Martian mantle signatures in Yamato nakhlites

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Abstract: We report nitrogen and heavy noble gas isotopic abundances in the Yamato nakhlites Y000593 and Y000749 and infer isotopic signatures for the magma source region in Mars. The nitrogen signature $\delta^{15}N=13\pm1\%$ appears in broad plateau releases of both nakhlites and also has previously been observed in Nakhla and in Chassigny. This signature differs from the primitive indigenous nitrogen signature $(\delta^{15}N = -30\%)$ and, strikingly, from nitrogen in the modern Martian atmosphere. It demonstrates that exchanges between the solid planet and its modern atmosphere have been very limited. The xenon isotopic records support this conclusion. In nakhlite Y000749 radiogenic ¹²⁹Xe is observed in one temperature fraction, while a five times larger component is observed in several steps of Y000593. The lack of an association with fission Xe or with indigenous Xe from the mantle source region suggests a crustal source. A crustal storage of the extinct ¹²⁹I was previously invoked to account for radiogenic ¹²⁹Xe in the Martian atmosphere. Fission Xe components due to extinct ²⁴⁴Pu were identified in both nakhlites. These records show that the magma source region had assimilated and retained fission gas since the early differentiation of Mars. The measured concentrations of ⁴⁰Ar exceed the amounts produced from the decay of ⁴⁰K in 1.3 Ga and document that the magma inherited some radiogenic ⁴⁰Ar, together with fission gas. CRE ages based on spallation ¹⁵N_c and ³⁸Ar are consistent with a reported ⁸¹Kr-⁸³Kr age and CRE ages for other nakhlites, confirming identical ejection ages for all nakhlites.

key words: Mars, nakhlites, fission xenon, radiogenic xenon, nitrogen signatures

1. Introduction

Chronologies based on extinct radionuclides in SNC meteorites (*e.g.* Halliday *et al.*, 2001) show that Mars accreted on time scales of several Ma. Constraints on the early evolution of Martian volatiles were obtained from fission xenon records in Chassigny and ALH84001 (Mathew and Marti, 2001) and in nakhlites (Mathew and Marti, 2002; Marty and Marti, 2002; Mathew *et al.*, 2003). The identification of mantle reservoirs is based on Chassigny data, which Mathew and Marti (2001) characterized as primitive component "Chass-S", with a solar-type isotopic signature of Xe and a light nitrogen signature ($\delta^{15}N = -30\%$). This component was enriched in an olivine separate of Chassigny, lacking radiogenic ¹²⁹Xe and fission Xe. These properties can either be due to a late incorporation, after decay of ¹²⁹I and ²⁴⁴Pu, or it may represent an interior

reservoir with substantial Xe concentrations, which could mask *in-situ* produced components.

Mathew and Marti (2001) noted that a second xenon component, Chass-E (Evolved), is related to Chass-S by the addition of fission Xe due to extinct ²⁴⁴Pu. This Chass-E xenon signature implied that fission Xe was mixed with Chass-S Xe at the time of, or prior to, its incorporation. The fission gas is not due to in-situ decay of ²⁴⁴Pu in Chassigny. Both Chass-S and Chass-E xenon components apparently represent indigenous reservoirs that are characterized by low ¹²⁹Xe/¹³²Xe (<1.07) ratios. In those Chassigny samples Mathew and Marti (2001) also found light N ($\delta^{15}N \le -21\%$) isotopic signatures (in the $\le 300^{\circ}$ C extractions), while the heaviest observed signature in the low-temperature range was $\delta^{15}N = +15\%$ at 400°C. Light N ($\delta^{15}N = -30\%$) was interpreted to represent a primitive indigenous nitrogen signature.

The nakhlites from Yamato Mountains (Y000593 and Y000749) offer new opportunities to probe the Martian mantle. The research is carried out in consortium mode and permits petrographic, chemical and isotopic investigations on the same material (Misawa *et al.*, 2003). Marty and Marti (2002) argued that the presence of ²⁴⁴Pu-derived fission Xe presents evidence for closed system evolution of the mantle, which indicates quite different geodynamic regimes for planets Earth and Mars. Records from these nakhlites may provide further insights into mantle characteristics, as well as data regarding the question of survival of extinct radionuclide signatures in events capable of resetting the ⁴⁰K-⁴⁰Ar, ⁸⁷Rb-⁸⁷Sr and ¹⁴⁷Sm-¹⁴³Nd clocks recorded in the 1.3 Ga ages of nakhlites (*e.g.* Nyquist *et al.*, 2001). If exchanges with atmospheric gases did occur, also information on paleoatmospheres may be secured.

