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Noble gases in two shergottites and one nakhlite from Antarctica: Y000027, Y000097, and Y000593

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Abstract

We have investigated secondary influences on the noble gas budget in rim and interior pairs of three Martian meteorites from Antarctica: the lherzolitic shergottites Y000027 and Y000097, and the nakhlite Y000593. Three factors have been found to influence the original Martian noble gas budget: shock metamorphic overprint, cosmic irradiation, and terrestrial weathering. The 3 He/⁴He ratio of the shergottites is between 0.189 and 0.217, which indicates almost complete loss of radiogenic 4 He. This is expected from the high shock pressure observed in the shergottite samples. The concentration of ⁴He in these shergottite samples ranges from 33.8 to $39.4 \times 10^{-8} \text{ ccSTP/g}$. ²²Ne in the shergottites is on the order of $14 \times 10^{-9} \text{ ccSTP/g}$. The nakhlite has $\sim 800 \times 10^{-8} \text{ ccSTP/g}^4$ He and $\sim 26 \times 10^{-9} \text{ ccSTP/g}^{22}$ Ne. An indication for solar cosmic ray contribution to the neon budget can be found in the shergottites. As Y000027 and Y000097 are reported to be paired we conclude the cosmic ray exposure (CRE) age $T_{(3+21)}$ of this shergottite to be 4.41 \pm 0.54 Ma. For the nakhlite Y000593 $T_{(3+21)}$ is 11.8 \pm 0.3 Ma. Heavy noble gas concentrations show large differences between rim and interior samples with the rim samples having 1.3–2.9, 1.7–38, and 1.4–20 times as much ³⁶Ar, ⁸⁴Kr, and ¹³²Xe, respectively. The enrichment of heavy noble gases in the rim samples indicates severe terrestrial contamination. The relation between 129 Xe/ 132 Xe and 84 Kr/ 132 Xe in the rim samples shows that the incorporation mechanism caused elemental fractionation of Kr and Xe to the extent that in the Y000027 shergottite samples any Martian signature is completely masked by terrestrial contamination, if the total is taken. Only the 1400 °C steps show clear evidence for Martian atmosphere. The Y000593 nakhlite interior sample, on the other hand, shows low 84 Kr/ 132 Xe in relation to 129 Xe/ 132 Xe, which is characteristic for fractionated Martian atmosphere observed in nakhlites. © 2009 Elsevier B.V. and NIPR. All rights reserved.

Keywords: Martian meteorite; Noble gas; Cosmic irradiation; Elemental fractionation

1. Introduction

Noble gases provide a powerful tool to reveal several aspects of the history of a Martian meteorite. First of all, they have been the first measured proof that linked the SNC meteorites to Mars, when D. Bogard (Bogard, 1982; Bogard and Johnson, 1983; Bogard et al., 1984) found the noble gas signature of the glassy lithology C of EETA 79001 to be similar to the Martian atmosphere as measured by the Viking lander (Owen et al., 1977). A Martian interior component was identified in Chassigny soon thereafter (Ott and Begemann, 1985). Furthermore, cosmic ray exposure ages (Eugster et al., 1997) tell about the delivery history; and

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"classical" K/Ar and Ar/Ar age dating (Bogard and Garrison, 1999) reveals the geologic history. Besides the Martian atmosphere and the Martian interior component, a fractionated Martian atmospheric component was found in the nakhlites (Drake et al., 1994; Ott, 1988); and results for ALHA84001 have been interpreted as showing the presence of ancient Martian atmosphere (Gilmour et al., 1998). Lately, a second Martian interior component was proposed by disentangling the signatures of mineral separates from three shergottites (Schwenzer et al., 2007a) and excess ⁴⁰Ar trapped from the magma source was found in the shergottites (Bogard and Park, 2008). Therefore, the noble gas components in Martian meteorites are a mixture of the Martian components atmosphere (fractionated in case of the nakhlites) and interior, with addition of radiogenic components especially to helium and argon, and fission components to xenon (e.g., Mathew et al., 2003). However, several factors are likely to have modified the original Martian signatures of the meteorites: The launch event disturbs the original signatures by causing loss and implantation, with the extent of the disturbance related to the degree of shock metamorphic overprint (Fritz et al., 2005a; Schwenzer et al., 2008b). During space travel cosmogenic nuclides are added and finally terrestrial air will contaminate the rock (Mohapatra et al., 2009).

The SNC meteorites, a.k.a. Martian meteorites, are divided into four petrologic groups: the shergottites. which are themselves subdivided (Goodrich, 2002), the nakhlites, the chassignites and the orthopyroxenite(s) (Meyer, 2008). To date 60 meteorites are classified as shergottites and carry individual names (Antarctic Meteorite Newsletter, 2007; Connolly et al., 2007a,b; Grossman, 2000; Grossman and Zipfel, 2001; Meteoritical Bulletin Database, 2008; Meyer, 2008; Russell et al., 2002, 2005). However, pairing reduces the number of independent individuals to 37. Seventeen of these shergottites -15 individuals - were found by Antarctic meteorite research campaigns. Two of the known nakhlite individuals stem from Antarctica (Treiman, 2005). Furthermore the oldest Martian sample, the pyroxenite ALHA 84001, has also been found in Antarctica (Treiman, 1998). This makes Antarctica an important source for Martian meteorites. The fact, however, that meteorites found in Antarctica are not falls but may have suffered changes in their noble gas budget such as loss of light noble gases due to cold desert weathering (Alexeev, 1998; Graf and Marti, 1995; Patzer and Schultz, 2001; Schwenzer et al., 2008a), can challenge the interpretation of noble gas results. Moreover, for the heavy noble gases

fractionated adsorption seems to be the rule rather than the exception (Mohapatra et al., 2009; Nagao and Park, 2008; Nagao et al., 2008; Scherer et al., 1994; Schwenzer et al., 2007b, 2008b). Therefore, studying Antarctic meteorites should also include a look at their terrestrial history and possible terrestrial influence on the noble gas budget.

As part of the consortium study initiated by the National Institute for Polar Research (NIPR), Japan, we present noble gas data on three Martian meteorites: the paired lherzolitic shergottites Yamato 000027 (Y000027) and Yamato 000097 (Y000097), and the nakhlite Yamato 000593 (Y000593). For Y000027 and Y000097 the information is mostly in abstract form so far (Mikouchi and Kurihara, 2007a; Misawa et al., 2008; Shirai and Ebihara, 2008; Schwenzer et al., 2008a), especially from the 2007 NIPR Symposium (Hoffmann et al., 2007; Ikeda and Imae, 2007; Imae and Ikeda, 2007; Mikouchi and Kurihara, 2007b; Misawa et al., 2007; Nagao et al., 2007; Shirai and Ebihara, 2007). Results obtained in the framework of the consortium study on the two shergottites are published in this journal (Mikouchi and Kurihara, 2008; Nagao et al., 2008; Shirai and Ebihara, 2009).

In addition to the shergottites, we include Y000593 in our study. The nakhlite was found in 2000 (Imae et al., 2003). Previous work includes petrological studies (e.g., Fritz et al., 2005a,b; Imae et al., 2003, 2005; Treiman, 2005), investigations of alteration phases (e.g., Treiman, 2008), as well as isotopic (Boctor et al., 2005; Misawa et al., 2005) and noble gas (Christen et al., 2005; Murty et al., 2003; Okazaki et al., 2003; Park et al., 2007) studies.

The focus of our study is on the factors influencing the noble gas budget after incorporation of the original Martian signatures. We disentangle the Martian, cosmic and terrestrial components in our data set. By investigating rim and interior samples, our experiments were designed to especially shed light on two details: cosmogenic nuclides and terrestrial contamination.

2. Samples and experimental

2.1. Samples

Three Martian meteorites have been investigated: the two lherzolitic shergottites Y000027 and Y000097 and the nakhlite Y000593. Two samples have been measured for each: a sample taken from the rim of the meteorite and a sample taken from the interior of the meteorite. Sample preparation was kept to a minimum, i.e., the chips obtained from NIPR were weighed on

Table 1 Results for He and Ne.

