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New constraints on the lithium isotope compositions of the Moon and terrestrial planets

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Abstract

High-precision lithium (Li) isotope data are reported for samples from the Earth, Moon, Mars and Vesta and provide evidence of broadly similar compositions that are slightly heavy relative to those of chondrites. Mare basalts exhibit a large range of Li isotope compositions ($\delta^7Li = +3.4‰$ to $+6.4‰$) that correlate with indices of magmatic differentiation. Three samples (quartz-normative basalts and picritic orange glass) that are thought to have formed by melting of relatively primitive source regions yield a mean $\delta^7Li = +3.8 \pm 0.4‰$ taken as the best estimate for the average composition of the Moon. Other samples are isotopically heavier correlating with increases in Rb and Hf and probably reflecting transport of isotopically heavy Li that formed in specific high-Ti cumulate–melt layers during crystallisation of the magma ocean. The most extreme lunar δ^7Li is found in a ferroan anorthosite ($+8.9‰$). Terrestrial mantle olivines fall into a tight range between $+3.6‰$ and $+3.8‰$. If these olivines reflect the composition of the bulk Earth, the Li isotope compositions of Earth and Moon are identical. The Li isotope compositions of samples from the Moon, Earth, Mars and Vesta provide no evidence for differences between large inner solar system mantle reservoirs. This in turn provides evidence that core formation, volatile loss and the presence of a crust and hydrosphere have not significantly influenced the bulk Li isotope composition of the mantles of these objects. The fact that chondrites are isotopically light compared with differentiated planetary bodies of the inner solar system is consistent with a small but significant Li isotope fractionation within the accretionary disc or chondrite parent bodies, the origin of which is presently unclear.
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1. Introduction

Theoretical models and isotope approaches for studying the origin of the solar system are becoming increasingly sophisticated and powerful [1–3], but a major issue of current debate is the origin of the heterogeneous distribution of volatiles, which it is now thought may partly relate to accretion processes. It has been proposed on the basis of Sr isotopes that there were significant losses of moderately volatile elements during the late (>10 Myrs) accretionary history of the material that formed the Earth and Moon [4]. More recently it has also been argued that the slightly heavier Fe isotope composition of basalts from the Moon, relative to those from Vesta and Mars, may reflect volatilisation of Fe

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during the Giant Impact [5]. Iron is only slightly volatile and the degree to which this effect reflects vaporisation of molten iron metal as opposed to silicate is unclear. If the effect is produced by volatilisation of silicate it should be present in other elements of similar half mass condensation temperature. Lithium is such a slightly volatile element. O'Neill [6] predicted complete or nearly complete condensation of Li while most Na is evaporated during formation of the Moon. Being very light, Li is expected to show sizeable isotope fractionations during partial volatile loss.

Lithium (Li) isotope abundances have already been reported from a few meteorites using high-precision multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) [7,8]. However, most of these are chondrites. The few existing analyses suggest that different chondrite groups may have distinct Li isotope compositions. This variation could reflect aqueous alteration on parent bodies resulting in isotopically light Li in the residual highly metamorphosed chondrites and isotopically heavy Li related to chondrites with high alteration index [7]. CM chondrites show large internal Li isotope variation [8] providing evidence of a complex history of evaporation and condensation of Ca- and Al-rich refractory inclusions and chondrules in the solar nebula. These two constituents of chondrites seem to have negative δ^7Li values resulting partly from incorporation of spallogenic Li into chondritic matter in the early solar system [9,10].

The exact Li isotope composition of the bulk silicate Earth or primitive mantle has proven problematic because the variation in Li isotope compositions in mantle rocks is large (−17‰ to >+10‰; [11–19]). Most estimates of the Li isotope composition of the terrestrial mantle are made on the basis of MORB and very limited data for Hawaii (δ^7Li of 4.2±0.8‰; [20]). Available analyses of peridotitic rocks seem to be consistent with a δ^7Li close to +4‰ for the Earth [14,21] although samples from the latter study may have been influenced by subduction zone processes with heavy Li. Isotope compositions of peridotites, calculated from mineral data, showed rather variable values (δ^7Li from −1.1‰ to +4.1‰; [14]). Two fertile lherzolites from Vitim (Russia) and Dreiser Weiher (Germany) have calculated bulk δ^7Li of +3.8‰ and +4.1‰, respectively [14], consistent with the above mantle value. Also Elliott et al. [22] stressed that the δ^7Li in N-MORB lavas displays a tight range of 3–4‰ with slightly higher values in OIB.

