H-isotopic composition of water in the martian crust at two endpoints separated by ~2.4 billion years.

Mars mantle geochemistry and the shergottites

Mars has been volcanically active over much of its history, and martian meteorites record ages of surface materials that span from 4.48 Ga to about 0.165 Ga^{20,70–72}. The oldest materials are presumed to come from the southern highlands and indicate that the crust is a geochemically enriched reservoir^{69,73,74} that has at least 1400 ppm H₂O⁹. The martian mantle is comprised of at least two geochemical reservoirs, including a geochemically depleted source and a geochemically

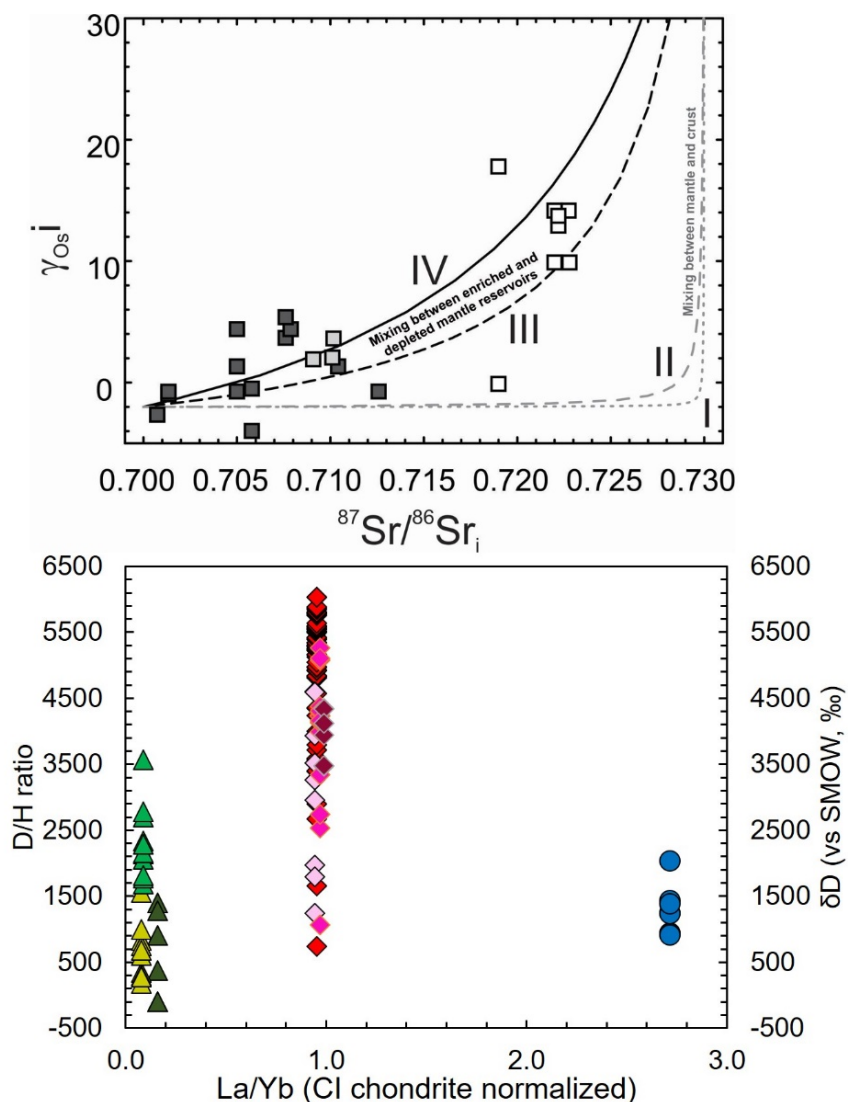
enriched source. The depleted source is characterized by low La/Yb ratios (~ 0.1), large and age-corrected positive $\varepsilon^{143}\text{Nd}$ values (e.g., $> +48$), low initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (~ 0.7013), and low magmatic oxygen fugacity ($f\text{O}_2$) near the IW buffer ($\Delta\text{IW} + 1$)^{36–38,75,76}. The enriched source is characterized by La/Yb ratios of ~ 1.5 , and slightly negative age-corrected $\varepsilon^{143}\text{Nd}$ values (i.e., as low as -8), more radiogenic initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (~ 0.7225), and higher magmatic $f\text{O}_2$ ($\Delta\text{IW} + 2$ to $+3$)^{36–38,75,76}.