Sample	Temperature	⁴ He	³ He/	²² Ne	²⁰ Ne/	²¹ Ne/
	(°C)		⁴ He		²² Ne	²² Ne
Y000027, 82	500	8.79	0.1792	1.01	1.821	0.669
shergottite	±	0.18	0.0023	0.01	0.055	0.004
49.86 mg rim	1000	23.65	0.1929	4.70	0.896	0.861
	±	0.47	0.0027	0.11	0.026	0.004
	1400	2.50	0.1821	7.74	0.844	0.873
	±	0.05	0.0029	0.18	0.024	0.004
	1800	_ ^a	^a	0.31	0.845	0.871
	±	24.04	0 1007	0.08	0.072	0.009
	Sum	34.94	0.1887	13.70	0.934	0.854
V000027 82	± 500	0.51	0.0019	0.20	0.017	0.003
shergottite	500 +	4.13	0.2129	0.23	4.110	0.000
50.07 mg	⊥ 1000	31.15	0.0030	2.58	0.140	0.009
interior	+	0.65	0.0031	0.06	0.027	0.004
interior	1400	4.17	0.2009	10.11	0.863	0.869
	±	0.09	0.0029	0.24	0.024	0.004
	1800	a	a	0.75	0.825	0.878
	±			0.02	0.037	0.006
	Sum	39.44	0.2159	13.67	0.926	0.864
	±	0.66	0.0025	0.25	0.019	0.003
Y000097, 92	500	6.59	0.2048	0.94	1.153	0.701
shergottite	±	0.15	0.0027	0.02	0.037	0.008
59.44 mg rim	1000	24.76	0.1993	4.00	0.860	0.846
	±	0.50	0.0027	0.09	0.026	0.007
	1400	2.54	0.1885	8.02	0.840	0.865
	±	0.07	0.0029	0.19	0.024	0.006
	1800	_"	_"	1.49	0.833	0.865
	±	22.00	0.1007	0.04	0.027	0.005
	Sum	33.90	0.1996	14.45	0.866	0.849
V000007 82	±	0.55	0.0021	0.22	1.627	0.004
shergottite	300 +	0.05	0.1930	0.01	1.027	0.085
100 76 mg	⊥ 1000	24.53	0.0030	2.02	0.040	0.000
interior	+	0.51	0.0031	0.07	0.052	0.005
interior	1400	3.18	0.1755	9.63	0.862	0.861
	±	0.10	0.0023	0.23	0.024	0.004
	1800	a	a	0.36	0.864	0.896
	±			0.01	0.038	0.012
	Sum	33.76	0.1901	13.73	0.900	0.846
	±	0.54	0.0023	0.24	0.020	0.004
Y000593,	500	501.55	0.0158	0.55	0.762	0.777
108 nakhlite	±	9.96	0.0002	0.01	0.025	0.009
98.15 mg rim	1000	238.96	0.0424	10.98	0.839	0.861
	±	4.79	0.0005	0.26	0.023	0.004
	1400	6.94	0.0952	14.68	0.827	0.856
	±	0.15	0.0012	0.34	0.023	0.004
	1800	_"	_"	0.11	0.777	0.838
	±	747 45	0.0250	0.01	0.090	0.018
	Sum	11.05	0.0250	20.32	0.016	0.850
V000502	± 500	702.47	0.0002	0.43	0.010	0.003
02 nakhlita	500 +	14.42	0.0182	0.09	0.766	0.820
92 nakilile 92 66 mg	1000	137.21	0.0003	12 41	0.020	0.009
interior	+	2.82	0.0006	0.29	0.023	0.004
interior	1400	3.25	0.1179	12.22	0.831	0.857
	±	0.07	0.0015	0.29	0.023	0.004
			(contin	ued on	next co	olumn)

Table 1 (continued)

Sample	Temperature (°C)	⁴ He	³ He/ ⁴ He	²² Ne	²⁰ Ne/ ²² Ne	²¹ Ne/ ²² Ne
	1800	0.05	0.1120	0.49	0.857	0.847
	±	0.02	0.0254	0.01	0.038	0.013
	Sum	843.98	0.0233	25.82	0.833	0.854
	±	14.70	0.0002	0.41	0.016	0.003

He concentrations in 10^{-8} , Ne concentrations in 10^{-9} ccSTP/g. Martian meteorite class, sample weight and rim/interior location are given in the first column.

^a Close to blank.

and wrapped into Pt-foil pre-degassed at 700 °C. If chips needed to be broken, clean pinchers were used. No crushing or grinding nor any liquids were applied.

2.2. Measurement procedures

The samples were loaded into the sample holder and preheated at 130 °C for two days to remove adsorbed terrestrial contamination. Step-heating experiments were performed with steps at 500, 1000, 1400, and 1800 °C (see Tables 1–4). Noble gas blanks were somewhat variable, typical values (for 1800 °C system blanks with Pt-foil) being ⁴He = 5×10^{-11} ccSTP, ²⁰Ne = 8×10^{-13} ccSTP, ³⁶Ar = 4×10^{-12} ccSTP, ⁴⁰Ar = 1.3×10^{-9} ccSTP, ⁸⁴Kr = 1.5×10^{-13} ccSTP, ¹³²Xe = 6×10^{-14} ccSTP. For analytical details see Schwenzer (2004) and Mohapatra et al. (2009).

2.3. Data reduction

The data reported below (see Section 3) have been corrected for blanks and mass discrimination. In addition, interference corrections were applied for HD and H₃ at ³He, for H₂¹⁸O, doubly charged argon and CO₂ in Ne, for HCl and hydrocarbons at ³⁶Ar and ³⁸Ar and also for hydrocarbons at ⁷⁸Kr. Errors in Tables 1–4 include: (a) uncertainties due to variations in blank amounts and composition; (b) uncertainties in the proper interference correction factors; and (c) variations in mass discrimination and (for the amounts) sensitivity.

2.4. Component resolution

Partitioning of the noble gases between trapped (plus radiogenic in the case of ⁴He and ⁴⁰Ar) and cosmogenic components was done for He, Ne, and Ar. In the following discussion "c" refers to cosmogenic, "tr" to trapped (+radiogenic), "rad" to the pure radiogenic component, where applicable. For this, ³He was taken to be 100% cosmogenic, together with

Table 2		
Results	for	Ar.

Sample	Temperature	³⁶ Ar	⁴⁰ Ar	³⁸ Ar/	⁴⁰ Ar/
~F	(°C)			³⁶ Ar	³⁶ Ar
Y000027. 82	500	3.47	1064	0.191	306
shergottite	±	0.24	72	0.001	2
49.86 mg rim	1000	1.54	967	0.443	627
ç	±	0.11	70	0.005	7
	1400	2.59	2364	0.750	913
	±	0.18	165	0.007	9
	1800	0.12	43	0.722	365
	±	0.04	12	0.033	8
	Sum	7.72	4438	0.437	575
	±	0.31	194	0.004	5
Y000027, 83	500	1.18	351	0.192	298
shergottite	±	0.08	25	0.001	2
50.07 mg	1000	0.17	225	0.835	1367
interior	±	0.04	51	0.039	65
	1400	1.20	586	1.089	487
	±	0.09	44	0.021	6
	1800	0.09	42	1.059	513
	±	0.04	18	0.049	16
	Sum	2.64	1203	0.671	460
	±	0.13	264	0.014	5
Y000097, 92	500	0.53	180	0.198	337
shergottite	±	0.04	13	0.004	2
59.44 mg rim	1000	1.00	1170	0.475	1167
	±	0.07	80	0.003	7
	1400	3.75	4989	0.586	1331
	±	0.25	339	0.002	7
	1800	0.15	128	1.177	867
	±	0.01	9	0.018	9
	Sum	5.43	6468	0.543	1191
	±	0.27	349	0.003	8
Y000097, 83	500	0.35	111	0.205	317
shergottite	±	0.02	8	0.004	2
100.76 mg	1000	0.42	357	1.000	855
interior	±	0.03	24	0.007	6
	1400	1.74	1427	0.988	820
	±	0.12	97	0.003	4
	1800	0.04	25	1.18/	680
	± 5	0.003	1010	0.041	14
	Sum	2.54	1919	0.880	/54
V000502 109	±	0.12	94	0.000	5 012
1000393, 108	300 -	0.95	805 50	0.280	915 7
08 15 mg rim	± 1000	0.00	6904	1 5 2 2	10 272
96.15 mg 1mi	1000	0.00	467	0.011	03
	⊥ 1400	6.44	407	1 475	93 66
	+	0.44	-23	0.004	04
	1800	_a	_a	_a	_a
	+				
	Sum	8.05	8094	1 339	1010
	+	0.03	624	0.008	54
Y000593 92 nakhlite	500	0.25	1511	0.887	6167
92 66 mg	+	0.20	119	0.017	145
interior	1000	0.73	5783	1.530	7879
	+	0.05	395	0.010	57
	 1400	9.38	275	1,467	29
	±	0.64	19	0.004	1
		(cont	inued a	on next	column)

