

Rb–Sr, Sm–Nd and Ar–Ar isotopic systematics of Martian dunite Chassigny

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Abstract

Isotopic analysis of the Martian meteorite Chassigny yields a Rb–Sr age of 1406 ± 14 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.702251 ± 0.000034 , a Sm–Nd age of 1386 ± 28 Ma with an initial $\varepsilon_{143\text{Nd}}$ -value of $+16.9 \pm 0.3$ and an ^{39}Ar – ^{40}Ar age of 1360_{-40}^{+20} Ma. The concordance of these ages and the Rb–Sr and Sm–Nd initial isotopic signatures suggest that Chassigny crystallized from low Rb/Sr, light rare earth element depleted source materials ~ 1390 Ma ago. The ages and $\varepsilon_{143\text{Nd}}$ -values of Chassigny and the nakhlites Governador Valadares and Lafayette overlap, suggesting that they could have come from very similar mantle sources. Nakhla, Northwest Africa 998 and Yamato 000593 appear to be from similar but distinct sources. Chassigny and all nakhlites so far studied have undergone similar evolution histories. That is, chassignites/nakhlites were derived from a region where volcanism lasted at least 50 Ma and crystallized from different lava flows or subsurface sills. They probably were launched from Mars by a single impact event. The trapped Martian atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in Chassigny, nakhlites and shergottite impact glass are similar and possibly indicate minimal change in this ratio over the past ≥ 600 Ma.

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1. Introduction

The chassignites, Chassigny and Northwest Africa (NWA) 2737, are Martian dunites mainly composed of cumulate olivine with minor amounts of pyroxene,

chromite, interstitial feldspar and accessory phases such as chlorapatite [1–4]. Among Martian meteorites, the clinopyroxenites (nakhlites) are least affected by shock metamorphism. Peak shock pressures for Lafayette and Yamato (Y) 000593 were determined to be below 14 GPa, whereas those for Nakhla and Governador Valadares lie in the range 14–20 GPa [5]. The same authors concluded that Chassigny has been subjected to a higher peak shock pressure in the range 26–32 GPa, slightly lower than the previously reported value of

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about 35 GPa [6]. Alteration products including carbonates [7] and sulphates [8,9] are less abundant in Chassigny compared to nakhlites. Rare earth element (REE) abundances in Chassigny are approximately one tenth of those in nakhlites. The prior chemical, K–Ar, Rb–Sr and Sm–Nd isotopic studies of Chassigny suggest that the meteorite crystallized ~ 1300 Ma ago and is closely related to nakhlites [11–18]. Furthermore, the ejection age of Chassigny (11.3 ± 0.6 Ma) is comparable to those of nakhlites, suggesting launch pairing of these meteorites [10]. Although the measured radiometric ages and cosmic-ray exposure (CRE) ages of Chassigny and several nakhlites are similar [10], suggesting that they were derived from a common location on Mars and were ejected in a single impact event, the reported radiometric ages for these meteorites using K–Ar, Rb–Sr, Sm–Nd and U–Pb systems show variations of at least 100 Ma. Furthermore, compared to other Martian meteorites there are limited isotopic data for Chassigny, and some of those data were obtained many years ago and were reported in abstracts [15,18]. To examine more closely the relationship of Chassigny to nakhlites, we have undertaken new Rb–Sr, Sm–Nd

and ^{39}Ar – ^{40}Ar isotopic analyses of Chassigny to more precisely determine its crystallization age and the strontium and neodymium isotopic signatures of its mantle source region. We compare the new results to those recently obtained for nakhlites and discuss possible genetic relationships between Chassigny and the nakhlites.

2. Sample and analytical procedures

The studied sample of Chassigny (USNM 624) was an ~ 1.7 -g chip having sawn surfaces. This sample was first washed in ethanol in an ultrasonic bath for 5 min to remove brownish surface deposits and rusts, and then processed by gently crushing to grain size $< 149 \mu\text{m}$ (Fig. 1). About 15% of the crushed material was taken as whole-rock samples (WR1, WR and reserve). The rest of this sample was further crushed and sieved into two size fractions, 149 – $74 \mu\text{m}$ and $< 74 \mu\text{m}$. Mineral separates were made from the finer fraction using heavy liquids. A feldspar-rich sample (FELD) was obtained from material floated in the 2.85 g/cm^3 heavy liquid. Pyroxene-rich (PX) and olivine-rich