We have analysed a range of samples to assess whether there are systematic differences in Li isotope composition between planetary objects, in particular the

Moon and to constrain a δ^7Li value for the bulk Earth. In addition to data for lunar basalts, eucrites, martian meteorites and chondrites, we present Li isotope ratios for a suite of olivines, clinopyroxenes and orthopyroxenes from spinel lherzolites in order to better estimate the δ^7Li of the Earth's mantle.

2. Methods and samples

All samples have been dissolved in a mixture of HF and HNO_3 (6 : 1 v/v) and after complete decomposition evaporated and refluxed with HNO_3 several times to remove fluorides. We used small-volume (2.1 ml) ion exchange columns packed with BioRad AG50W-X8 (mesh 200–400) cation-exchange resin and employed 1M HNO_3–80% methanol (v/v) mixture as an elution media. Isotope measurements were performed on the large-geometry high-resolution multiple-collector ICPMS Nu1700 (Nu Instruments). Details of analytical and mass spectrometric procedures are given in Magna et al. [23].

Additional small columns (0.6 ml) packed with BioRad AG50W-X12 (mesh 200–400) were used for final cleaning and effective removal of large quantities of chromium that appeared in the Li fraction after the first step. This problem was notable for clinopyroxenes from spinel lherzolites which contain up to 1–2% Cr. The use of 0.5 M HNO_3 eluted all Cr in 2 ml such that the subsequent Li fraction was completely "clean" (see Fig. 1). Although this second step was precautionary and we did not quantify the influence of Cr on the accuracy of Li isotope measurements, it appears to be important for the acquisition of high quality data.

Lithium abundances were measured using a PQ-2 quadrupole ICPMS (VG Elemental) with beryllium as an internal standard for matrix effect corrections. Other trace element data for lunar rocks, eucrites, Allende and martian meteorites were obtained using the PQ-2 quadrupole ICPMS (VG Elemental) with rhodium as an internal standard. Basaltic reference standards were measured prior to samples and 2σ errors (two standard deviations) were better than 5% for most elements. Uncertainties in U and Pb determinations were better than 10% (2σ), Cs determinations were better than 20% (2σ). The Eu anomaly Eu_N/Eu* was calculated from the interpolated Eu* defined by the chondrite-normalised abundances of Sm and Gd.

Terrestrial samples comprise mineral separates of olivine, clinopyroxene and orthopyroxene extracted from spinel lherzolites from San Carlos and Kilbourne Hole (USA), Vitim (Russia), Atsagin-Dush and Tariat (Mongolia). Additionally, three lherzolites and one
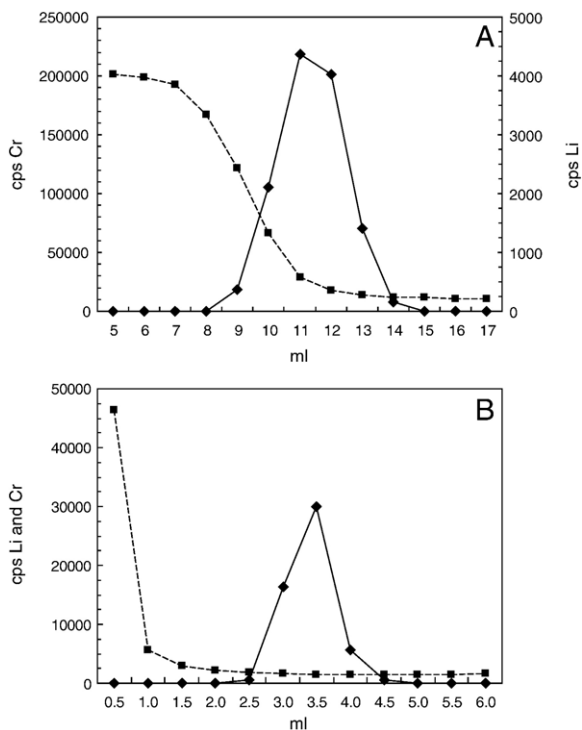
Fig. 1. Two-stage Li elution and purification from clinopyroxene 8520-09. Panel A displays first step of Li elution where Cr dominates Li fraction. Note two-order difference of magnitude in counts per second (cps) for Cr and Li. BioRad AG 50W-X8 cation-exchange resin was used and elution media 1 M HNO_3 in 80% (v/v) methanol provided excellent separation of Li from other matrix and trace elements apart from Cr. Second step (panel B) used 0.5 M HNO_3 to separate Li form Cr successfully with employing BioRad AG 50W-X12 resin. Chromium is marked as squares with dotted line, lithium as diamonds with solid line.