Table 2 (continued)

× /					
Sample	Temperature (°C)	³⁶ Ar	⁴⁰ Ar	³⁸ Ar/ ³⁶ Ar	⁴⁰ Ar/ ³⁶ Ar
	1800	0.45	4	1.495	8
	±	0.03	1	0.008	1
	Sum	10.81	7573	1.459	701
	±	0.67	413	0.008	123

Concentrations are given in 10^{-9} ccSTP/g. Martian meteorite class, sample weight and rim/interior location are given in the first column. ^a Close to blank.

a ratio of $({}^{4}\text{He}/{}^{3}\text{He})_{c} = 4.1$ (Schwenzer et al., 2007a). Abundances of trapped ²⁰Ne and cosmogenic ²¹Ne as well as estimates for the cosmogenic $({}^{22}Ne/{}^{21}Ne)_c$ ratio $(^{20}\text{Ne}/^{22}\text{Ne})_{\text{tr}} = 10 \pm 1,$ derived using were $(^{21}\text{Ne}/^{22}\text{Ne})_{tr} = 0.032 \pm 0.005$ (these values cover both air and most published values for Martian atmosphere), and $({}^{20}\text{Ne}/{}^{22}\text{Ne})_c = 0.80 \pm 0.05$ (GCR, chondritic range; Wieler, 2002). If the low $({}^{20}\text{Ne}/{}^{22}\text{Ne})$ value of 7 for Martian atmosphere suggested by Garrison et al. (1995) and Park and Nagao (2006) is used, the resulting cosmogenic ²¹Ne and $({}^{22}Ne/{}^{21}Ne)_c$ become slightly lower, but remain identical within error in most cases.

For argon, air or Martian atmosphere are possible choices as trapped component; different choices for $({}^{38}\text{Ar}/{}^{36}\text{Ar})_{tr}$ within the range given in the literature for Martian atmosphere (0.268, Bogard, 1997; 0.244, Wiens, 1988) change calculated ${}^{38}Ar_c$ and ${}^{36}Ar_{tr}$ abundances to various degrees. We calculated the partitioning with the values of Wiens (1988). Taking terrestrial atmospheric composition (0.188; Nier, 1950) instead results in (slightly) lower ³⁶Artr and consequently higher ⁴⁰Ar/³⁶Ar_{tr} values. For comparison: The 36 Ar_{tr} in Y000027 rim is 6.53×10^{-9} ccSTP/g when with the Wiens-values, partitioned and 6.26×10^{-9} ccSTP/g when air is taken, which is a discrepancy within error limits. The same check with a "less weathered" sample, Y000027 interior, results in a larger difference in the ${}^{36}Ar_{tr}$: 1.55×10^{-10} (with Wiens-value) and 2.74×10^{-10} ccSTP/g (with airvalue). The ${}^{38}\text{Ar}_c$, however, remains close: 1.33×10^{-9} and 1.44×10^{-9} ccSTP/g. Note, that the total of ³⁶Ar_{tr} is about an order of magnitude larger (Tsteps ≥ 1000 °C, and three to four times in the sum of all T-steps) in rim than in interior, while ³⁸Ar_c does not differ that much and is slightly larger in the rim sample of the shergottite. The nakhlite shows a similar pattern: ³⁶Ar_{tr} of the rim sample is about three times the amount found in the interior. Cosmogenic ${}^{38}Ar_c$, however, does not differ much in the nakhlite samples, too. It is important to note that the choice is critical for

Table 3
Results for krypton.

Sample	Temperature (°C)	⁸⁴ Kr	⁷⁸ Kr/ ⁸⁴ Kr	⁸⁰ Kr/ ⁸⁴ Kr	82Kr/84Kr	⁸³ Kr/ ⁸⁴ Kr	⁸⁶ Kr/ ⁸⁴ Kr
Y000027, 82	500	1169.35	0.0061	0.0393	0.2020	0.2030	0.3067
shergottite	±	22.65	0.0003	0.0004	0.0013	0.0014	0.0015
49.86 mg rim	1000	62.48	0.0046	0.0415	0.2059	0.2125	0.3045
	±	1.69	0.0039	0.0020	0.0056	0.0055	0.0057
	1400	75.68	0.0068	0.0508	0.2106	0.2104	0.2912
	±	1.91	0.0032	0.0021	0.0059	0.0042	0.0081
	1800	17.73	0.0003	0.0381	0.2087	0.1926	0.2922
	±	1.17	0.0136	0.0033	0.0136	0.0102	0.0096
	Sum	1325.24	0.0060	0.0401	0.2028	0.2038	0.3055
	±	22.82	0.0004	0.0004	0.0012	0.0013	0.0014
Y000027, 83	500	31.12	0.0058	0.0398	0.2022	0.2042	0.3118
shergottite	±	6.21	0.0008	0.0008	0.0021	0.0024	0.0025
50.07 mg	1000	1.40	a	0.0495	0.2076	0.2069	0.2926
interior	±	1.16		0.0062	0.0184	0.0128	0.0134
	1400	1.67	a	0.0406	0.2325	0.2135	0.2946
	±	1.17		0.0040	0.0146	0.0115	0.0152
	1800	0.23	a	0.0463	0.1902	0.2022	0.2842
	±	1.10		0.0241	0.0527	0.0725	0.0629
	Sum	34.42	a	0.0403	0.2038	0.2047	0.3100
	\pm	6.52		0.0008	0.0022	0.0023	0.0025
Y000097, 92	500	143.07	0.0063	0.0401	0.2066	0.2025	0.3006
shergottite	±	3.02	0.0015	0.0009	0.0014	0.0022	0.0028
59.44 mg rim	1000	23.66	0.0025	0.0549	0.2125	0.2082	0.3200
8	±	1.08	0.0084	0.0026	0.0081	0.0099	0.0085
	1400	91.51	0.0062	0.0466	0.2094	0.2080	0.3041
	+	2.02	0.0022	0.0014	0.0019	0.0031	0.0035
	1800	2.62	_a	0.0285	0.2348	0.1774	0.2507
	+	0.93		0.0176	0.0539	0.0462	0.0504
	Sum	260.86		0.0436	0.2084	0.2047	0.3031
	+	3.91		0.0007	0.0014	0.0019	0.0021
Y000097, 83	500	117.30	0.0054	0.0403	0.2009	0.2086	0.3021
shergottite	+	2.44	0.0010	0.0011	0.0029	0.0021	0.0053
100 76 mg	1000	9.75	_a	0.0524	0.1961	0.2173	0.3151
interior	+	0.61		0.0034	0.0112	0.0095	0.0115
	1400	24 97	0.0067	0.0579	0.2267	0.2363	0.2988
	+	0.76	0.0049	0.0021	0.0024	0.0038	0.0029
	1800	_a,b	_a,b	_a,b	_a,b	_a,b	a,b
	Sum	152.02		0.0440	0.2048	0.2137	0.3024
	+	2.63		0.0010	0.0024	0.0018	0.0042
Y000593 108	500	305.68	0.0058	0.0399	0.2041	0.2053	0.3064
nakhlite	+	5 96	0.0004	0.0006	0.0013	0.0022	0.0016
98 15 mg rim	1000	18.80	0.0184	0.0938	0.2722	0.2917	0.2977
yours mg min	+	0.68	0.0069	0.0031	0.0050	0.0062	0.0078
	1400	2.85	0.1006	0.4104	0.6569	0.8744	0.1635
	+	0.57	0.0420	0.0374	0.0444	0.0641	0.0321
	1800	_a,b	_a,b	_a,b	_a,b	_a,b	_a,b
	Sum	327 33	0.0074	0.0462	0.2119	0.2160	0 3046
	+	6.02	0.0007	0.0007	0.0013	0.0022	0.0016
Y000593 92		6.91	a	0.0386	0.2058	0.2122	0.3253
nakhlite	+	0.63		0.0041	0.0089	0.0110	0.0123
92 66 mg	1000	5 67	0.0815	0.2690	0 4977	0 5893	0.2180
interior	+	0.61	0.0217	0.0173	0.0238	0.0311	0.0174
menor	 1400	3 35	0.0217	0.4300	0.7368	0.0210	0 1373
	+	0.60	0.1450	0.0373	0.0467	0.0219	0.0374
	⊥ 1800	_a,b	_a,b	_a,b	a,b	_a,b	_a,b
	Sum	15.02		0.2050	0.4214	0.4958	0 2475
		10.95		0.2050	0.1/3	0.10/	0.0115
	<u> </u>	1.00		0.0107	0.0175	0.01)+	0.0115