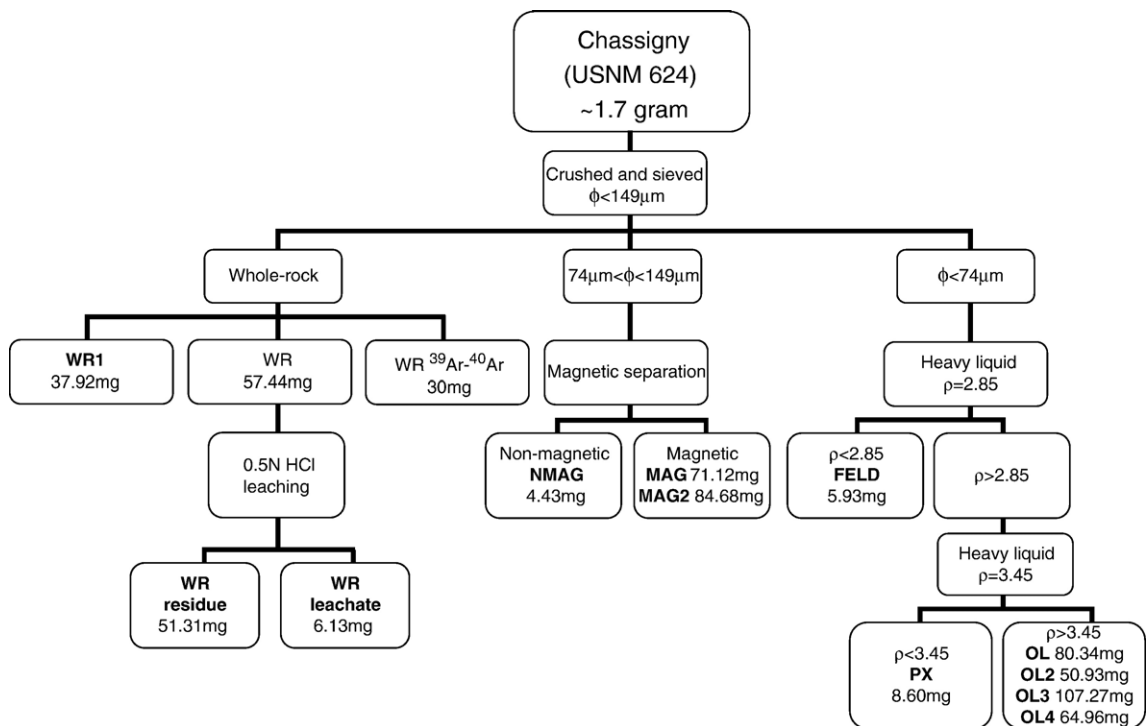


Fig. 1. Flow diagram of sample processing. The WR sample was washed with 0.5 N HCl in an ultrasonic bath for 10 min. Magnetic separation was performed using a Frantz isodynamic separator at 0.8 A. A non-magnetic (NMAG) and two magnetic (MAG, MAG2) fractions were obtained. Mineral separation was made from the finer fraction sample by density separation using heavy liquids (bromoform: $\rho = 2.85 \text{ g/cm}^3$ and Clerici's solutions: $\rho = 3.45 \text{ g/cm}^3$). At $\rho < 2.85 \text{ g/cm}^3$, we obtained a feldspar sample (FELD). A pyroxene sample (PX) was obtained with $2.85 \text{ g/cm}^3 < \rho < 3.45 \text{ g/cm}^3$. From the heavier fraction ($\rho > 3.45 \text{ g/cm}^3$), we obtained four olivine samples (OL, OL2, OL3, OL4).

(OL) samples were prepared using a heavy liquid of density 3.45 g/cm³. Most pyroxenes floated in this heavy liquid, whereas most olivines sank. From the coarser fraction, we obtained non-magnetic (NMAG) and magnetic (MAG and MAG2) samples using a Frantz isodynamic magnetic separator. The WR sample was washed with 0.5 N HCl in an ultrasonic bath for 10 min to leach out phosphates.

Both the residue and the leachate of the whole-rock sample, WR(r) and WR(l), respectively, plus unleached samples were analyzed for rubidium, strontium, samarium and neodymium isotopes following the procedures of [19,20]. All isotopic measurements were made on Finnigan-MAT multi-collector mass spectrometers, either 261 or 262, following the procedures of [19]. The average value of ⁸⁷Sr/⁸⁶Sr measured for NBS 987 during the course of the study was 0.710249±0.000027 (2σ_p, 38 analyses, σ_p=standard deviation of the population). The ⁸⁷Sr/⁸⁶Sr results reported here were renormalized to ⁸⁷Sr/⁸⁶Sr=0.710250 for NBS 987 [19]. Samarium and neodymium were analyzed as SmO⁺ and NdO⁺ except the samarium concentration measurements for MAG and MAG2 for which samarium was analyzed as Sm⁺. The average value of ¹⁴³Nd/¹⁴⁴Nd during the course of the study for our Ames neodymium standard, which has the same neodymium isotopic composition as the Caltech neodymium standard n(Nd)β [20], was 0.511120±0.000015 (2σ_p) normalized to ¹⁴⁶Nd/¹⁴⁴Nd=0.724140 for one series of seven NdO⁺ analyses and 0.511113±0.000016 (2σ_p) for a second series of nine analyses of NdO⁺. The latter value applies to samples MAG and MAG2 only. The ¹⁴³Nd/¹⁴⁴Nd

values reported here for samples were further normalized to ¹⁴³Nd/¹⁴⁴Nd=0.511138 for the Caltech neodymium standard n(Nd)β [21].

We neutron-irradiated a 30-mg whole-rock (WR) sample of Chassigny, along with several samples of the NL-25 hornblende age standard at the University of Missouri Research Reactor. The irradiation constant (*J* value) for Chassigny was 0.02070±0.00015. Argon was released by stepwise temperature extraction in an induction furnace equipped with a thermocouple and its isotopic composition was measured on a mass spectrometer. After application of system blanks and decay and reactor corrections, the ³⁹Ar–⁴⁰Ar age at each extraction was calculated from the ⁴⁰Ar/³⁹Ar ratio, relative to this ratio in the age standard. Experimental details are given in Bogard et al. [22].

3. Results

3.1. Rubidium–strontium systematics

The rubidium and strontium concentrations and ⁸⁷Sr/⁸⁶Sr data for whole-rock and mineral separate samples are given in Table 1. The rubidium and strontium abundances of WR1 are 0.618 ppm and 11.9 ppm, respectively, and are in good agreement with the previous results obtained by isotope dilution mass spectrometry [14] and by conventional spark source mass spectrometry (SSMS) (Rb=0.69 ppm, Sr=11.9 ppm) [15], except the strontium data of Nakamura et al. [14] (Sr=8.29 ppm), which is ~30% lower than the present data and the previous SSMS results [16]. The calculated rubidium

Table 1
The Rb–Sr analytical results for Chassigny

Sample ^a	Wt. (mg)	Rb (ppm)	Sr (ppm)	⁸⁷ Rb/ ⁸⁶ Sr ^b	⁸⁷ Sr/ ⁸⁶ Sr ^c
WR1	37.92	0.6184	11.89	0.1505±12	0.705219±10
WR(r)	51.31	0.5789	10.20	0.1642±14	0.705526±10
WR(l)	6.13	0.5120	8.058	0.1838±13	0.705773±10
FELD	5.93	6.869	108.2	0.1836±14	0.705864±10
NMAG	4.43	27.36	680.3	0.1164±13	0.704602±10
PX	8.60	5.029	89.95	0.1618±18	0.705492±10
OL2	50.93	0.1388	1.062	0.3781±28	0.709797±10
OL3	107.27	0.1585	1.181	0.3886±63	0.710011±24
OL4	61.96	0.1253	0.9506	0.3815±54	0.709915±22
MAG	71.12	0.4922	10.10	0.1410±17	0.705090±10
MAG2	84.68	0.4313	8.549	0.1460±17	0.705149±11
NBS 987 Sr standard: Sr ⁺ (38 analyses)					0.710249±27 ^d

^a WR=whole-rock, WR(r)=whole-rock residue, WR(l)=whole-rock leachate, FELD=ρ<2.85 g/cm³ fraction mainly composed of feldspar, NMAG=non-magnetic fraction, PX=pyroxene, OL=olivine, MAG=magnetic fraction.

^b Uncertainties correspond to last figures and represent ±2σ_m error limits. σ_m=standard deviation of the mean.

^c Normalized to ⁸⁸Sr/⁸⁶Sr=8.37521 and adjusted to ⁸⁷Sr/⁸⁶Sr=0.710250 of the NBS 987 Sr standard [19]. Uncertainties correspond to last figures and represent ±2σ_m error limits.

^d Uncertainties correspond to last figures and represent ±2σ_p error limits. σ_p=standard deviation of the population.