The Xe signatures observed in ALH84001 were interpreted to represent those of an ancient Martian atmosphere (Gilmour et al., 1998; Mathew and Marti, 2001), while a more recent atmospheric signature, consistent with that of the modern atmosphere, was identified in a few temperature fractions of Nakhla (Mathew and Marti, 2002). The component with Chass-S xenon composition shows strong elemental fractionation in the heavy noble gas abundances: ³⁶Ar/¹³²Xe and ⁸⁴Kr/¹³²Xe ratios were constrained to be <5 and <1.1, respectively (Mathew and Marti, 2001), and may be compared with estimated solar ratios ³⁶Ar/¹³²Xe and ⁸⁴Kr/¹³²Xe of 67000 and 20, respectively (Anders and Grevesse, 1989). If representative of the mantle, this evidence for noble gas fractionation may help to characterize differentiation processes during the formation of Mars. For example, an origin due to adsorption by carbon-rich matter during accretion of the Martian protoplanetesimals would favor heavy noble gases, and carbon sub-micron grains are efficient noble gas trappers (Niemeyer and Marti, 1981). These authors showed that trapped noble gases are loosely bound and elementally strongly fractionated, while no isotopic fractionations were detected. Their results also suggest, that if carbon-rich phases were in fact carriers of noble gases from early solar system reservoirs, the observed similarities in elemental fractionations for the atmospheres of planets Earth and Mars could be understood, even for fairly different trapping conditions. An identification of paleoatmospheric components could provide information for an assessment of isotopic evolutions during the period of heavy bombardment (Mathew et al., 1998).

2. Mass spectrometry

Several fragments of both nakhlites Y000593 and Y000749 were wrapped in Au foils and loaded into the gas extraction and purification system. The meteorites were step-heated by an external resistance heater up to 1040°C in a double walled quartz system within a separately pumped vacuum jacket. Samples were then transferred *in vacuo* into a Mo crucible, mounted in a double walled quartz system with cooling water, for step-heating by radio frequency up to the melting temperature. Extraction blanks were measured at the same temperatures between sample measurements. The extraction blanks for N were 0.1–0.4 ng for the $\leq 1400^{\circ}$ C steps and was of atmospheric composition (δ^{15} N=0±3‰). Typical blanks for ³⁶Ar and ¹³²Xe (of atmospheric composition) were 1–3×10⁻¹² cm³STP/g and 1–2×10⁻¹⁴ cm³STP/g, respectively. Details of the analyzing procedure were described previously (Mathew and Marti, 2002). The propagated uncertainties in the isotope ratios include statistical errors and uncertainties in the discrimination and in blank corrections.

3. Fission Xe in nakhlites

A remarkable feature of the 1.3 Ga old NC meteorites, Chassigny as well as the nakhlites Nakhla and NWA817, is that they contain fission Xe components produced mostly by the decay of extinct ²⁴⁴Pu. The Xe gas was released at temperatures above 900°C and was well mixed with indigenous (Chass-S) Xe. A model calculation of the initial ²⁴⁴Pu content of Mars (Marty and Marti, 2002) suggests that it was consistent with the chondritic abundance. Since nakhlites are considered to represent cumulates of magmas derived from mantle reservoirs, Mathew *et al.* (2003) used Nd and U as adequate geochemical proxies for Pu to trace the behavior of Pu during fractionation processes. In a study of Xe isotopes in the Yamato nakhlites Okazaki *et al.* (2003) noted excesses in ¹³⁶Xe and suggested that fission xenon may be present.

We now discuss the Yamato nakhlite Xe data (Table 1) which show correlated excesses on all heavy Xe isotopes, and the relative yields identify the source as fission Xe from extinct ²⁴⁴Pu, as was observed for other nakhlites (Mathew and Marti, 2002; Mathew et al., 2003). We take the approach used by these authors to disentangle the various Xe components. In a first step, the spallation Xe component has to be evaluated and subtracted from the measured data. The Y000593 Xe data in the 800° and 900°C steps (Table 1) show only very small spallation components. For the higher temperature steps the subtraction method is used for fractions with constant fission to indigenous xenon ratios, but variable spallation components. The evaluated spallation Xe spectra show minor differences in the relative spallation yields, especially for the early releases. A slightly steeper spectrum and a very low relative ¹³¹Xe yield may signal spallation yields from fractionated LREE in phosphates and glassy mesostasis (Wadhwa and Crozaz, 2003). Therefore, we adopt inferred spallation spectra as given in Appendix A, which reports the spallation-corrected Xe data. We see from the isotopic correlation of spallation-corrected ratios (Fig. 1) that all data plot close to the tie-line of Chass-S Xe and fission Xe. We further note in this figure that, although well-mixed components were reported in nakhlites (Mathew and Marti, 2002; Mathew