 $\frac{\pm}{1.06}$ $\frac{1.06}{0.0107}$ $\frac{1.06}{0.0107}$ $\frac{1.06}{0.0107}$ $\frac{1.06}{0.0143}$ $\frac{1.0194}{0.0194}$ $\frac{1.06}{0.0194}$ $\frac{1.06}{0.019$

Table	4
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Results for xenon.

Sample	Temperature (°C)	¹³² Xe	¹²⁴ Xe/ ¹³² Xe	¹²⁶ Xe/ ¹³² Xe	¹²⁸ Xe/ ¹³² Xe	¹²⁹ Xe/ ¹³² Xe	¹³⁰ Xe/ ¹³² Xe	¹³¹ Xe/ ¹³² Xe	¹³⁴ Xe/ ¹³² Xe	¹³⁶ Xe/ ¹³² Xe
Y000027, 82 shergottite	500	417.79	0.00354	0.00339	0.07216	0.9836	0.1523	0.7923	0.3890	0.3296
49.86 mg rim	±	8.74	0.00011	0.00010	0.00071	0.0070	0.0009	0.0034	0.0015	0.0017
	1000	58.70	0.00403	0.00389	0.07121	0.9822	0.1509	0.7957	0.3892	0.3315
	±	1.27	0.00025	0.00030	0.00265	0.0126	0.0026	0.0084	0.0059	0.0037
	1400	25.76	0.00417	0.00521	0.07097	1.1258	0.1552	0.7808	0.3877	0.3328
	±	0.64	0.00057	0.00041	0.00419	0.0187	0.0056	0.0137	0.0079	0.0077
	1800	10.80	0.00394	0.00304	0.06611	0.9755	0.1583	0.7592	0.3849	0.3390
	±	0.53	0.00074	0.00075	0.00607	0.0330	0.0083	0.0201	0.0101	0.0152
	sum	513.04	0.00364	0.00353	0.07187	0.9904	0.1524	0.7914	0.3889	0.3302
	±	8.87	0.00010	0.00010	0.00070	0.0060	0.0009	0.0030	0.0015	0.0016
Y000027, 83 shergottite	500	88.16	0.00398	0.00318	0.07100	0.9934	0.1500	0.8009	0.3820	0.3303
50.07 mg interior	±	1.80	0.00023	0.00024	0.00197	0.0079	0.0026	0.0055	0.0024	0.0039
	1000	16.78	0.00330	0.00310	0.06910	0.9779	0.1479	0.7751	0.3822	0.3311
	±	0.58	0.00067	0.00059	0.00414	0.0194	0.0059	0.0161	0.0075	0.0070
	1400	5.34	0.00605	0.00531	0.07556	1.1390	0.1431	0.8228	0.3838	0.3572
	±	0.50	0.00137	0.00104	0.00975	0.0606	0.0120	0.0282	0.0190	0.0156
	1800	4.26	a	0.00516	0.06970	0.9793	0.1282	0.7810	0.3530	0.3235
	±	0.50		0.00166	0.01300	0.0439	0.0156	0.0534	0.0206	0.0201
	Sum	114.54		0.00334	0.07088	0.9974	0.1486	0.7974	0.3810	0.3315
	±	2.02		0.00022	0.00176	0.0074	0.0023	0.0054	0.0024	0.0034
Y000097, 92 shergottite	500	54.59	0.00348	0.00302	0.07387	0.9727	0.1533	0.7921	0.3735	0.3305
59.44 mg rim	±	1.19	0.00022	0.00016	0.00113	0.0085	0.0021	0.0032	0.0067	0.0041
-	1000	17.35	0.00508	0.00426	0.06635	1.0283	0.1528	0.7641	0.3797	0.3467
	±	0.53	0.00038	0.00042	0.00310	0.0141	0.0043	0.0070	0.0086	0.0072
	1400	9.25	0.00630	0.00482	0.08205	1.6169	0.1385	0.7576	0.3847	0.3515
	±	0.43	0.00075	0.00090	0.00771	0.0364	0.0061	0.0212	0.0083	0.0080
	1800	3.18	0.00269	0.00388	0.07975	1.0261	0.1464	0.7679	0.3890	0.3007
	±	0.42	0.00220	0.00161	0.01325	0.0579	0.0145	0.0566	0.0277	0.0263
	Sum	84.38	0.00409	0.00350	0.07344	1.0567	0.1513	0.7817	0.3766	0.3350
	±	1.43	0.00020	0.00018	0.00138	0.0077	0.0018	0.0040	0.0049	0.0033
Y000097, 83 shergottite	500	41.71	0.00386	0.00290	0.07275	1.0012	0.1541	0.7820	0.3898	0.3303
100.76 mg interior	±	0.86	0.00012	0.00020	0.00190	0.0052	0.0010	0.0041	0.0015	0.0018
e	1000	13.61	0.00456	0.00367	0.06973	0.9903	0.1472	0.7701	0.3763	0.3404
	±	0.36	0.00020	0.00054	0.00239	0.0159	0.0037	0.0099	0.0053	0.0078
	1400	5.34	0.00794	0.01376	0.08208	1.2239	0.1603	0.7638	0.3668	0.3250
	±	0.26	0.00097	0.00113	0.00459	0.0293	0.0074	0.0146	0.0129	0.0072
	1800	0.31	0.00196	0.00491	0.03612	1.3422	0.1198	0.9351	0.4061	0.3618
	±	0.24	0.00741	0.00644	0.06739	0.2398	0.0892	0.1858	0.0692	0.0839
	Sum	60.96	0.00437	0.00403	0.07271	1.0200	0.1529	0.7785	0.3849	0.3322
	±	1.00	0.00013	0.00021	0.00150	0.0058	0.0013	0.0039	0.0020	0.0023