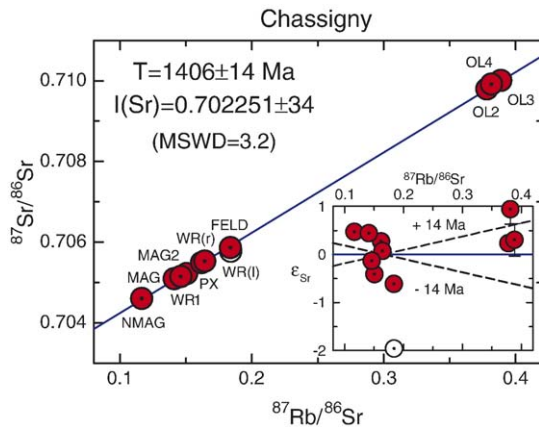


Fig. 2. Rubidium–strontium isotopic data for whole-rock and mineral separates from Chassigny. Ten data points, excluding whole-rock leachate WR(l), define a linear array corresponding to a Rb–Sr age of 1406 ± 14 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.702251 \pm 0.000034$ (MSWD=3.2) for $\lambda(^{87}\text{Rb}) = 1.402 \times 10^{-11} \text{ yr}^{-1}$ using the Williamson regression program [23]. If the Isoplot/Ex program [24] were used, a Rb–Sr age of 1411 ± 21 Ma (MSWD=3.2) with an initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.702243 \pm 0.000058$ would be obtained from these 10 data points. The inset shows deviations of $^{87}\text{Sr}/^{86}\text{Sr}$ in parts in 10^4 (ϵ -units) for whole-rock and mineral separates of Chassigny relative to the 1406 Ma isochron. Dotted lines on either side of the best-fit line correspond to ± 14 Ma. The WR(l) point deviates downward and/or to the right of the isochron by 2 ϵ -units, suggesting a minor isotopic disturbance possibly due to shock metamorphism [5,6], or terrestrial or Martian rubidium contamination.

and strontium concentrations for the WR sample, i.e., WR(l) plus WR(r), are 7% and 16%, respectively, lower than those of the unleached WR1 sample, suggesting slightly heterogeneous distribution of alkali and alkaline

earth elements among 50-mg sized whole-rock samples. Fig. 2 shows $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ data for two whole-rock and eight mineral samples of Chassigny: pyroxene (PX), feldspar (FELD), olivines (OL2, OL3, OL4), as well as non-magnetic (NMAG) and magnetic (MAG, MAG2) fractions. A total of 11 data points, including whole-rock leachate WR(l) and residue WR(r), define a linear array corresponding to a Rb–Sr age of 1406 ± 14 Ma (mean square of weighted deviates: MSWD=12) for $\lambda(^{87}\text{Rb}) = 1.402 \times 10^{-11} \text{ yr}^{-1}$ using the Williamson regression program [23]. The WR(l) point deviates downward from the isochron and/or to the right of it, suggesting a minor isotopic disturbance possibly due to shock metamorphism [5,6], or minor terrestrial or Martian rubidium contamination. Excluding the WR(l) point, a Rb–Sr age of 1406 ± 14 Ma (MSWD=3.2) with an initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.702251 \pm 0.000034$ (if the Isoplot/Ex program [24] were used, a Rb–Sr age of 1411 ± 21 Ma (MSWD=3.2) with an initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.702243 \pm 0.000058$) would be obtained from these 10 data points.

3.2. Samarium–neodymium systematics

The samarium and neodymium analytical results are given in Table 2 for two whole-rock and seven mineral samples of Chassigny: pyroxene (PX), feldspar (FELD), olivines (OL, OL2), and non-magnetic (NMAG) and magnetic (MAG, MAG2) fractions. The neodymium and samarium concentrations of the whole-rock sample (WR1) of Chassigny are in good agreement with the

Table 2
The Sm–Nd analytical results for Chassigny

Sample ^a	Wt. (mg)	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$ ^b	$^{143}\text{Nd}/^{144}\text{Nd}$ ^c
WR1	37.92	0.1242	0.6082	0.12349 ± 19	0.512039 ± 10
WR(r)	51.31	0.0603	0.2170	0.16791 ± 35	0.512443 ± 13
WR(l)	6.13	0.5218	3.241	0.09736 ± 19	0.511791 ± 10
FELD	5.93	0.5618	3.326	0.10216 ± 19	0.511882 ± 12
NMAG	4.43	2.393	15.29	0.09469 ± 13	0.511787 ± 10
PX	8.60	1.443	6.236	0.13998 ± 15	0.512187 ± 10
OL	80.34	0.0261	0.1272	0.12429 ± 34	0.512046 ± 17
OL2	50.93	0.0251	0.1239	0.12249 ± 53	0.512031 ± 13
MAG	71.12	0.1227	0.5849	0.12687 ± 15	0.512082 ± 10
MAG2	84.68	0.1062	0.5097	0.12596 ± 15	0.512070 ± 10
Ames Nd standard: NdO ⁺		(7 analyses, 11/2004) ^d			0.511120 ± 15 ^e
		(9 analyses, 03/2005, for MAG and MAG2 only) ^d			0.511113 ± 16 ^e

^a WR=whole-rock, WR(r)=whole-rock residue, WR(l)=whole-rock leachate, FELD= $\rho < 2.85 \text{ g/cm}^3$ fraction mainly composed of feldspar, NMAG=non-magnetic fraction, PX=pyroxene, OL=olivine, MAG=magnetic fraction.

^b Uncertainties correspond to last figures and represent $\pm 2\sigma_m$ error limits. σ_m =standard deviation of the mean.

^c Normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.724140$ and adjusted to $^{143}\text{Nd}/^{144}\text{Nd} = 0.511138$ of the Ames Nd standard [19]. Uncertainties correspond to last figures and represent $\pm 2\sigma_m$ error limits.

^d Neodymium standard data were obtained in different analytical sessions.

^e Uncertainties correspond to last figures and represent $\pm 2\sigma_p$ error limits. σ_p =standard deviation of the population.

previous results for this meteorite [12–16] (Fig. 3a). Because REE abundances of chlorapatite in Chassigny usually exceed $\sim 1000\times$ CI-chondrite abundances [23], we tried to selectively leach out chlorapatite by washing with 0.5 N HCl. However, the leachate, WR(l), does not show a large REE enrichment ($<10\times$ CI-chondrite). The leaching results show that the WR(l) sample does not contain much chlorapatite, and that some olivine and/or feldspar were also dissolved by the procedure. The neodymium and samarium concentrations in the PX sample are in close agreement with the data for the Chassigny augite obtained by ion microprobe [25] (Fig. 3b). Compared to the data obtained by ion microprobe, our FELD sample seems to be impure and contains some REE-carrier phases (Fig. 3b). The olivine fractions (OL and OL2) possess the lowest REE abundances among all the mineral concentrates but their Sm/Nd

ratios are almost identical to that of WR1. The samarium and neodymium abundances of MAG and MAG2 are $0.7\text{--}1.2\times$ CI, suggesting that our magnetic sample is a mixture of pyroxene and olivine. The NMAG sample is the most REE-rich phase we separated ($20\text{--}35\times$ CI). All the samples, including the acid leachate and residue of the whole-rock, show light REE (LREE)-enriched signatures. Nevertheless, we obtained a significant variation in $^{147}\text{Sm}/^{144}\text{Nd}$ ratios from 0.0947 to 0.168 exceeding that previously obtained by acid leaching (0.107 to 0.151) [18].