harzburgite from Atsagin-Dush were analysed for whole-rock δ^7Li composition. San Carlos is a primitive spinel lherzolite from Arizona, USA, studied for its major and trace elements by Jagoutz et al. [24]. Vitim (Siberia, Russia) has been depicted as a fertile off-craton peridotite and in detail studied by Ionov et al. [25]. Samples from Atsagin-Dush, Mongolia, were previously described in detail by Wiechert et al. [26]. 8520-09 is a spinel lherzolite for which Li concentration and isotope data for olivine and orthopyroxene were acquired. 8520-12, -19 and -20 are spinel lherzolites whereas 8520-30 is a harzburgite. Tariat spinel lherzolite is located in Tariat depression, Mongolia, and has been described in detail by Press et al. [27]. Kilbourne Hole (New Mexico, USA) is a spinel lherzolite, another aliquot of which has been studied by Jagoutz et al. [24]. Mineral separates from spinel lherzolites were ultrasonically cleaned in weak HCl for 20 min to remove surface contamination, subsequently rinsed with de-ionised water and ultrasonically

washed for 30 min in de-ionised water. The lunar samples include the more important magmatic rock types collected during various Apollo missions: high-Ti mare basalts, picritic glasses, olivine-, ilmenite- and quartz-normative basalts as well as one ferroan anorthosite. In addition, 2 martian meteorites, 6 eucrites and 2 chondrites were analysed.

Lithium isotope compositions were calculated using the following formula: δ^7Li (‰)=$[(^7Li/^6Li)_{sample}/(^7Li/^6Li)_{standard} - 1] \times 1000$. We used L-SVEC as a reference standard [28]. Accuracy and precision of the method has been monitored by multiple analyses (full replication including sample dissolution) of BHVO-2 and JB-2, two international reference rocks of the US and Japanese Geological Surveys, and OK-1 an in-house eclogite standard from Münchberg (Germany) with well-defined $\delta^7Li=-8.27\pm0.20$‰ [23]. During this study δ^7Li values of 4.52 ± 0.18‰ (2σ; $n=10$), 4.65 ± 0.39‰ (2σ; $n=9$) and -8.24 ± 0.33‰ (2σ; $n=3$) have been obtained for BHVO-2, JB-2 and OK-1, respectively. These values are in good agreement with previously published data and results reported by other groups [29–31].

3. Results

Lithium abundances and isotope compositions for non-terrestrial samples are given in Table 1. Trace element data for non-terrestrial samples are provided in Table 2. Two chondrites Allende (CV3) and Bruderheim (L6) contain 2.1 and 2.7 ppm Li, respectively. Nakhla, a martian clinopyroxene cumulate, and Zagami, a martian shergottitic basalt, contain 4.8 and 4.0 ppm Li, respectively. Eucrites show substantially higher Li abundances (8.3–13.1 ppm) as do lunar rocks and glasses (6.0–13.3 ppm). Two ferroan anorthosites have 0.8 ppm Li (62255) and 0.14 ppm Li (65315), respectively. Total repeat analyses of five samples including the full analytical procedure, replicated very well (see Table 1).