Temp.	¹³² Xe				¹³² Xe =	1.00			
(°C)	$10^{-12} \text{ cm}^3/\text{g}$	¹²⁴ Xe	¹²⁶ Xe	¹²⁸ Xe	¹²⁹ Xe	¹³⁰ Xe	¹³¹ Xe	¹³⁴ Xe	¹³⁶ Xe
			Yamato Na	khlite Y0007	49,51 (381	mg)			
800	0.859	0.0044	0.0040	0.0827	1.024	0.1570	0.7980	0.3880	0.3270
		± 7	9	27	13	25	130	30	23
1000	4.217	0.0089	0.0138	0.0975	1.020	0.1660	0.8450	0.3840	0.3260
		±3	3	9	7	15	110	20	11
1200	7.678	0.0077	0.0087	0.0897	1.026	0.1634	0.7980	0.3880	0.3290
		± 3	2	6	4	8	45	25	15
1400	3.941	0.0312	0.0483	0.1406	1.160	0.1902	0.9160	0.3974	0.3300
		±10	15	15	4	13	25	12	10
1550	2.370	0.0116	0.0147	0.0945	1.035	0.1620	0.8240	0.3910	0.3320
		± 6	7	16	6	15	35	20	16
			Yamato Na	akhlite Y0005	593,85 (484 i	mg)			
600	0.643	0.0037	0.0036	0.0796	1.096	0.1530	0.8090	0.3870	0.3319
		± 8	7	18	10	15	100	52	43
800	0.815	0.0042	0.0033	0.0813	1.174	0.1560	0.8150	0.3852	0.3284
		± 7	7	13	9	14	95	48	41
900	0.786	0.0044	0.0038	0.0822	1.203	0.1573	0.8180	0.3861	0.3281
		± 8	7	14	10	14	96	45	39
1000	1.928	0.0258	0.0422	0.1376	1.278	0.1840	0.8570	0.3880	0.3300
		±10	11	12	9	11	74	37	30
1200	1.080	0.0078	0.0105	0.0889	1.047	0.1580	0.8220	0.3908	0.3371
		± 6	7	11	8	12	85	38	32
1400	5.130	0.0166	0.0256	0.1082	1.253	0.1680	0.8410	0.3946	0.3365
		± 8	9	9	7	10	76	33	29
1550	4.676	0.0565	0.0916	0.2019	1.329	0.2290	0.9450	0.3923	0.3183
		±10	13	10	7	10	80	31	27
1650	0.458	0.0546	0.0904	0.1992	1.319	0.2241	0.9510	0.3918	0.3207
		±12	14	13	11	13	91	38	33

Table 1. Measured Xe isotopic abundances in Yamato nakhlites.

The ¹³²Xe concentrations are in units $(10^{-12} \text{ cm}^3 \text{STP/g})$; only data for temperature steps $\geq 800^{\circ}\text{C}$ are given (low temperature extractions were consistent with terrestrial Xe). Uncertainties included are those in the least significant figures of the isotopic ratios (95% confidence levels).

et al., 2003), some variability is present in the Yamato nakhlites. Some temperature fractions plot halfway between data of Chass-E and the other Yamato temperature fractions and reveal fission Xe/Chass-S Xe mixing ratios which are smaller. These systematics indicate that although fission gas has generally been well assimilated in the nakhlite magma, complete mixing with indigenous Chass-S Xe was not achieved. The isotope ratios shown in Fig. 2 permit the identification of the fission source. First, we note a confirmation of varying mixing ratios fission Xe/indigenous Xe and a trend line which documents that the fission component is dominated by Xe from extinct ²⁴⁴Pu, but minor contributions from ²³⁸U can not be excluded. However, *in situ*-produced fission Xe from ²³⁸U during 1.3 Ga, based on the measured U abundance of 55 ppb (Dreibus *et al.*, 2003) can only account for ~5% of the observed fission Xe (Table 1). Figures 1



Fig. 1. Spallation-corrected ¹³⁰Xe/¹³⁶Xe vs. ¹²⁸Xe/¹³⁶Xe ratios (Appendix A) in Y000749, Y000593 and other nakhlites. Isotopic shifts due to the addition of fission Xe components to Chass-S Xe are not uniform, but the observed shifts exceed those due to fission of ²³⁸U in 1.3 Ga. NWA 817 data are from Mathew et al. (2003), Nakhla data are from Mathew and Marti (2002) and Chass-S and Chass-E data are from Mathew and Marti (2001).

and 2 further illustrate that Y000749 Xe data cannot be explained as mixtures of modern Martian atmospheric Xe components with fission gas. We return to this issue again when we discuss ¹²⁹Xe data.