The Sm–Nd isochron diagram for Chassigny is presented in Fig. 4. Ten data points, including whole-rock leachate, WR(l), and residue, WR(r), define a linear array corresponding to a Sm–Nd age of 1354 ± 27 Ma (MSWD=3.9) for $\lambda(^{147}\text{Sm})=6.54\times 10^{-12}$ yr $^{-1}$ using the Williamson regression program [23]. The FELD point slightly deviates upward from the isochron and/or to the left of it, suggesting a minor isotopic disturbance possibly due to shock metamorphism [5,6], or terrestrial or Martian REE contamination. Excluding FELD, a Sm–Nd age of 1386 ± 28 Ma (MSWD=2.2) with an initial $\varepsilon_{143\text{Nd}}=+16.9\pm 0.3$ (if the Isoplot/Ex program [24] were used, a Sm–Nd age of 1385 ± 47 Ma (MSWD=2.2) with an initial $\varepsilon_{143\text{Nd}}=+16.9\pm 0.4$) would be obtained from these nine data points.

3.3. $^{39}\text{Ar}\text{--}^{40}\text{Ar}$ age

Fig. 5 plots the $^{39}\text{Ar}\text{--}^{40}\text{Ar}$ age and K/Ca ratio in Chassigny against the cumulative release of ^{39}Ar . The minimum ages observed are 1387 ± 10 Ma for two extractions releasing 10–30% of the ^{39}Ar . The first three extractions (up to 475 °C) released a small amount of adsorbed terrestrial argon, which makes two of these ages appear slightly older. Above $\sim 50\%$ of the ^{39}Ar release, the $^{39}\text{Ar}\text{--}^{40}\text{Ar}$ age increases significantly to a maximum apparent value of ~ 3600 Ma. The high extraction temperatures and low K/Ca ratios for the oldest ages above $\sim 90\%$ ^{39}Ar release suggest that they are associated with olivine and produced by the release of trapped Martian ^{40}Ar .

Fig. 6 is an isochron plot of $^{40}\text{Ar}/^{36}\text{Ar}$ versus $^{39}\text{Ar}/^{36}\text{Ar}$ for 12 extractions showing an approximately constant K/Ca ratio and releasing $\sim 10\text{--}86\%$ of the total ^{39}Ar . The isochron slope is strongly linear ($R^2=0.9984$), has an $^{40}\text{Ar}/^{36}\text{Ar}$ intercept of 1452 ± 168 and gives an $^{39}\text{Ar}\text{--}^{40}\text{Ar}$ age of 1354 ± 13 Ma. This $^{40}\text{Ar}/^{36}\text{Ar}$ intercept ratio is similar to that of trapped Martian atmospheric argon deduced from studies of Martian shergottites [26]. Because of significant variability in the $^{36}\text{Ar}/^{37}\text{Ar}/^{38}\text{Ar}$ isotopic ratios for these Chassigny extractions and

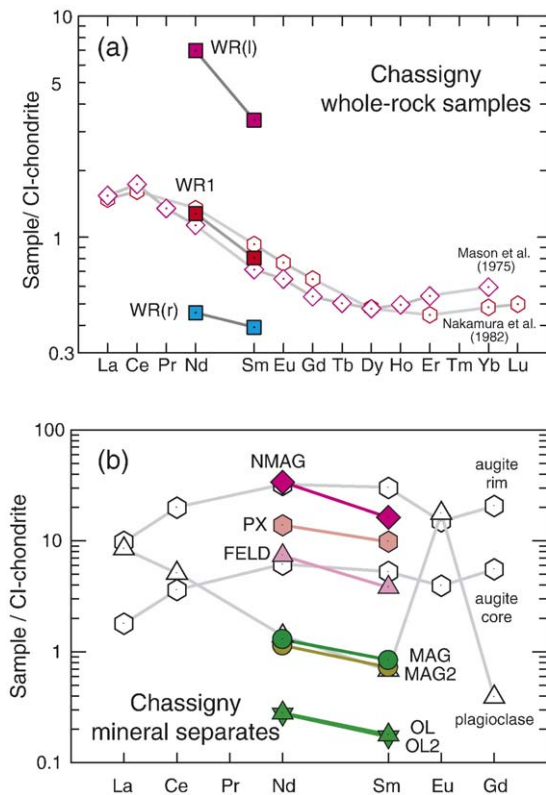


Fig. 3. (a) Samarium and neodymium abundances of whole-rock (WR1), whole-rock leachate WR(l) and whole-rock residue WR(r) samples of Chassigny. The REE abundance patterns of Chassigny by Mason et al. [12] and by Nakamura et al. [14] (La=0.376, Ce=1.04, Nd=0.642, Sm=0.143, Eu=0.0450, Gd=0.132, Dy=0.121, Er=0.0740, Yb=0.0810, Lu=0.0126, values are in ppm) are shown by open symbols for comparison. (b) Samarium and neodymium abundances of mineral separate samples of Chassigny. The light-to-middle REE abundances of constituent phases of Chassigny obtained by ion microprobe [25] are also shown for comparison.

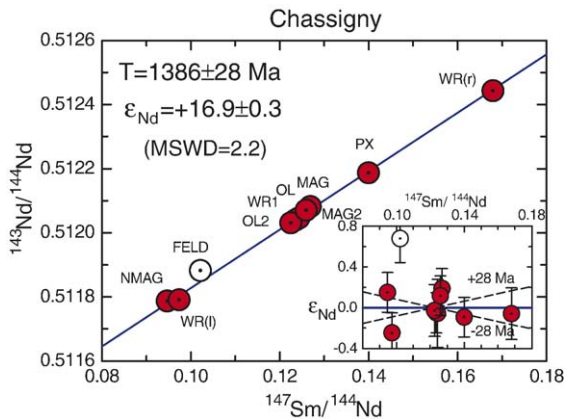


Fig. 4. Samarium–neodymium isotopic data for whole-rock and mineral separates from Chassigny. Nine data points, excluding FELD, define a linear array corresponding to a Sm–Nd age of 1386 ± 28 Ma with an initial $\epsilon_{143\text{Nd}} = +16.9 \pm 0.3$ (MSWD=2.2) for $\lambda(^{147}\text{Sm}) = 6.54 \times 10^{-12} \text{ yr}^{-1}$ using the Williamson regression program [23]. If the Isoplot/Ex program [24] were used, a Sm–Nd age of 1385 ± 47 Ma (MSWD=2.2) with an initial $\epsilon_{143\text{Nd}} = +16.9 \pm 0.4$ would be obtained from these nine data points. The inset shows deviations of $^{143}\text{Nd}/^{144}\text{Nd}$ in ϵ -units for whole-rock and mineral separates of Chassigny relative to the 1386 Ma isochron. Dotted lines on either side of the best-fit line correspond to ± 28 Ma. The FELD point slightly deviates upward from the isochron and/or to the left of it by 0.7 ϵ -units, suggesting a minor isotopic disturbance possibly due to shock metamorphism [5,6], or terrestrial or Martian REE contamination.