The Li isotope compositions of the samples range from +1.5‰ to +8.9‰ δ^7Li (Fig. 2). The chondrites are isotopically light relative to all the other samples, Bruderheim (L6) yielding $\delta^7Li=+1.5$‰, whereas two duplicate measurements of Allende (CV3) average $\delta^7Li=+3.1$‰. Although this is an inadequate characterisation of chondrites, the data are fully consistent with the recent and more comprehensive study of chondrites reported by McDonough et al. [7], who also report compositions that are variable but light relative to the values for the various silicate samples reported in Table 1. The best estimate for average chondritic compositions is $\delta^7Li=+2.0\pm1.5$‰ (W. McDonough,

Table 1
Lithium concentrations and isotope compositions of non-terrestrial samples

	Sample	Split	Li (ppm)	δ^7Li (‰)	2σ
Moon					
Anorthosites					
Fe-anorthosites	62255	134	0.8	8.89	0.18
	65315	30	0.14	n.a.	
Basalts					
High-Ti mare basalts	70035	164	8.6	5.09	0.09
	Replicate			5.11	0.10
	74255	178	9.2	6.39	0.41
	75075	158	10.3	5.48	0.15
	Replicate			5.21	0.31
Qz-normative basalts	15058		7.7	3.74	0.12
	15475	31	7.2	3.35	0.26
Ilm-normative basalt	12045	13	9.5	4.43	0.09
	Replicate			4.28	0.07
Ol-normative basalt	15555	115	6.0	4.32	0.16
Glasses					
Green glass	15426	163	6.7	4.74	0.19
Orange glass	74220	804	13.3	4.19	0.30
Grey glass	74240	17	10.5	5.60	0.15
Mars					
Nakhla			4.8	4.99	0.47
Zagami			4.0	3.88	0.18
Vesta					
Bereba			10.6	4.23	0.22
Bouvante			13.1	3.84	0.48
Cachari			10.5	5.75	0.89
Juvinas			9.0	3.65	0.29
	Replicate			3.61	0.34
Pasamonte			10.1	3.65	0.20
ALHA 78132			8.3	3.04	0.24
Chondrites					
Allende			2.1	3.13	0.25
	Replicate			3.08	0.19
Bruderheim			2.7	1.49	0.29

n.a. — not analysed.

personal communication to ANH, 2005). The martian meteorites Nakhla and Zagami yield δ^7Li=+5.0‰ and +3.9‰, respectively. Eucrites span a narrow range from +3.0‰ to +4.2‰ excluding Cachari with a high δ^7Li. The same aliquot of Cachari also has anomalously heavy oxygen [32]. The range of δ^7Li values in lunar basalts and glasses (i.e. excluding the anorthosites) exceeds 3‰ (+3.4‰ to +6.4‰) and appears to vary with lithology. Quartz-normative basalts have the lightest Li isotope compositions whereas high-Ti mare basalts are isotopically heavy. Picritic glasses, olivine- and ilmenite-normative basalts have intermediate δ^7Li values. An extreme δ^7Li value of +8.9‰ has been measured in a ferroan anorthosite (62255).

Lithium abundances and isotope compositions of terrestrial samples are given in Table 3. Terrestrial basalts, e.g. MORB and OIB, are variable in Li concentrations but most have 3–6 ppm Li consistent with the comprehensive study of Ryan and Langmuir [33]. Olivines from spinel lherzolites are notably homogeneous with 1.5–2.0 ppm Li. Pyroxenes are depleted in Li compared to olivines, and orthopyroxenes are more depleted than clinopyroxenes, consistent with findings of Seitz and Woodland [34] for peridotitic lithologies. All olivines and bulk peridotites have δ^7Li values indistinguishable from the currently accepted mantle δ^7Li of 4.2 ± 0.8‰ [20]. Olivine separates are particularly homogeneous with δ^7Li ranging from 3.6‰ to 3.8‰. Whole-rock analyses of peridotites from Mongolia show constant Li abundances of 1.4–1.7 ppm Li and a remarkably narrow range of δ^7Li=3.8–4.3‰. The δ^7Li of the harzburgite is slightly lighter (by ~0.4‰) than the values for spinel lherzolites.

In contrast to these uniform values, pyroxenes show a considerable range in δ^7Li from 2.6‰ to 6.0‰ and two reference peridotites measured during the course of this study show completely distinct δ^7Li values. JP-1 (GSJ) has δ^7Li=3.97 ± 0.41‰, consistent with the olivine and Mongolian bulk peridotite data, whereas PCC-1 (USGS) yields δ^7Li=8.85 ± 0.41‰ (see Table 3) which is indistinguishable from a value of 8.9‰ for this reference rock given by Seitz et al. [14]. However, PCC-1 is a partially serpentinised harzburgite, which can readily account for its heavier δ^7Li value compared to the other peridotites. Bulk Li isotope compositions of peridotitic rocks must be considered with caution as they may be influenced by metasomatism and alteration at various possible stages.