4. Radiogenic ¹²⁹Xe_r on Mars

There has been controversy in the literature (Drake *et al.*, 1994; Okazaki *et al.*, 2003) regarding the origin of the ¹²⁹Xe excesses in nakhlites, since the data do not fit a



Fig. 2. Xe isotopic ratios (Appendix A) ¹³²Xe/¹³⁶Xe vs. ¹²⁸Xe/¹³⁶Xe in Y000749, Y000593 and other nakhlites. The shifts due to a fission Xe component identify extinct ²⁴⁴Pu as the major contributor. NWA817, Nakhla and Chassigny data are from the same sources as Fig. 1.

tie-line of Chass-S (Mars mantle) and Mars atmosphere (Fig. 3), as observed in shergottite glasses. Therefore, the suggestion was made that nakhlite xenon data are affected by iddingsite with a low ratio 84 Kr/ 132 Xe=6, which might suggest elemental fractionation in the iddingsite formation process on Mars. On the other hand, Mathew and Marti (2002) in their study of Nakhla showed that Xe data in the temperature steps 800° to 1000° C fit such a tie-line and probably represent a modern atmospheric component. However, the >1000°C data of Nakhla show indigenous Xe with the Chass-S isotopic composition, and are inconsistent with isotopic signatures of modern atmospheric gases. A different source for radiogenic 129 Xe excesses is required, as



Fig. 3. Plot of the spallation-corrected ¹²⁹Xe/¹³²Xe vs. ¹³⁶Xe/¹³²Xe ratios (Appendix A) in Y000749, Y000593 and other nakhlites. Mixtures of Chass-S Xe with Martian atmospheric Xe cannot explain the observed trends. Figure also shows that radiogenic ¹²⁹Xe excesses and fission excesses are decoupled.

mantle (Chass-S) Xe does not carry such excesses. Mathew *et al.* (2003) confirmed variable excesses of radiogenic ¹²⁹Xe_r in recently discovered SNC meteorites which are not related to the modern Martian atmosphere. The observed excesses of radiogenic ¹²⁹Xe in nakhlites indicate a source inside the solid planet.

More information on the source of radiogenic ¹²⁹Xe can be found by analyzing the associations with interior components. We discussed the fission component in the Yamato nakhlites and can use the data in Appendix A to assess a correlation of ¹²⁹Xe_r with fission gas. ¹²⁹I ($t_{1/2}$ =16 Ma) and ²⁴⁴Pu are now extinct, but radiogenic and fission Xe components recorded decay processes in the early history of Mars. If the observed radiogenic ¹²⁹Xe_r component was cycled through the mantle, it should be well mixed with the fission component which in turn was rather well mixed with indigenous mantle Xe, as discussed earlier. In Fig. 3 (see also Table 1) we observe variable ratios ¹²⁹Xe/¹³²Xe, which are decoupled from those of fission Xe and indigenous mantle gas. While in nakhlite Y000749 only the 1400°C step shows a radiogenic component. Radiogenic ¹²⁹Xe (3.0×10^{-12} cm³STP/g) is about 5× larger than in Y000749, and ratios ¹²⁹Xe_r/¹³⁶Xe_f are 4.4 and 0.7, respectively. This record shows that although radiogenic ¹²⁹Xe was not stored and mixed in the nakhlite magma source, it represents a radiogenic

component from extinct ¹²⁹I and must have been stored in the solid planet. In their study of xenon isotope correlations in nakhlites Y000593, Y000749 and Y000802, Okazaki *et al.* (2003) noted that there is no simple correlation between excesses of fission ¹³⁶Xe and radiogenic ¹²⁹Xe, and they suggest that the excess could come from the Mars atmosphere. However, this interpretation has to be rejected, since indigenous Xe in the nakhlites has the isotopic signature of Chass-S xenon and differs from atmospheric Xe.