uncertainties in the trapped Martian $^{36}\text{Ar}/^{38}\text{Ar}$ ratio, making corrections to these isochron data for cosmogenic ^{36}Ar is not straightforward, and the ^{36}Ar values for this isochron were not so corrected. If we assume that the minimum measured $^{36}\text{Ar}/^{37}\text{Ar}$ ratio (observed at 600 °C) released only cosmogenic ^{36}Ar , we can use this ratio as a

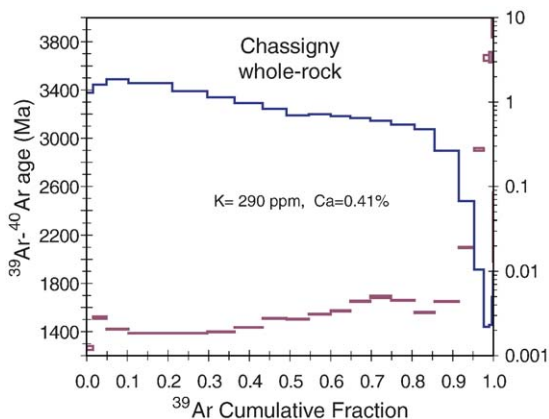


Fig. 5. ^{39}Ar – ^{40}Ar ages (rectangles, left scale) and K/Ca ratios (stepped line, right scale) plotted against cumulative release of ^{39}Ar for stepwise temperature extractions of a sample of Chassigny. The concentrations of potassium and calcium in this sample are indicated on the figure. The widths of age rectangles indicate individual age uncertainties.

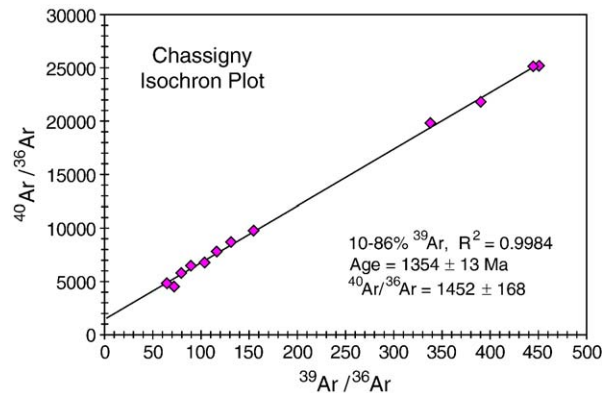


Fig. 6. Isochron plot of $^{40}\text{Ar}/^{36}\text{Ar}$ versus $^{39}\text{Ar}/^{36}\text{Ar}$ for those extractions of Chassigny releasing 10–86% of the total ^{39}Ar . The isochron slope defines an ^{39}Ar – ^{40}Ar age of 1354 ± 13 Ma and a trapped $^{40}\text{Ar}/^{36}\text{Ar}$ intercept of 1452 ± 168 . See text for effects of corrections for cosmogenic ^{36}Ar on this isochron.

basis to apply a maximum correction to the remaining isochron data for cosmogenic ^{36}Ar . With this correction, the isochron age becomes 1415 ± 13 Ma and the isochron intercept becomes 1787 ± 845 (the isochron R^2 value becomes 0.9988). Both the corrected isochron age and $^{40}\text{Ar}/^{36}\text{Ar}$ intercept would be upper limits, as the extraction used to correct for cosmogenic ^{36}Ar likely also released some trapped ^{36}Ar . Further, the 1390 ± 10 Ma age given by extractions releasing ~ 10 –30% of the ^{39}Ar would limit the age to < 1400 Ma. Thus, we conclude that the ^{39}Ar – ^{40}Ar age of Chassigny lies between 1340 and ~ 1400 Ma or 1360_{-20}^{+40} Ma. The less precise Chassigny ^{39}Ar – ^{40}Ar age (1320 ± 70 Ma) measured almost three decades ago and presented by Bogard and Garrison [26] is consistent with this age range. The Sm–Nd isochron age for Chassigny of 1386 ± 28 Ma is identical within error limits with the ^{39}Ar – ^{40}Ar age.

We also examined in an isochron plot ($R^2 = 0.9783$) for those high temperature extractions releasing 86% to $> 99\%$ of the ^{39}Ar and suggesting much older ages. This plot, with corrections for cosmogenic ^{36}Ar applied as above, gives somewhat different results from those of Fig. 6. For these high temperature extractions, the isochron age is 1540 ± 20 Ma and the $^{40}\text{Ar}/^{36}\text{Ar}$ intercept is 518 ± 127 . We do not interpret this slightly older age and lower intercept as being real. Rather we suggest that this high temperature phase of Chassigny contains both trapped Martian interior argon, with a much lower $^{40}\text{Ar}/^{36}\text{Ar}$ ratio than the Martian atmosphere [27] and a component of excess radiogenic ^{40}Ar . Chassigny also contains Martian interior xenon whose isotopic composition is quite different from Martian atmospheric xenon [27]. All these components likely were dissolved in the melt when Chassigny crystallized,

and the trapped ^{40}Ar is more apparent in the olivine because of its much lower potassium content.

4. Discussion

4.1. Isotopic disturbance due to secondary effects

Chassigny experienced shock metamorphism possibly related to its launch from the Martian surface. Shock effects are observed in olivine mosaicism, planar deformation and maskelynitized plagioclase. Shock effects on isotopic systems are limited in Chassigny, compared to those in shergottites. Almost all whole-rock samples and mineral fractions analyzed plot on the Rb–Sr and Sm–Nd isochrons. Moreover, the ^{39}Ar – ^{40}Ar systematics of Chassigny do not show any disturbance. These facts strongly suggest that the K–Ar, Rb–Sr and Sm–Nd systems of Chassigny did not undergo open system behavior during shock metamorphism.

Alteration products including carbonates and sulphates have been reported in Chassigny [7–9] and are considered to have been formed during aqueous alteration event(s) in the Martian surface environment. Compared to the Sm–Nd system, the Rb–Sr system is more susceptible to aqueous alterations. The Rb–Sr isotopic systems of the nakhlites, Nakhla, Lafayette and Y 000593, are disturbed by alteration [28–31]. All the data points for Chassigny, except the WR(l) point which deviates from the 1406 Ma isochron by -2ϵ -units, plot

on the isochron within $\pm 1 \epsilon$ -units, suggesting that isotopic disturbance due to aqueous alteration on the Martian surface, if any, was minor.