Prior work has shown that crustal contamination cannot explain the variation in Os, Nd, or Sr isotope compositions of martian samples and distinct mantle reservoirs (i.e., mantle heterogeneity) are therefore required to explain the variation in bulk-rock isotope data (e.g.,^{77,78}). While we do not expect correlations to exist between Os, Sr, or Nd and D/H, one might expect a correlation to exist between a crustal tracer like bulk-rock La/Yb and D/H in apatite. From this comparison we would expect rocks with extreme crustal contamination or those from the crust to show the highest La/Yb ratio and most fractionated D/H ratio, if the crust was the ‘heavy D/H end-member’ being mixed with a light D/H (and low La/Yb) mantle. Instead, the crust (as defined by NWA 7034) has the highest La/Yb ratio but an intermediate D/H ratio (Supplementary Figure 10). This illustrates the conclusions of this work, that the crust is enriched in incompatible trace elements like La, but it has an intermediate D/H ratio. This intermediate crustal H isotope composition is best explained by isotopic mixing of at least two distinct (in D/H ratio) mantle reservoirs (e.g., Figure 4).

Inhomogeneity in other volatiles: Noble gases

In addition to these geochemical indicators, heterogeneities among Martian mantle materials are indicated by noble gas analyses of Martian meteorites. One case is argon, where Bogard and Garrison⁷¹ and Schwenzer et al.⁷² found in the shergottites variable “trapped” (i.e., non-radiogenic) $^{40}\text{Ar}/^{36}\text{Ar}$ ratios. This may indicate that the shergottites, in addition to containing atmospheric Ar, have been tapping into mantle reservoirs with variable Ar isotopic composition⁷⁹. More straightforward are the observations on Xe isotopes (of presumably mantle origin), which are present in the shergottites (and nakhlites), where they are mixed with Martian atmospheric gas, and in pure form in Chassigny. Xenon in Chassigny comes in two varieties^{79–81}: Chass-S, which is indistinguishable in composition from solar wind Xe; and an evolved component Chass-E, with added contributions from the decay of now extinct ^{129}I and fission of now extinct ^{244}Pu . Given the short half-lives of the precursors, the difference between the mantle reservoirs that host Chass-S and Chass-E, must have been established early in Martian history (i.e., probably no later than about 4 Ga ago) and they must have remained isolated from each other since then.

Supplementary Figure 10. Bulk-rock isotope versus in-situ D/H compositions for martian lithologies. Panel-a shows crystallization-age corrected Sr vs Os isotope data for martian shergottites (modified from ⁷⁷). Panel-a shows mixing between a depleted shergottite mantle source with a hypothetical crust of varying Os and Sr composition (curves I and II), and depleted mantle with a hypothetical enriched mantle reservoir (curves III and IV). This plot shows that the variation in bulk-rock compositions of shergottites is best explained by mantle heterogeneity rather than crustal assimilation. Panel-b shows H isotope compositions vs bulk-rock La/Yb ratio of NWA 7034 (circles), depleted shergottites (triangles: Queen Alexandra Range 94201, Yamato 980459, Tissint), and enriched shergottites (diamonds: Shergotty, Larkman Nunatak 06319, Los Angeles, Grove Mountains 020090). Bulk-rock La/Yb data and H isotope data are compiled in Supplementary Table 2.



Ages of Martian materials

Supplementary Information Table 3. Ages of martian materials used to construct Figure 2 in the main manuscript. *denotes depleted shergottite. For impact glass H-isotope data and ages see Usui et al.¹⁸.

Sample/reservoir	Target	Age (Ma)	System	Reference
ALH 84001	Bulk	4091± 30	Lu-Hf	Lapen et al. ¹⁰
	Carbonate	3900 ± 40	Pb-Pb	Borg et al. ¹²
NWA 7034	Apatite	1490 ± 90	U-Pb	McCubbin et al. ¹⁴
Tissint *	Bulk	574 ± 20	Rb-Sr, Sm-Nd	Brennecka et al. ⁸²
Yamato 980459 *	Bulk	290 ± 40	Rb-Sr, Sm-Nd	Shih et al. ⁸³
<i>Enriched shergottites (ES)</i>				
GRV 020090	Baddeleyite	192 ± 10	U-Pb	Jiang and Hsu ⁸⁴
Shergotty	Bulk	165 ± 11	Rb-Sr	Shih et al. ⁸⁵
Los Angeles	Bulk	170 ± 8	Rb-Sr	Nyquist et al. ⁸⁶
EETA 79001	Bulk	173 ± 10	Rb-Sr	Wooden et al. ⁸⁷
LAR 06319	Bulk	183 ± 12	Sm-Nd	Shafer et al. ⁸⁸
	Bulk	197 ± 29	Lu-Hf	Shafer et al. ⁸⁸
	Bulk	190 ± 26	Sm-Nd	Shih et al. ⁸⁹
	Bulk	207 ± 14	Lu-Hf	Shih et al. ⁸⁹
Average ± standard deviation	194 ± 10 million years			
Range used for ES	165 to 194 million years			
MSL Mudstone	~2900-3500 million years ⁸			
GRV – Grove Mountains, EETA – Elephant Moraine, LAR – Larkman Nunatak				

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