Martian crustal storage and assimilation into the ascending magma is an option. The ¹²⁹I storage in the crust during the early differentiation of Mars, and a release of radiogenic ¹²⁹Xe_r after its decay were suggested by Dreibus and Wänke (1987) and by Musselwhite and Drake (2000) to account for the high ratio ¹²⁹Xe/¹³²Xe in the present atmosphere. Dreibus and Wänke (1987) noted that iodine is an incompatible and highly volatile element which could have been extracted from hot rock in the interior, in the presence of water, and incorporated into crustal rock. Musselwhite and Drake (2000) determined the solubility of iodine in a range of synthetic basaltic liquids and found values which exceed the solubility of Xe by a few orders of magnitude. They suggest that in a second stage of outgassing the atmospheric ¹²⁹Xe/¹³²Xe can be explained, if it follows a stage of an efficient removal of atmospheric gases by hydrodynamic escape and impact erosion. In these models assimilation of crustal radiogenic xenon into the lava (probably by means of a crustal carrier) may account for variable amounts in the two paired nakhlites, as well as the observed lack of correlation between radiogenic and fission components. Depletion of iodine in the mantle during the early large-scale differentiation event (e.g. Halliday et al., 2001; Blichert-Toft et al., 1999), is supported by the near absence of radiogenic $^{129}Xe_r$ in Chass-S xenon. Since an assimilation of crustal material in lavas is here implied, are there other records which support such an origin? The heavy nitrogen signature in the modern Martian atmosphere contrasts with light ancient nitrogen ($\delta^{15}N \sim -30\%$) as observed in ALH84001 (Marti and Mathew, 2000), but nitrogen signatures in the Martian crust have not been studied.

5. Nitrogen in nakhlites

Nitrogen concentrations in Yamato nakhlites (Table 2) are similar to those in Nakhla, but smaller than in NWA 817 (Mathew *et al.*, 2003). The isotopic signatures observed in stepwise pyrolysis of the Yamato nakhlites are reported in Table 2 and are shown in Fig. 4. The low-temperature data ($<300^{\circ}$ C) are afflicted by terrestrial contaminants; the temperature fractions in Y000749 show a small component of light nitrogen. In Y000749 a broad release plateau (500° to 1040° C) with signature δ^{15} N = +13% was observed. A high-resolution investigation of this component was carried out in nakhlite Y000593. The broad plateau with δ^{15} N = +13% was confirmed in a total of 13 steps over an intermediate temperature range from 350° to 1040° C, before a spallation 15 N_c component appears in steps above this temperature. This nitrogen component is not only observed in the Yamato nakhlites, but also in the plateau-release of Nakhla (Mathew and Marti, 2002), in Chassigny (Mathew and Marti, 2001), and apparently also in high-temperature steps of NWA817 (Mathew *et al.*, 2003). These

Sample	T (°C)	N	δ ¹⁵ N (‰)	Sample	T (°C)	Ν	δ ¹⁵ N (‰)
		(ppm)				(ppm)	
Nakhlite	180	0.005	-3.4 ±3.9	Nakhlite	120	0.007	3.9 ±4.4
Y000749,51	250	0.12	-2.4 ±3.7	Y000593,85	200	0.032	0.1 ±1.7
(381 mg)	300	0.06	-3.4 ±2.4	(484 mg)	250	0.038	1.0 ± 2.2
	400	0.01	6.0 ± 3.1		300	0.082	3.3 ±1.4
	500	0.04	6.1 ± 2.0		350	0.102	6.7 ±1.8
	600	0.17	10.8 ± 1.2		400	0.072	13.9 ± 1.6
	700	0.14	12.4 ±3.2		450	0.061	13.7 ± 2.4
	450C	0.10	2.0 ± 0.8		500	0.052	13.3 ±3.5
	800	0.061	12.0 ± 0.5		550	0.074	13.8 ± 1.2
	900	0.017	13.1 ±4.7		600	0.081	13.2 ± 1.5
	1040	0.026	12.8 ± 3.0		650	0.089	13.7 ± 1.4
	1200	0.116	60.3 ±2.2		700	0.119	13.2 ± 1.6
	1400	0.191	114.0 ± 2.8		750	0.126	13.0 ± 0.8
	1650	0.054	95.3 ±4.9		800	0.076	13.2 ±0.9
	Total	1.11			850	0.087	13.8 ± 1.4
					900	0.091	12.9 ± 1.0
					950	0.030	13.5 ± 1.3
					1040	0.031	13.1 ± 1.8
					1200	0.084	59.1 ±2.5
					1400	0.162	68.2 ± 2.0
					1550	0.176	109.0 ±2.2
					1650	0.019	65.6 ±4.2
					Total	1.691	

Table 2. N concentrations and isotopic signatures in the Yamato nakhlites Y000749,51 and Y000593,85.

data show the presence of nitrogen with this signature in nakhlite magma sources in the Martian mantle.