4.2. Crystallization age of Chassigny

The new Sm–Nd, Rb–Sr and ^{39}Ar – ^{40}Ar ages are concordant within analytical uncertainties (Table 3). Thus we adopt the Sm–Nd age of 1386 ± 28 Ma as the crystallization age of Chassigny. This age also is in agreement with the two-point Sm–Nd tie-line age (1362 ± 62 Ma) previously obtained by an acid leaching experiment [18], but is ~ 150 Ma older than the Rb–Sr age of 1249 ± 18 Ma (recalculated using $\lambda(^{87}\text{Rb}) = 1.402 \times 10^{-11} \text{ yr}^{-1}$) obtained by Nakamura et al. [15]. Among Chassigny/nakhlite suite rocks so far studied, Chassigny shows the oldest crystallization age.

4.3. Evolution of Martian atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$

Because of the significant potassium and iodine contents of the Martian crust and the elevated $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{129}\text{Xe}/^{132}\text{Xe}$ ratios in the Martian atmosphere compared to Martian interior gases trapped in meteorites, it is conceivable that these isotopic ratios have increased substantially in the Martian atmosphere over time. Estimated Martian atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in shergottites and in Chassigny/nakhlites permit us to

Table 3
Summary of radiometric ages of Chassigny and nakhlites

Meteorite	K–Ar (Ma)	Ar–Ar (Ma)	Rb–Sr* (Ma)	Initial $^{87}\text{Sr}/^{86}\text{Sr}$ **	Sm–Nd (Ma)	Initial $\epsilon_{143\text{Nd}}$	References
Chassigny	1420 \pm 170		1249 \pm 18	0.702543 \pm 51	1362 \pm 62	+15.2 \pm 0.5	[11] [15] [18]
		1320 \pm 70					[26]
		1360 $^{+20}_{-40}$	1406 \pm 14	0.702251 \pm 34	1386 \pm 28	+16.9 \pm 0.3	this work
Nakhla		\sim 1300					[47]
			1299 \pm 139	0.70281 \pm 34			[28]
			1330 \pm 76	0.70254 \pm 23			[28]
			1361 \pm 14	0.702319 \pm 54			[28]
			1230 \pm 18	0.702542 \pm 29			[29]
					1254 \pm 87	+14.7 \pm 0.7	[36]
		1332 \pm 10, 1323 \pm 11					[48]
Governador			1320 \pm 10	0.702362 \pm 13			[49]
Valadares			1190 \pm 24	0.702741 \pm 50	1362 \pm 36	+16.7 \pm 0.3	[20]
Lafayette			1246 \pm 54	0.70258 \pm 10	1320 \pm 33	+16.3 \pm 0.3	[30]
		1322 \pm 10					[48]
Yamato 000593		\leq 1360	1301 \pm 24	0.702525 \pm 27	1315 \pm 18	+15.8 \pm 0.2	[31]
NWA 998					1290 \pm 50	+15.3 \pm 0.9	[43]

* Rb–Sr ages are calculated for the decay constant of $\lambda(^{87}\text{Rb}) = 1.402 \times 10^{-11} \text{ yr}^{-1}$.

** Errors apply last digits.

examine this question. Among Martian meteorites, shergottites display significantly higher shock levels than do nakhlites and Chassigny has an intermediate shock level [5,10]. Trapped atmospheric gases in some shergottites radiometrically dated at less than 200 Ma in age mainly occur in shock-produced glass inclusions and veins [32]. It is generally assumed that shock glass in shergottites formed during meteorite ejection from Mars a few Ma ago. However, trapped Martian atmospheric noble gases (argon, krypton and xenon) in nakhlites are associated not with shock glass but with surfaces of mineral grains and with Martian weathering products radiometrically dated at ~ 600 Ma [30,31,33,34]. Thus, there is a good possibility that Martian atmospheric gases in nakhlites and Chassigny were incorporated at much earlier times than in shergottites.

Above we obtain trapped $^{40}\text{Ar}/^{36}\text{Ar}$ for Chassigny of ~ 1450 without applied cosmogenic ^{36}Ar corrections and ~ 1790 when cosmogenic corrections are applied. We recently reported $^{39}\text{Ar}-^{40}\text{Ar}$ data for nakhlite Y 000593 [31], which also released trapped Martian argon. A highly linear isochron plot, corrected for cosmogenic ^{36}Ar , gave an $^{39}\text{Ar}-^{40}\text{Ar}$ age of 1395 ± 5 Ma and a $^{40}\text{Ar}/^{36}\text{Ar}$ intercept of 1502 ± 159 . Bogard and Garrison [26] suggested that trapped Martian atmospheric argon in some shergottites had a $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of ~ 1750 and that this ratio is not greater than ~ 1900 . In contrast, an analysis of the very highly shocked Martian dunite NWA 2737 did not indicate any trapped Martian atmospheric argon [35]. The general similarity in trapped $^{40}\text{Ar}/^{36}\text{Ar}$ ratios between shergottites and chassignites/nakhlites suggests that this ratio may not have changed appreciably over the past ≥ 600 Ma, implying low degassing rates of radiogenic ^{40}Ar from the Martian surface over this time.

4.4. Isotopic characteristics of the source material

The source materials for the Martian dunite/clinopyroxenite meteorite suite (Chassigny and the nakhlites) have been modeled on the basis of trace element abundances as well as isotopic signatures, and have been suggested to have been derived from early differentiated, LREE-depleted mantle sources, e.g., [15,17,20,36].

Here we assume that the Martian mantle formed at $T_0=4553$ Ma, which is ~ 14 Ma after solar system formation ~ 4567 Ma ago, assuming differentiation of Martian mantle occurred at a very early stage (between ~ 10 and 25 Ma after beginning of the solar system) based on recent $^{182}\text{Hf}-^{182}\text{W}$ and $^{146}\text{Sm}-^{142}\text{Nd}$ isotopic

studies [37–39]. We also assume a chondritic uniform reservoir (i.e., CHUR) with an initial $^{143}\text{Nd}/^{144}\text{Nd}=0.505902$ at the time of differentiation (4553 Ma). Further, we assume a mantle with a uniform Martian initial $^{87}\text{Sr}/^{86}\text{Sr}=0.698972$ at 4543 Ma, derived from $^{87}\text{Sr}/^{86}\text{Sr}=0.698972 \pm 0.000008$ [19] for the 4558 Ma angrite Lewis Cliff (LEW) 86010 [19]. We also assume $^{87}\text{Rb}/^{86}\text{Sr}=0.13$ for bulk Mars [20]. Then, a two-stage model for Chassigny and nakhlites (Nakhla, Governador Valadares, Lafayette, NWA 998 and Y 000593) shows that the time-averaged $^{87}\text{Rb}/^{86}\text{Sr}$ ratios for the sources of Chassigny and nakhlites are 0.073 and 0.073–0.082 (Fig. 7a), respectively, and the time-averaged $^{147}\text{Sm}/^{144}\text{Nd}$ ratio for the mantle source of Chassigny is 0.240 (Fig. 7b,c). Selection of the time of Chassigny/nakhlite source formation (between ~ 10 and 25 Ma after beginning of the solar system) does not affect calculated $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios for the mantle sources (usually variations are less than 0.5%). Present-day $\varepsilon_{87\text{Sr}}$ and $\varepsilon_{143\text{Nd}}$ values of Chassigny are -33 (Fig. 7a) and $+4$ (Fig. 7b,c), respectively.