Y000593, 108 nakhlite	500	232.56	0.00372	0.00333	0.07122	0.9885	0.1536	0.7885	0.3895	0.3310
98.15 mg rim	++	4.89	0.00008	0.00008	0.00124	0.0035	0.0007	0.0030	0.0016	0.0014
	1000	40.77	0.00499	0.00663	0.07609	1.0275	0.1561	0.8159	0.3957	0.3418
	++	0.83	0.00036	0.00034	0.00244	0.0089	0.0025	0.0066	0.0040	0.0037
	1400	7.00	0.03421	0.05149	0.14459	1.0787	0.1927	0.8704	0.3972	0.3161
	Ŧ	0.28	0.00238	0.00254	0.00890	0.0248	0.0049	0.0246	0.0066	0.0111
	1800	a 	_a	a	a	_a	a	a 	_a	a
	++									
	Sum	280.32	0.00466	0.00501	0.07376	0.9964	0.1549	0.7946	0.3906	0.3322
	Ŧ	4.97	0.00010	0.00011	0.00111	0.0032	0.0007	0.0027	0.0015	0.0013
Y000593, 52 nakhlite	500	8.82	0.00459	0.00307	0.07158	1.1104	0.1511	0.7541	0.4018	0.3234
92.66 mg interior	++	0.32	0.00057	0.00068	0.00443	0.0239	0.0052	0.0296	0.0106	0.0077
	1000	3.70	0.04445	0.06905	0.15272	1.5465	0.2232	0.8868	0.3926	0.3184
	++	0.27	0.00277	0.00400	0.01083	0.0425	0.0095	0.0250	0.0150	0.0158
	1400	1.71	0.15425	0.28040	0.44582	1.6767	0.3945	1.3370	0.3328	0.2445
	++	0.27	0.01447	0.02502	0.03890	0.0847	0.0383	0.0912	0.0156	0.0200
	1800	a I	_a	_a	_a	-a	a	a	-a	a I
	Ŧ									
	Sum	14.23	0.03291	0.05350	0.13758	1.2917	0.1991	0.8585	0.3912	0.3127
	÷	0.50	0.00194	0.00326	0.00616	0.0212	0.0062	0.0223	0.0079	0.0067
Concentrations in $10^{-12} cc$ ^a Close to or below blan	cSTP/g. Martian me k.	steorite class	s, sample weight	and rim/interior	location are give	n in the first col	umn.			

 38 Ar_c, which comes out low, when the correction is done with the values of Bogard (1997) or Wiens (1988), resulting in an even larger discrepancy with exposure ages based on ³He and ²¹Ne (cf. Table 5). Thus, for the calculation of cosmic ray exposure ages the trapped component is taken as terrestrial atmosphere.

3. Results

3.1. Helium and neon

More than 89% of the ⁴He from the two shergottites degasses in the first two temperature steps (see Table 1). For the nakhlite Y000593 the effect is even more pronounced with >99% of ⁴He degassing in the first two steps. Loss of ${}^{4}\text{He}$ – most likely due to terrestrial, cold desert weathering – is observed in Y000027 and Y000593: 34.9×10^{-8} and 39.4×10^{-8} ccSTP/g in Y000027 rim and interior, respectively, and 747 and 844×10^{-8} ccSTP/g in Y000593 rim and interior, respectively. In contrast, rim and interior of Y000097 contain similar amounts of ⁴He (33.9 and 33.8×10^{-8} ccSTP/g). Note, that the ⁴He concentration in both Y000097 samples is lower than in the rim sample of Y000027. As the meteorites are paired, they should contain equal amounts of ⁴He. This observation points at a more pervasive weathering in Y000097 compared to Y000027.

Neon (22 Ne total, i.e., including trapped and cosmogenic contributions) is degassed more evenly in the four temperature steps, with the main release occurring in the 1000 and 1400 °C steps. The concentration in the nakhlite is about twice that in the shergottites. The slightly higher amount of 20 Ne in the 500 °C step of the rim sample of Y000027 is likely caused by adsorption of terrestrial air, while otherwise the amounts of trapped neon are similar in rim and interior samples. As for 21 Ne, the amount degassed in the first temperature step is about the same in all samples except Y000027 interior. It degasses by far the smallest amount of 22 Ne and with it even less 21 Ne. Overall, 21 Ne seems to be less affected by weathering than helium and argon.

3.2. Argon, krypton, xenon

Fig. 1 shows cumulative release plots for ${}^{40}\text{Ar}/{}^{36}\text{Ar}_{tr}$ and ${}^{129}\text{Xe}/{}^{132}\text{Xe}$ (see also Tables 2 and 4). It reveals that degassing for xenon is quite similar in all three samples: At least 62% and up to 83% of ${}^{132}\text{Xe}$ is released in the 500 °C step already. This is in

ı.

Concentration	ns of cosmogenic isotopes (cc	STP/g), production rates P (ccS	TP/g Ma) and cosmic ray expc	osure ages T (Ma) determined ir	n this study.	
	Y000027 rim	Y000027 interior	Y000097 rim	Y000097 interior	Y000593 rim	Y000593 interior
³ He _c P ₃	$(6.59\pm 0.12)*10^{-8}$ $163.0*10^{-10}$	$(8.52\pm0.18)*10^{-8}$ $163.0*10^{-10}$	$(6.77\pm0.13)*10^{-8}$ $163.4*10^{-10}$	$(6.42 \pm 0.14) * 10^{-8}$ $163.9 * 10^{-10}$	$(1.87\pm 0.03)*10^{-7}$ $161.9*10^{-10}$	$(1.96\pm 0.04)*10^{-7}$ $161.7*10^{-10}$
J.	4.04	5.20	4.16	3.94	11.55	12.12
²¹ Ne _c	$(1.17\pm0.02)*10^{-8}$	$(1.18\pm 0.02)*10^{-8}$	$(1.23\pm 0.02)*10^{-8}$	$(1.16\pm 0.02)*10^{-8}$	$(2.25\pm 0.04)*10^{-8}$	$(2.20\pm 0.04)*10^{-8}$
\mathbf{P}_{21}	$27.0 * 10^{-10}$	28.3 * 10 ⁻¹⁰	25.4 * 10 ^{- 10}	25.4 * 10 ⁻¹⁰	18.90×10^{-10}	$18.74 * 10^{-10}$
$^{38}_{38}$ Ar _c	$(2.20 \pm 0.12) * 10^{-9}$	$(1.44 \pm 0.10) * 10^{-9}$	$(2.21 \pm 0.11) * 10^{-9}$	$(2.03 \pm 0.11) * 10^{-9}$	$(1.09\pm0.07)*10^{-8}$	$(1.57\pm0.12)*10^{-8}$
P_{38}	$7.5 * 10^{-10}$	$7.5 * 10^{-10}$	$7.5 * 10^{-10}$	$7.5 * 10^{-10}$	$21.5 * 10^{-10}$	$21.5 * 10^{-10}$
T_{38}	3.06	1.92	2.95	2.71	5.07	7.32
T_{3-21}		4.41 =	E 0.54		11.8	3 ± 0.29
T_{3-38}		3.82 =	E 0.58		9.9	5 ± 4.00
Elemental da	ta for production rates from T	reiman (2005) for Y000593, an	d Shirai and Ebihara (2009) fo	or Y000027 and Y000097.		

Table

accordance with the observations of Nagao et al. (2008): >62% of the ¹³²Xe is degassed in their (400 + 600) °C steps. Note further that the amount of ¹³²Xe released in total from the rim is at least 1.4 (Y000097) and at maximum ~20 (Y000593) times as much as that released from the interior sample (Fig. 1, Table 4). For krypton the situation is similar, as between 44 and 94% of ⁸⁴Kr is released in the first T-step already, and the difference between interior and rim varies between a factor of 1.7 (Y000097) and 39 (Y000027) (see Table 3).