From the observed excesses in δ^{15} N (relative to the $\pm 13\%$ signature) in steps above 1040°C we calculate spallation concentrations ${}^{15}N_c = 134$ and 118 pg in Y000593 and Y000749, respectively. This yields an average CRE age of 11 ± 1 Ma, if a production rate $P_{15}=11.6$ pgMa⁻¹ for ${}^{15}N_c$ (Mathew *et al.*, 2003) is used. The ${}^{15}N_c$ -derived CRE age is consistent with reported CRE ages of other nakhlites (Nyquist *et al.*, 2001;



Fig. 4. Release systematics of nitrogen in the nakhlites Y000749 and Y000593. The plateau release in the $<1040^{\circ}C$ steps show the indigenous N signature and the excursions to heavy N in the high temperature steps signal spallation ${}^{15}N_c$. The cosmic ray exposure age calculated from these spallation ${}^{15}N_c$ excesses is consistent with the other CRE ages of nakhlites. Extraction temperatures (in hundreds of degrees) are marked close to the data bars. For Y000749 a combustion step in oxygen (at 450°C, marked 4.5C in upper panel) was sequentially added after the 700°C pyrolysis step and is not considered part of the plateau.

Mathew *et al.*, 2003; Okazaki *et al.*, 2003). This supports the implicit assumption that indigenous N in the high-temperature steps and in the plateau steps are the same component.

6. K-Ar ages and ejection times from Mars

The time of ejection from Mars is calculated as the sum of the CRE and the terrestrial age. Okazaki *et al.* (2003) determined a 81 Kr- 83 Kr age of 11.8 ± 1.0 Ma for Y000593 and give a limit for the terrestrial age < 0.04 Ma. These authors use produc-

Sample	T (°C)	³⁶ Ar	40Ar/36Ar	³⁶ Ar ^{/38} Ar	³⁸ Ar _C	¹³² Xe	¹²⁹ Xe/ ¹³² Xe	³⁶ Ar/ ¹³² Xe	⁸⁴ Kr/ ¹³² Xe
Nakhlite	180	0.118	303 ±26	5.30 ±0.15		0.1	0.98	118	3.8
Y000749,51	250	0.452	316 ±21	5.30 ±0.09		0.31	0.98	145	3.2
(381 mg)	350	0.754	358 ±16	4.58 ±0.05	0.03	0.93	0.98	79	3.6
	450	3.50	525 ±10	4.28 ±0.04	0.18	4.12	0.98	82	3.8
	550	2.10	4160 ±8	3.80 ±0.03	0.18	1.40	0.98	142	4.0
	700	1.73	8660 ±19	2.10 ±0.02	0.57	1.59	0.98	85	4.1
	800	4.02	$10280 \hspace{0.1cm} \pm 32$	1.15 ±0.02	3.12	0.86	1.024	232	4.1
	1000	3.54	9980 ±15	1.32 ±0.03	2.30	4.22	1.02	49	3.8
	1200	7.03	1355 ±8	1.36 ±0.02	4.38	7.68	1.026	54	3.8
	1400	98.8	28 ±1.3	0.683 ±0.004	144.4	3.94	1.16	126	4.1
	1550	30.3	48 ±1.4	0.708 ±0.005	42.1	2.37	1.035	123	4.1
	>550	145			197	20.7			
Nakhlite	200	0.120	298 ±21	5.20 ±0.20		0.10	0.98	120	3.8
Y000593,85	300	0.351	305 ±12	5.20 ±0.15		0.31	0.98	113	3.6
(484 mg)	400	0.364	420 ±11	4.2 ±0.20	0.02	0.40	0.98	88	3.4
	500	3.11	528 ±6	4.28 ±0.08	0.16	4.12	0.98	73	3.8
	600	0.830	4860 ±6	1.40 ±0.03	0.50	0.64	1.096	79	3.9
	800	1.50	8860 ±9	0.841 ±0.008	1.72	0.82	1.174	48	4.0
	900	3.65	10800 ±9	0.859 ±0.005	4.06	0.79	1.203	129	3.6
	1000	4.66	6880 ±8	0.823 ±0.005	5.48	1.93	1.278	57	3.6
	1200	4.13	3870 +5	0 734 +0 0 004	5.56	1.08	1.047	50	3.7

Table 3. Measured heavy noble gas concentrations and Ar isotopic ratios (95% confidence limits).

The data are corrected for blanks and mass discrimination. The ^{36}Ar and $^{38}Ar_c$ abundances are in units $10^{-10}\,cm^3 STP/g$ and a spallation ratio $^{36}Ar/^{38}Ar{=}0.65$ is adopted, the ^{132}Xe abundances are in $10^{-12}\,cm^3 STP/g$.