On the basis of the Sm–Nd isotopic signatures of Chassigny and the nakhlites, some characteristics of the parent magmas and mantle source materials of these meteorites can be inferred as follows. Chassigny, Governador Valadares and possibly Lafayette could have come from very similar mantle sources because they appear to be the same age and have the same initial neodymium isotopic composition within analytical error limits (Table 3 and Fig. 7c). Nakhla, NWA 998 and Y 000593 appear to be from similar but distinct sources at different times (see Table 3) with time-averaged $^{147}\text{Sm}/^{144}\text{Nd}$ ratios in the range 0.233–0.236 (Fig. 7c). As already has been suggested, the mantle sources of Chassigny and the nakhlites were highly depleted in LREE and rubidium. Parent/daughter fractionations (Sm/Nd and Rb/Sr, respectively) during basalt generation (i.e., partial melting of source materials) were different among the Chassigny–nakhlite suite rocks.

4.5. Possible source crater of chassignites–nakhlites

Chassigny and all nakhlites so far studied have undergone a similar evolution history and are commonly considered to have been launched from Mars by a single impact event. A possible source crater of Chassigny and nakhlites might be expected to contain chassignite–nakhlite signatures, i.e., olivine (Fo_{25-35} or Fo_{68-79}) plus clinopyroxene assemblages. Chassigny and some nakhlites may represent samples of slightly different ages (see Table 3) and neodymium isotopic signatures as shown above. This indicates that the Chassigny–

nakhlite suite does not represent a single cumulate pile but several different lava flows at different times, although some workers favored origins of nakhrites at different depths within a single cumulate pile. [40,41]. Magmatic activities in the region probably continued for at least 50 Ma (Fig. 7c).

Although the radiometric ages of the Chassigny/nakhrites are in general well-defined, some isotopic disturbances are clearly observed in the Rb–Sr system of nakhrites. Nakhlite alteration products including carbonates, sulphates and iddingsite could be the cause of this problem. Unfortunately, it is still unclear whether iddingsite formed during a single alteration event or during multiple events. If the iddingsite Rb–Sr ages

observed in Lafayette and Y 000593 represent formation of alteration material as final brine evaporates possessing relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.7042–0.7046 [30,31], then a final aqueous alteration occurred within the region at ~ 650 Ma ago. A crater size larger than 7 km in diameter is expected to be required to produce a sufficient number of fragments of the correct size to account for nine chassignite–nakhlite meteorites having a total weight of ~ 30 kg [42].

5. Conclusions

We have undertaken new Rb–Sr, Sm–Nd and ^{39}Ar – ^{40}Ar isotopic analyses of Chassigny and have precisely determined its crystallization age of 1386 ± 28 Ma, the oldest Sm–Nd age so far reported for chassignite/nakhlite suite rocks. The obtained age and initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $\epsilon_{143}\text{Nd}$ isotopic signatures suggest that Chassigny crystallized from low Rb/Sr, LREE depleted source materials ~ 1390 Ma ago, and that chassignite/nakhlite volcanism lasted at least 50 Ma.