For argon the case is more complicated (Fig. 1, Table 2). All samples release less than 1% of their 38 Ar_c in the 500 °C step. The main amount is released in the 1400 °C step (75-87%). Trapped ³⁶Ar_{tr} (Fig. 1) is more variable, with Y000027 rim (55%), Y000027 interior (71%), and Y000593 rim (85%) showing more than 50% trapped $^{36}Ar_{tr}$ in the 500 $^\circ C$ step. For Y000097 rim and interior and Y000593 interior the main degassing step is 1400 °C (>56% at least). Thus Y000027 and Y000593 show what is expected from the assumption that a weathered rim contains abundant adsorbed air (also, the accompanying ${}^{40}\text{Ar}/{}^{36}\text{Ar}_{tr}$ ratios are low in the 500 °C steps), while the interior is less contaminated. For Y000097 the pattern is more complicated, since its rim sample releases only 13% of the ³⁶Ar_{tr} in the 500 °C step, while 66% degas in the 1400 °C step. As already seen in He and also apparent in Xe (see discussion below), Y000097 appears to be pervasively weathered. In general, all samples release very little, if any, gas in the 1800 °C step.

4. Discussion

4.1. Cosmic ray exposure ages

We calculated cosmic ray exposure ages using the isotopes ³He, ²¹Ne, and ³⁸Ar following the method of Eugster and Michel (1995) and Eugster et al. (1997) (Table 5). Chemical data are taken from Treiman (2005) for Y000593, and from Shirai and Ebihara (2009) for the shergottites. As Y000027 and Y000097 are claimed to be paired (Mikouchi and Kurihara, 2007a,b) we conclude $T_{(3+21)}$ of this shergottite to be 4.41 ± 0.54 Ma. $T_{(3+21+38)}$ is 3.82 \pm 0.58 Ma, but cosmogenic argon may be compromised by the influence of weathering. Our value is in accord with the cosmic ray exposure ages for other lherzolitic shergottites, e.g., ALHA 77005 (Eugster et al., 1997; Schwenzer, 2004) and also in good agreement with the previously reported values for Y000027/000097: 4.90 (± 1.28) Ma (Nagao et al., 2007) and 4.6 \pm 1.5 Ma (Nagao et al., 2008).



Fig. 1. Cumulative release plots for trapped 36 Ar_{tr} and 132 Xe. Numbers at the steps are temperatures in °C. Black solid lines: rim, grey dashed lines: interior, black dotted line: air ratio. Degassing temperatures are given adjacent to the lines in grey and black numbers with color of the numbers corresponding to the line color. Also, the total concentration is given for the rim and interior samples in 10^{-9} ccSTP/g for 36 Ar_{tr}, and 10^{-12} ccSTP/g for 132 Xe.

For the nakhlite Y000593 we obtain a cosmic ray exposure age of $T_{(3+21)} = 11.8 \pm 0.3$ Ma, which is in sound agreement with the exposure ages of the nakhlites and the idea that the nakhlites were ejected in a single ejection event (see Treiman, 2005 for summary). We exclude T_{38} here as it is significantly lower than T_3 and T_{21} and furthermore varies between the rim and interior sample (Table 5), indicative of weathering influence or chemical inhomogeneities. Our T_{21} matches the cosmic ray exposure age of Y000593 reported in the literature (11.2 Ma, average CRE age, Christen et al., 2005; 11.7 Ma T_{21} age, Okazaki et al., 2003; 11.83 Ma, T_{21} , our study) perfectly.

4.2. Helium loss

Helium is lost most easily due to weathering as well as due to shock metamorphic overprinting (Fritz et al., 2005a) during the launch of a meteoroid from Mars. It has been shown that shock metamorphic overprint and helium loss correlate in a systematic manner (Schwenzer et al., 2008b).

Comparing rim and interior samples, the Y000027 shergottite and the Y000593 nakhlite show only 89% of the ⁴He amount of the interior in the rim samples (Table 1). The observed difference is most likely due to weathering (Graf and Marti, 1995; Alexeev, 1998). The 11% loss observed here is larger than the $5 \pm 3\%$ that have been reported for L and H chondrites found in Antarctica (Alexeev, 1998). Also, Antarctic weathering can account for the spread of helium and neon results obtained for Y000593 so far; the measured (total) concentrations of ⁴He, for example, range from 480 to 1304×10^{-8} ccSTP/g (Murty et al., 2003; Okazaki et al., 2003, this study; Fig. 2). The rim of Y000027 rim contains 23% less ³He than the interior pointing at helium loss after accumulation of



Fig. 2. "Bern-plot" (Eberhardt et al., 1966), showing (a) the results of the Y000593 measurement of this study together with the available literature data, and (b) Y000027 and Y000097 of this study. Also shown are "Leya-lines". For Y000593 these are calculated after Leya et al. (2000) taking the bulk chemical compositions from Treiman (2005), for the shergottites they are calculated with the chemical compositions of Y000097 as measured by Shirai and Ebihara (2009).

the cosmic ray produced nuclides. For Y000097 the picture is less clear, but both rim and interior are low compared to Y000027 interior, which is another piece of evidence that Y000097 has experienced pervasive weathering. In the nakhlite Y000593 the rim sample contains about 5% less ³He than the sample from the interior. The nakhlite, being a much bigger sample, may show weathering as well as irradiation differences between its rim and interior. Using the "Bernplot" (${}^{3}\text{He}/{}^{21}\text{Ne})_{c}$ vs. (${}^{22}\text{Ne}/{}^{21}\text{Ne})_{c}$ (Eberhardt et al., 1966) and combining it with theoretical production rate calculations using the method of Leya et al. (2000) allows to evaluate ³He loss more strictly, since in combination with the neon data differences in irradiation conditions are taken into account. Fig. 2

shows that for the shergottite Y000027 and the nakhlite Y000593 the samples taken from the interior match the theoretical value within measurement uncertainty while the samples from the rim fall below the line. This pattern, i.e., a lower $({}^{3}\text{He}/{}^{21}\text{Ne})_{c}$ ratio in the rim compared to the interior sample, is especially pronounced in Y000027. As already noticed for ⁴He. terrestrial influence on helium in the complete Y000097 sample is observed, in contrast to the pronounced difference between rim and interior in case of Y000027 and Y000593. Coming back to the question of terrestrial loss, those samples with ³He loss must either have suffered terrestrial weathering loss or solar heating, where we regard weathering as the more likely cause. This inference is based on our observations of the heavy noble gases which show severe terrestrial influence especially in the rim samples (see below).

Looking at the ³He/⁴He ratios (Fig. 3) displays another aspect: The measured ratios are essentially identical to the cosmogenic ³He/⁴He ratio, which is taken as 0.244 here (for details see Schwenzer et al., 2008b). The nakhlite, in contrast, shows additional, i.e., radiogenic, ⁴He. The most likely reason for the loss of radiogenic ⁴He is shock metamorphism. This is in accordance with our findings on a larger set of Martian meteorites, for which we could demonstrate a correlation of the degree of ⁴He_{rad} loss with shock pressure that is independent from the initial amount of ⁴He, thus independent of U and Th in the sample (Schwenzer et al., 2008b). Other noble gases are affected, too, but the mechanisms are more complicated: e.g., argon and xenon can be implanted from



Fig. 3. ³He vs. ⁴He of the two shergottites Y000027 and Y000097, and the nakhlite Y000593.

the Martian atmosphere as well as lost from the sample. Details are beyond the scope of this paper, especially as the samples in hand are affected by terrestrial processes that modified the heavy noble gas budget.