 0.720 ± 0.003

 0.682 ± 0.003

 0.664 ± 0.003

23.5

108.9

37.25

186.3

5.13

4.68

0.46

15.5

1.253

1.329

1.319

37

85

129

3.7

3.7

3.8

1400

1550

1650

>500

17.2

74.50

24.64

131

 $640~{\pm}4$

45 ±1.3

 $42 \hspace{0.1in} \pm 1.4$

tion rates according to Eugster and Michel (1995) for the ²¹Ne—ages of 11.9 Ma for both Y000593 and Y000749, consistent with the ⁸¹Kr-⁸³Kr age and with CRE ages obtained for other nakhlites (Nyquist *et al.*, 2001; Mathew *et al.*, 2003). This also confirms the identical ejection ages for all nakhlites.

The spallation ${}^{38}\text{Ar}_c$ component is released as early as 350°C and peaks at 1400° to 1550°C. The ${}^{38}\text{Ar}_c$ concentrations (Table 3) are 18.6×10^{-9} and 19.7×10^{-9} cm³STP/g

for Y000593 and Y000749 are both consistent with the reported CRE age.

Okazaki *et al.* (2003), assuming a negligible contribution from Martian atmospheric ⁴⁰Ar, reported K-⁴⁰Ar age of 1.24 ± 0.22 Ga. This assumption appears appropriate, since nitrogen and xenon records do not show an atmospheric component. A nonradiogenic ⁴⁰Ar/³⁶Ar ratio similar to the indigenous ratio ⁴⁰Ar/³⁶Ar=207 ratio (Mathew and Marti, 2001) is inferred from the data (Table 3), a ratio which does not affect the budget. From measured ⁴⁰Ar concentrations (Table 3) and concentration of K (Dreibus *et al.*, 2003; Oura *et al.*, 2003) we calculate crystallization ages in excess of the reported 1.3 Ga age for nakhlites (Nyquist *et al.*, 2001), ~1.6 Ga for Y000593 and ~1.5 Ga for Y000749. These excesses suggest that radiogenic ⁴⁰Ar was inherited by the magma.

7. Magmatic fractionation

Two scenarios were considered by Mathew et al. (2003) for the presence of ²⁴⁴Puderived fission Xe in nakhlites. In the first option Xe components, consisting of fission Xe gas mixed with indigenous mantle Xe, were either added in variable proportions to nakhlite parent magmas, or fractionated to variable extents. A magmatic fractionation is implied by the composition of nakhlites, which could have taken place at any time after ²⁴⁴Pu decay. A second option was mentioned suggesting that ²⁴⁴Pu was still alive during magmatic episodes, an option consistent with the apparent trend that fission Xe is enriched in nakhlites together with U and the REE. In both scenarios the Xe components were enriched in the liquid during the course of magma generation. We may model the evolution of the fission component in the mantle during the period from the early differentiation to the recorded 1.3 Ga event, assuming a U abundance of 12 ppb. The size of this fission component is ${}^{136}Xe_f = 26 \times 10^{-15} \text{ cm}^3 \text{STP/g}$. The component produced after differentiation (during the past 1.3 Ga) using a U concentration of 55 ppb (Dreibus et al., 2003), would add 42×10^{-15} cm³STP/g, but the total fission component would only amount to $\sim 8\%$ of the observed average fission component $(0.8 \times 10^{-12} \text{ cm}^3 \text{STP/g})$. An inferred shift due to a calculated ²³⁸U-fission component would be difficult to observe in Fig. 2. Yamashita et al. (2003) report Pb isotopic systematics in Y000593 which indicate that no isotopic equilibration was achieved, but they suggest that the source material was subjected to two differentiation events. The first event represents the initial differentiation as recorded in the products of extinct ²⁴⁴Pu, ¹⁴⁶Sm and ¹⁸²Hf. Closed-system behavior of noble gases in the mantle requires sufficient pressure and, therefore, depth for the evolving liquids, of quantities which are not well known for Mars. Since LREE, as proxies for ²⁴⁴Pu, are strongly enriched in the mesostasis and in phosphates (Wadhwa and Crozaz, 2003), the observed trend of an enrichment of fission Xe in NWA817 (Mathew et al., 2003) simply may reflect variable mesostasis abundance (Imae et al., 2003; Mikouchi et al., 2003).

8. Conclusions

1) Isotopic abundances of nitrogen and of heavy noble gases in nakhlites Y000593 and Y000749 were studied for signatures of the magma source region. A nitrogen

component with $\delta^{15}N = 13 \pm 1\%$ is observed in plateau releases of both Yamato nakhlites; it has previously been observed in Nakhla and also in Chassigny.

2) In nakhlite Y000749 radiogenic ¹²⁹Xe is observed in one temperature fraction, while a much larger component is observed in several steps of Y000593. The lack of an association with fission Xe as well as with indigenous Xe from the mantle source region indicates a crustal source.