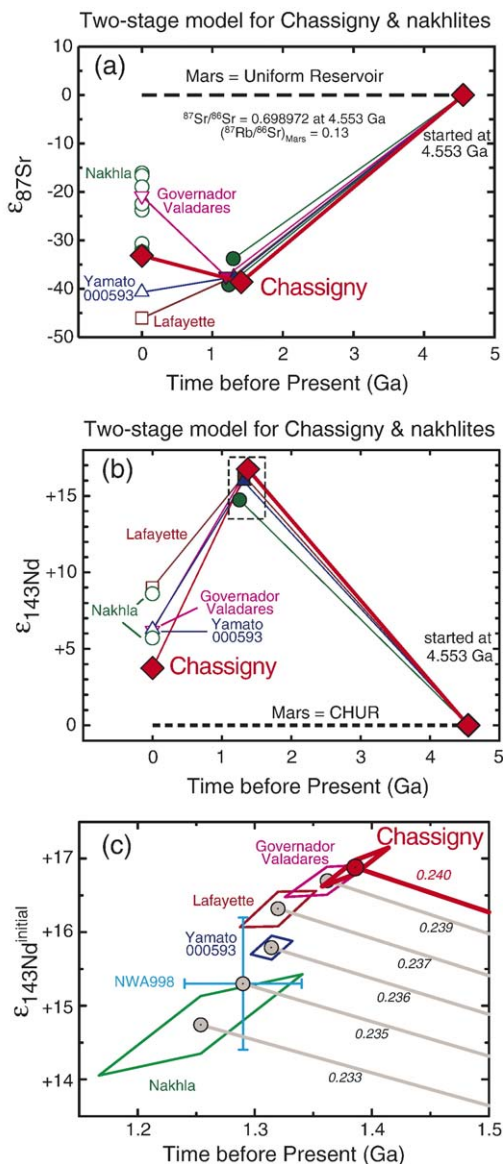


Fig. 7. A simple two-stage model for T (ages) versus initial (a) $^{87}\text{Sr}/^{86}\text{Sr}$ and (b, c) $^{143}\text{Nd}/^{144}\text{Nd}$ evolution diagrams for Chassigny and nakhrites (Nakhla, Governorador Valadares, Lafayette, NWA 998 and Y 000593). Initial values are represented in ϵ -units. Nakhrites data are from [20,28–31,43]. Present-day $\epsilon_{87}\text{Sr}$ and $\epsilon_{143}\text{Nd}$ values are calculated from whole-rock samples. Nakhla whole-rock samples show wide variations of the present-day $\epsilon_{87}\text{Sr}$ and $\epsilon_{143}\text{Nd}$ values. We assume that the Martian mantle formed at $T_0 = 4553$ Ma, which is ~ 14 Ma after solar system formation 4567 Ma ago. (a) A mantle with a uniform Martian initial $^{87}\text{Sr}/^{86}\text{Sr} = 0.698972$ at 4553 Ma, derived from $^{87}\text{Sr}/^{86}\text{Sr} = 0.698972 \pm 0.00008$ measured by Nyquist et al. [19] for the 4558 Ma angrite LEW 86010 [44], is assumed. We also assume $^{87}\text{Rb}/^{86}\text{Sr} = 0.13$ for bulk Mars [20] to calculate the $\epsilon_{87}\text{Sr}$ values. The large negative initial $\epsilon_{87}\text{Sr}$ values at 1200–1400 Ma for Chassigny and nakhrites indicate that the mantle sources of Chassigny/nakhrites were highly depleted in Rb/Sr relative to estimated bulk Mars. The present-day $\epsilon_{87}\text{Sr}$ values of Nakhla vary from -30 to -15 depending on the whole-rock samples used [28,29]. (b) A Martian mantle with a chondritic uniform reservoir (CHUR) with an initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.505902 at 4553 Ma (i.e., present-day $^{143}\text{Nd}/^{144}\text{Nd} = 0.511847$) is assumed [45]. The $\epsilon_{143}\text{Nd}$ values were calculated relative to the present-day $^{143}\text{Nd}/^{144}\text{Nd} = 0.511847$ and $^{147}\text{Sm}/^{144}\text{Nd} = 0.1967$ [45,46]. The present-day $\epsilon_{143}\text{Nd}$ values of the Nakhla whole-rock samples, WR-1 and WR-2, are $+5.7$ and $+8.8$, respectively [36]. (c) Enlarged view of data in the dotted square in (b). The data for individual meteorites are represented by parallelograms constructed according to their ages and initial $\epsilon_{143}\text{Nd}$ parameters. Values in italics represent time-averaged source $^{147}\text{Sm}/^{144}\text{Nd}$ ratios. Error parallelograms for Chassigny (this work), Governorador Valadares [20] and possibly Lafayette [30] overlap, suggesting that these meteorites could have come from very similar LREE-depleted mantle sources. Distinct data for Nakhla [36], NWA 998 [43] and Y 000593 [31] suggest that they represent different lava flows at different times from very similar LREE-depleted mantle sources.

The chassignite/nakhlite suite rocks derived from different lava flows or subsurface sills and they probably were launched from Mars by a single impact event. The trapped Martian atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in Chassigny, nakhlites and shergottite impact glass are similar and possibly suggest minimal change in this ratio over the past ≥ 600 Ma.

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Appendix A. Argon isotopic data for Chassigny

Temp. (°C)	^{39}Ar (cm ³ STP/g)	Age (Ma) ± error	K/Ca ratio ± error	$^{40}\text{Ar}/^{39}\text{Ar}$ ± error	$^{38}\text{Ar}/^{39}\text{Ar}$ ± error	$^{37}\text{Ar}/^{39}\text{Ar}$ ± error	$^{36}\text{Ar}/^{39}\text{Ar}$ ± error
300	6.991E-10	1280	1.294	49.06	0.340	0.425	0.0434
		17	0.034	0.90	0.007	0.011	0.0031
400	1.394E-09	1534	1.611	63.67	1.150	0.341	0.00839
		10	0.027	0.59	0.012	0.0058	0.00120
475	2.315E-09	1437	1.870	57.83	0.565	0.294	0.00543
		5.6	0.024	0.27	0.003	0.0037	0.00090
550	4.659E-09	1403	1.670	55.88	0.403	0.329	0.00256
		3.8	0.018	0.11	0.002	0.0035	0.00042
580	3.664E-09	1403	1.350	55.91	0.337	0.407	0.00222
		3.8	0.014	0.12	0.002	0.0044	0.00066
600	2.908E-09	1414	1.142	56.54	0.298	0.482	0.00225
		4.0	0.012	0.14	0.002	0.0052	0.00056
620	2.951E-09	1451	0.969	58.69	0.285	0.567	0.00296
		4.3	0.010	0.16	0.002	0.0061	0.00051
635	2.545E-09	1526	0.8316	63.18	0.298	0.661	0.00647
		4.6	0.0090	0.19	0.002	0.0072	0.00068
650	2.342E-09	1521	0.6918	62.90	0.348	0.795	0.0139
		4.6	0.0075	0.19	0.002	0.0086	0.00079
665	2.319E-09	1562	0.7152	65.39	0.251	0.769	0.00964
		4.6	0.0078	0.19	0.002	0.0084	0.00080
680	2.093E-09	1589	0.6824	67.13	0.232	0.806	0.00860
		6.2	0.0080	0.32	0.002	0.0095	0.00130
700	2.107E-09	1670	0.6475	72.37	0.252	0.849	0.0112
		6.3	0.0076	0.34	0.002	0.0099	0.00096
725	2.195E-09	1707	0.6032	74.84	0.278	0.912	0.0155
		11	0.0087	0.74	0.003	0.013	0.00091
760	2.486E-09	1679	0.5405	72.97	0.372	1.02	0.0126
		5.1	0.0059	0.24	0.002	0.011	0.00072
800	2.122E-09	1577	0.4747	66.34	0.573	1.16	0.00762
		5.4	0.0053	0.26	0.003	0.013	0.00085
890	2.557E-09	1670	0.2639	72.35	1.684	2.08	0.0246
		4.9	0.0028	0.22	0.006	0.022	0.00049
1000	1.636E-09	2117	0.06708	106.12	3.627	8.20	0.0984
		6.6	0.00074	0.44	0.016	0.09	0.0013
1100	9.936E-10	2932	0.01051	193.8	7.624	52.3	0.385
		12	0.00014	1.5	0.076	0.70	0.0056
1200	5.642E-10	3691	0.00220	320.1	5.992	250	1.20
		25	0.00004	4.9	0.094	4.7	0.021

(continued on next page)

Appendix A (continued)

Temp. (°C)	³⁹ Ar (cm ³ STP/g)	Age (Ma) ± error	K/Ca ratio ± error	⁴⁰ Ar/ ³⁹ Ar ± error	³⁸ Ar/ ³⁹ Ar ± error	³⁷ Ar/ ³⁹ Ar ± error	³⁶ Ar/ ³⁹ Ar ± error
1300	2.853E-10	3698 43	0.00232 0.00007	321.5 8.7	40.7 1.1	237 7.2	1.85 0.053
1400	1.124E-10	3958 95	0.00496 0.00031	379 22	3.98 0.24	111 7.0	2.03 0.13
1500	5.296E-11	2290 290	0.01000 0.00250	121 27	2.02 0.49	55.0 14.0	1.28 0.31

Columns give (left to right) extraction temperature (in °C), ³⁹Ar concentration (in cm³ STP/g), calculated ³⁹Ar–⁴⁰Ar age (in Ma), K/Ca ratio, and ⁴⁰Ar/³⁹Ar, ³⁸Ar/³⁹Ar, ³⁷Ar/³⁹Ar and ³⁶Ar/³⁹Ar ratios. Uncertainties are given beneath each age and each ratio.

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