4.3. Cosmic ray fingerprints

Looking more closely at the neon isotope systematic reveals that there potentially is a solar cosmic ray (SCR) contribution to the shergottites' neon (as common; e.g., Schwenzer et al., 2007a; and observed in these samples by Nagao et al., 2008). In Fig. 4 most points plot in the range of 0.80-0.95 for 21 Ne/ 22 Ne, i.e., the GCR spallation composition in bulk chondrites (e.g., Wieler, 2002). The five data points showing lower 21 Ne/ 22 Ne ratios are all 500 °C steps. One of them (Y000027 interior) shows also a high 20 Ne/ 22 Ne ratio, which indicates presence of a trapped component, either Martian or (more likely in this case) terrestrial atmosphere (Fig. 4) (see also Nagao et al., 2008). Some, but not all of the other 500 °C data points can be explained marginally, if a low 20 Ne/ 22 Ne ratio is



Fig. 4. Neon three isotopes plot showing all T-steps measured. The ones falling off the grey line are all 500 °C steps. In the upper left part the trapped components air (lower black dot) and Martian atmosphere (upper black dot; Garrison and Bogard, 1998; Swindle, 2002; for a more in depth discussion see Schwenzer et al., 2007a) are shown. Also shown is the SCR–Ne signature (after Garrison et al., 1995; data from Reedy, 1992) as well as the ²¹Ne/²²Ne ratio derived by Smith and Huneke (1975) for pure sodium spallation.

assumed for the trapped component, for example ~ 7 as suggested for Martian atmosphere by Bogard and Garrison (1998) and Nagao and Park (2008). No indication for this is observed in the other temperature releases, however.

On the other hand, the release of solar cosmic ray (SCR) produced neon can explain the data (Fig. 4). To further evaluate this possibility, we calculated the cosmogenic $({}^{21}\text{Ne}/{}^{22}\text{Ne})_c$ ratios. In accordance with the discussion above, remarkably low $({}^{21}\text{Ne}/{}^{22}\text{Ne})_c$ is found for the 500 °C step of four samples: Y000027 rim (0.749 \pm 0.013), both Y000097 samples (0.728 \pm 0.010 rim, 0.747 \pm 0.012 interior), and notably also the rim sample of nakhlite Y000593 (0.774 \pm 0.010). Two conclusions can be drawn from the results as demonstrated in Fig. 5. First, reassuringly, data for the shergottites confirm a pre-atmospheric radius larger than the size of the recovered meteorites. Second, the 500 °C



Fig. 5. Cosmogenic $(^{21}\text{Ne}/^{22}\text{Ne})_c$ for the three Martian meteorites shown in Fig. 2 as derived from measured Ne, compared with the range of possible ratios according to production rates of Leya et al. (2000) for GCR spallation and the chemical composition of the respective meteorites [bulk chemical compositions of Y000593 from Treiman (2005), for the shergottites the chemical compositions of Y000097 as measured by Shirai and Ebihara (2009)]. Thick grey lines show range of ratios for radii up to 40 cm (see text). Dotted black lines indicate the theoretical $^{21}\text{Ne}/^{22}\text{Ne}$ range for the size, which fits most closely to the calculated minimum radius derived from the recovered mass. This is a meteoroid radius of 5 cm for the shergottites and 10–15 cm for the nakhlite, respectively.

releases with $({}^{21}\text{Ne}/{}^{22}\text{Ne})_c$ lower than the "allowed" range indicate a possible contribution from solar cosmic rays. Although solar cosmic rays penetrate only few cm into a rock (Wieler, 2002), it may not be too surprising to see SCR influence in the interior of shergottite Y000097 for two reasons. (1) Solar cosmic ray influence is commonly observed in shergottites of all subtypes (Schwenzer et al., 2007a). (2) The meteoroid radius may have been as small as 1.25 cm (taken from its find mass of 24.48 g and assuming a density of 3 g/cm³) and can not have been more than 15 cm in radius judging from a comparison of its total (${}^{21}\text{Ne}/{}^{22}\text{Ne})_c$ with theoretical (${}^{21}\text{Ne}/{}^{22}\text{Ne})_c$ ratios calculated for its chemical composition (Fig. 5; Leya et al., 2000; Shirai and Ebihara, 2009).

Alternatively there is the option of degassing of a single Na-rich phase at 500 °C (comp. the pure sodium spallation ratio for production by GCR (Smith and Huneke, 1975) in Fig. 4). In evaluating both possibilities, it needs to be taken into account that the low $(^{21}\text{Ne}/^{22}\text{Ne})_c$ ratios have been observed here in one temperature step of the respective samples only and are not obvious in the totals, which is in contrast to other cases (Garrison et al., 1995; Schwenzer et al., 2007a); also, the meteoroid radius is currently unknown. Hence the case for SCR is weak at this time. Plagioclase is present as maskelynite with an abundance of ~ 9% (Mikouchi and Kurihara, 2008). Calculating its contribution to the production of ²¹Ne (after Leya et al., 2000) results in (5.2-6.4) $\times 10^{-10} \text{ ccSTP/g}_{\text{whole rock}}$ of ²¹Ne in 4.4 Ma, which agrees well with the abundance observed in our first T-step [Y000097: rim $(6.59 \pm 0.18) \times 10^{-10}$ ccSTP/g; interior $(5.53 \pm 0.14) \times 10^{-10}$ ccSTP/g]. Calculating the theoretical ²¹Ne_c from pure GCR for the (whole rock minus plagioclase)-chemical composition results in $(6.57-8.09) \times 10^{-9} \text{ ccSTP/g}^{21}$ Ne in 4.4 Ma, which is in good agreement with the value for the complete whole rock $[(6.62-8.11) \times 10^{-9} \text{ ccSTP/g};$ chemical composition from Mikouchi and Kurihara (2008), production rates after Leva et al. (2000), calculated for rim and interior of an 5 cm radius object]. These values are too low to explain the measured concentrations of ²¹Ne_c, which are $(1.23 \pm 0.02) \times 10^{-8}$ ccSTP/g and (1.16 ± 0.02) $\times 10^{-8}$ ccSTP/g for Y000097 rim and interior, respectively. However, with a bigger, 15-25 cm radius preatmospheric object, the production rates calculated with the Leya-method (Leya et al., 2000) match those obtained with the Eugster-method (Eugster et al., 1997). This choice would also increase the amount of ²¹Ne from plagioclase. Overall, the ²¹Ne/²²Ne ratios calculated for the sizes of objects that would fit the amount of ²¹Ne are higher than the measured ones for most of the cases,

which may *de facto* support the assumption of SCR contribution. Note that Nagao et al. (2008) also propose SCR influence from their measurements of these two shergottite specimens.

4.4. Terrestrial and Martian atmosphere in Martian meteorites

Because all three investigated Martian meteorites are Antarctic finds, they may have a long terrestrial age. While no data are available for the shergottite specimens yet, for the nakhlite Y000593 the terrestrial age has been given as <0.04 Ma (Okazaki et al., 2003) and 55 ± 20 ka (Nishiizumi and Hillegonds, 2004). From this and the occurrence of secondary minerals of terrestrial origin (Treiman and Goodrich, 2002), terrestrial weathering influence, i.e., adsorption of terrestrial atmosphere, is a concern. In earlier studies we found incorporation of terrestrial atmosphere in hot and cold desert derived samples to result in elemental fractionation leading to 84 Kr/ 132 Xe ratios as low as ~1 or even lower (Schwenzer, 2004; Schwenzer et al., 2007b). The 129 Xe/ 132 Xe isotopic ratio of terrestrial atmosphere remains unfractionated of course (0.9832, Ozima and Podosek, 2002). As the Martian interior component as measured in Chassigny has a similarly low 84 Kr/ 132 Kr (~1.1, Ott, 1988) and the 129 Xe/ 132 Xe ratio (1.03, Ott, 1988) is similarly low as in terrestrial atmosphere, it often becomes difficult to recognize whether a Martian interior component is present or if one is dealing with fractionated air.