3) Fission Xe components due to extinct ²⁴⁴Pu are identified in both nakhlites. The records show that the magma source region had assimilated and retained fission gas since the early differentiation of Mars.

4) The measured concentrations of 40 Ar exceed the amounts produced from the decay of 40 K in 1.3 Ga and suggest that the magma inherited some radiogenic 40 Ar.

5) CRE ages based on spallation ${}^{15}N_c$ and ${}^{38}Ar$ are consistent with the ${}^{81}Kr \cdot {}^{83}Kr$ age (Okazaki *et al.*, 2003) and CRE ages for other nakhlites (Nyquist *et al.*, 2001; Mathew *et al.*, 2003), confirming identical ejection ages for all nakhlites.

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¹³² Xe	136 Xe = 1.00								
$10^{-12} \text{ cm}^3/\text{g}$	¹²⁴ Xe	¹²⁶ Xe	¹²⁸ Xe	¹²⁹ Xe	¹³⁰ Xe	¹³¹ Xe	¹³² Xe	¹³⁴ Xe	
		Yamato	Nakhlite	Y000749,51					
0.858	0.0130	0.0113	0.2514	3.1299	0.4793	2.4386	3.0572	1.1863	
	±21	28	83	397	76	397	560	214	
4.181	0.0103	0.0113	0.2495	3.0762	0.4798	2.5332	3.0365	1.1686	
	±27	9	36	227	58	358	181	63	
7.645	0.0146	0.0112	0.2506	3.0942	0.4815	2.3936	3.0274	1.1748	
	±18	6	27	132	33	148	217	85	
3.792	0.0162	0.0112	0.2301	3.2989	0.4547	2.4919	2.9222	1.1637	
	±41	44	74	126	53	103	161	64	
2.348	0.0157	0.0111	0.2366	3.0645	0.4581	2.4123	2.9855	1.1678	
	±33	21	57	174	51	116	183	71	
		Yamato	Nakhlite Y	Y000593.85	5				
0.643	0.0111	0.0108	0.2398	3.3022	0.4610	2.4375	3.0130	1.1660	
	±24	21	54	301	45	301	390	157	
0.815	0.0128	0.0100	0.2476	3.5749	0.4750	2.4817	3.0451	1.1730	
	±21	21	40	286	43	289	380	146	
0.786	0.0132	0.0113	0.2500	3.6660	0.4791	2.4926	3.0475	1.1767	
	±24	21	43	305	43	293	362	137	
1.918	0.0140	0.0112	0.2303	3.6744	0.4584	2.3753	2.9136	1.1408	
	±41	33	61	277	61	244	242	126	
1.079	0.0120	0.0110	0.2314	3.0716	0.4516	2.4001	2.9463	1.1532	
	±26	21	37	248	46	261	269	119	
5.114	0.0116	0.0110	0.2272	3.6195	0.4439	2.3626	2.9197	1.1531	

Appendix A. Spallation-corrected Xe isotopic ratios in Y000749,51 and Y000593,85.

Temp. (°C)

800*

1000*

1200#

1400#

1550#

600

800

900

1000*

1200*

1400#

1550#

1650#

4.637

0.458

 ± 34

 ± 43

±39

0.0173

0.0135

27

41

44

0.0116

0.0115

The ¹³²Xe data are corrected for spallation adopting a spallation spectrum obtained by the subtraction method.

41

46

54

0.2339

0.2291

207

232

354

3.7335

3.6803

43

47

46

0.4520

0.4503

238

254

261

2.3890

2.3977

263

251

306

2.9208

2.9019

108

113

123

1.1496

1.1406

* Adopted spallation spectrum of ¹²⁴Xe: ¹²⁶Xe: ¹²⁸Xe: ¹²⁹Xe: ¹³⁰Xe: ¹³¹Xe: ¹³¹Xe: ¹³⁴Xe=0.55±0.10: =1.00: 1.60 ± 0.10 : 1.70 ± 0.20 : 0.95 ± 0.10 : 1.90 ± 0.30 : 1.0 ± 0.3 : 0.3 ± 0.1 .

Adopted spallation spectrum of ¹²⁴Xe: ¹²⁶Xe: ¹²⁸Xe: ¹²⁹Xe: ¹³⁰Xe: ¹³¹Xe: ¹³²Xe: ¹³⁴Xe=0.58±0.10: =1.00: 1.45±0.05: 1.60±0.15: 0.85±0.06: 2.1±0.3: 0.8±0.2: 0.3±0.1.

Uncertainties listed are those in the least significant figures of the isotopic ratios (95% confidence levels). The uncertainties in the isotopic ratios include variations by assuming lower (and upper) limits of the spallation spectrum.