Fractionation between Kr and Xe reducing the Kr/Xe ratio by a factor of ~ 2 is well known for air in terrestrial waters (Ozima and Podosek, 2002). Terrestrial fractionation of Kr from Xe had also been seen in meteorites (e.g., Schelhaas et al., 1990, L chondrite ALHA77214/81030; Scherer et al., 1994). The first indication for the presence of extremely low ⁸⁴Kr/¹³²Xe ratios – later termed elementally fractionated air (EFA) - in Martian meteorites was found in the Dar al Gani (DaG) and Sayh al Uhaymir (SaU) Martian meteorites (Mohapatra et al., 2002). From this an endmember for EFA with a 84 Kr/ 132 Xe ratio of ~1 (and atmospheric isotopic composition) was suggested. The results obtained on meteorites were subsequently confirmed by measurements of purely terrestrial sand samples from the DaG and SaU regions (Mohapatra et al., 2009; Schwenzer et al., 2002, 2003, 2007c). Terrestrial samples from the cold desert of Antarctica (as the meteorites investigated here) show similar trends, with the fractionation becoming more severe in locations with multiple freeze-thaw cycles (Schwenzer et al., 2007b). In the analyses of the two Yamato shergottites it can be seen that the rim samples are dominated by air in a way that no discernible evidence for the presence of a Martian atmospheric component is left, if one looks at the sum of all degassing steps (Fig. 6, Table 4). Only in the 1400 °C T-steps (and, with large error, the 1800 °C step of Y000097 interior) recognizable evidence for Martian atmospheric contribution can be found in the form of enhanced 129 Xe/ 132 Xe. As both recovered shergottites are small (find masses are 9.68 and 24.48 g for Y000027 and Y000097, respectively) the dominance of EFA may indicate essentially complete penetration of the meteorite by cold desert weathering processes. Our findings agree with the observations of Nagao et al. (2008), where presence of Martian atmosphere is only indicated in a small percentage of the Xe released in some higher temperature steps. The nakhlite Y000593, on the other hand, is a bigger specimen (find mass \sim 15 kg, with a single piece of 13.7 kg). In our data set



Fig. 6. In Xe/In Xe vs. or Kr/10-Xe. Shown are all temperature steps above blank. Numbers next to the data points indicate the corresponding degassing temperature. Endmembers are Chassigny (Ott, 1988), Martian atmosphere (Swindle, 2002) and terrestrial atmosphere (Ozima and Podosek, 2002). Also indicated is a range for the maximum fractionation of terrestrial air observed in our previous studies (see text) and the fractionated Martian atmosphere as evaluated by Schwenzer and Ott (2006). Insert: full range. Main figure: lower left extended. Abbreviations in the insert: FMA: fractionated Martian atmosphere (Schwenzer and Ott, 2006), MA: Martian atmosphere (Swindle, 2002), crush: component released upon crushing EETA79001 (Wiens, 1988), AIR: terrestrial atmosphere (Ozima and Podosek, 2002), MI: Martian interior (Ott, 1988).

the sample from its rim is dominated by EFA (Figs. 1 and 6), whereas the sample from the interior shows 129 Xe/ 132 Xe ratios up to 1.68, the highest value observed in this study. Therefore, weathering – although observed in thin section (Treiman and Goodrich, 2002) – may not have penetrated this sample completely, leaving the interior only moderately disturbed. To further evaluate this, the measurement of mineral separates may be helpful, but chemical treatments such as leaching may worsen the problem rather than being of help (Ott, 2008; Schwenzer et al., 2005).

The nature of the heavy noble gases can be further explored by looking at the 136 Xe/ 132 Xe ratio (Fig. 7). Interestingly, the nakhlite Y000593 interior sample shows contribution of Martian atmosphere in all T-steps (500, 1000 and 1400 °C), thereby making it



Fig. 7. 129 Xe/ 132 Xe vs. 136 Xe/ 132 Xe. Shown are all temperature steps where released gas amounts were clearly above blank. Numbers next to the data points indicate the corresponding degassing temperature. Endmembers are Chassigny (Ott, 1988), Martian atmosphere (Swindle, 2002) and terrestrial atmosphere (Ozima and Podosek, 2002). Top: full range. Bottom: lower left extended.

a comparably fresh sample. Its signatures are compatible with releasing a pure mixture of Chassigny and Martian atmospheric type gases in the 1400 °C step. Shifts to higher 136 Xe/ 132 Xe may indicate presence of a fission component (e.g., Mathew et al., 2003). Not much hint at Martian components is found in the rim of the nakhlite, where all T-steps are dominated by air. This finding demonstrates the importance of careful sample choice in concert with stepwise heating experiments. For the shergottites the 1400 °C steps and the 1800 °C step of Y000097 are the only steps showing Martian atmospheric signatures, which — as noted above — can be explained by a more penetrating terrestrial influence due to the small sample size.

There are additional interesting observations on the Martian components (Fig. 6). For the 500 °C step of Y000593 interior the observed shift to low 84 Kr/ 132 Xe ratios may have been enhanced by contamination with EFA, which is observed also in all other samples. In the higher T-steps, the nakhlite shows very low ⁸⁴Kr/¹³²Xe ratios, which are accompanied by high 129Xe/132Xe ratios. Those temperature steps, especially the 1400 °C steps of the interior sample, are influenced by Martian atmosphere. Within error limits the data plot on the mixing line between the "nakhlitic" fractionated Martian atmosphere as derived by Schwenzer and Ott (2006) and Chassigny (Martian interior; Ott, 1988) indicating the action of secondary, presumably aqueous, processes on Mars introducing a fractionated atmosphere. This is supported by the fact that Y000593 contains pre-terrestrial alteration minerals (Treiman and Goodrich, 2002; Treiman, 2008) and the disturbance of the Rb-Sr systematic (Misawa et al., 2005). In contrast to the fractionated Martian atmosphere incorporated into the nakhlites through alteration processes, the shergottites show evidence of implanted, unfractionated Martian atmosphere in their 1400 °C steps (Fig. 6). The excess ¹²⁹Xe (over the Martian interior 129 Xe/ 132 Xe = 1.03, Ott, 1988) thereby is the decisive feature pointing to their Martian descent (Bogard, 1982; Bogard et al., 1984). Implantation of Martian atmosphere into these samples is supported by the "severe" (Mikouchi and Kurihara, 2007a,b) shock pressure and melt veins (Imae and Ikeda, 2007) observed in the meteorite. In detail, however, the 1400 °C steps fall to slightly higher ⁸⁴Kr/¹³²Xe ratios than expected from pure mixing of Chassigny and Martian atmosphere. Overall, our dataset nicely demonstrates the contrast between alteration-incorporated fractionated Martian atmosphere in the nakhlites vs. shock-implanted, unfractionated Martian atmosphere in the shergottites.

5. Conclusions

Our study of rim and interior sample pairs of three Yamato Martian meteorites allows insights into several processes that affected the Martian meteorites in the course of their history.

5.1. Nakhlite

The nakhlite Y000593 (interior sample) shows addition of (fractionated) Martian atmosphere in its heavy noble gas signature, which is in agreement with findings for other nakhlites. One of the T-steps (1400 °C interior) is consistent with a pure mixture of the Chassigny and fractionated Martian atmosphere endmembers. Also in agreement with previous studies on other nakhlites is the fact that shock metamorphic overprint did not cause much loss of helium from this meteorite. The terrestrial contamination of Y000593 is not penetrating the whole specimen to the same degree as the much smaller shergottites, because the interior sample shows much less contribution from fractionated terrestrial atmosphere than the rim sample. Kr and Xe of the interior sample can be pictured as a mixture of Chassigny type gas and fractionated Martian atmosphere with some addition of air contamination and fission xenon.

5.2. Shergottites

Looking at the shergottites' histories, presence of Martian interior and unfractionated Martian atmosphere is indicated in some of the temperature steps that are not overwhelmed by air contamination. As most shergottites, both samples show severe loss of radiogenic helium most likely due to shock metamorphic overprint. While terrestrial contamination is overwhelming in all samples, the 1400 °C steps still reveal the presence of Martian components, containing a Chassigny (Martian interior) type gas and unfractionated (in terms of the ⁸⁴Kr/¹³²Xe ratio) Martian atmosphere component. From the xenon isotopic signatures alone, however, only the presence of air and Martian atmosphere is obvious.

Overall, our study sheds light on the fact that samples from Antarctica have to be evaluated carefully for terrestrial contamination, which compromises the interpretation of noble gas results. Small samples thereby may be penetrated completely. However, stepwise heating — and more so the measurement of mineral separates — allows looking through the terrestrial signatures at the Martian components.

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