4. Discussion

4.1. Lunar Li and the isotope effects of exposure

Among the various analysed planetary bodies most Li isotope variation is found in lunar materials (Table 1). This could of course reflect the fact that we have analysed many more lunar samples. The variability on the Moon is still surprising however. Oxygen isotopes provide evidence that the Earth and Moon formed from the same raw material [35]. Therefore, the Li isotope compositions for the total Earth and Moon should be identical, assuming Li isotopes have not been fractionated by the putative Moon-forming Giant Impact. Lithium isotope fractionation on Earth is dominated by the large effects associated with the hydrosphere. Therefore, Li isotope fractionation within the dry Moon is expected to be much smaller with basaltic compositions

Table 2
Measured trace elements concentrations of non-terrestrial samples

	12045	15058	15426	15475	15555	62255	70035	74220	74240	74255	75075
Li	9.5	7.7	6.7	7.2	6.0	0.81	8.6	13.3	10.5	9.2	10.3
Co	55	44	69	114	67	1.9	17	66	31	25	25
Ni	55	32	195	1341	67	9.2	6.6	72	94	9.0	8.2
Cu	19	10	10	11	25	–	44	36	32	40	43
Ga	4.8	3.6	3.5	4.1	3.9	–	4.1	8.7	8.1	5.2	5.3
Rb	1.2	0.88	1.3	0.92	0.93	0.33	1.2	1.5	2.3	2.2	1.3
Sr	149	98	65	91	44	170	89	215	152	181	183
Y	53	24	24	23	27	0.35	82	49	76	97	81
Zr	124	73	88	63	89	2.6	231	173	216	246	211
Nb	7.1	5.2	6.6	5.0	6.9	0.10	23	16	19	25	23
Cs	0.04	0.04	0.04	0.04	0.04	0.003	0.03	0.05	0.10	0.07	0.03
Ba	61	50	72	45	47	8.6	54	85	103	85	72
Hf	3.9	1.9	2.1	1.5	2.3	0.03	7.6	5.2	6.3	8.0	7.0
Pb	0.28	0.20	0.70	0.22	0.22	0.57	0.16	0.93	1.0	0.28	0.21
U	0.17	0.11	0.25	0.10	0.13	0.002	0.09	0.15	0.37	0.16	0.09
La	5.9	4.5	6.0	4.0	5.0	0.17	4.4	6.3	9.0	7.2	5.2
Ce	17	12	15	11	13	0.44	15	19	26	24	17
Pr	3.0	1.9	2.2	1.6	2.1	0.05	3.1	3.4	4.3	4.6	3.4
Nd	16	9.7	10	8.2	11	0.23	18	19	22	28	20
Sm	6.1	3.1	3.0	2.8	3.6	0.10	8.0	6.8	8.5	11	8.1
Eu	1.5	0.93	0.60	0.78	0.58	0.67	1.2	2.0	1.6	2.1	2.0
Gd	7.7	3.8	3.5	3.5	4.4	0.06	11	8.2	10	14	11
Tb	1.6	0.71	0.67	0.63	0.84	0.01	2.3	1.6	2.1	2.8	2.3
Dy	9.5	4.2	4.2	4.0	4.8	0.05	14	9.2	13	17	14
Ho	2.2	0.91	0.90	0.88	1.0	0.01	3.2	1.9	2.9	3.7	3.1
Er	5.6	2.4	2.4	2.4	2.7	0.04	8.7	4.7	7.8	9.8	8.4
Tm	0.84	0.36	0.39	0.36	0.38	0.005	1.4	0.70	1.2	1.4	1.2
Yb	5.5	2.3	2.6	2.4	2.4	0.03	8.8	4.4	7.9	9.5	8.2
Lu	0.77	0.34	0.39	0.33	0.37	0.005	1.3	0.64	1.2	1.3	1.2

	Allende	Bruderheim	Bereba	Bouvante	Cachari	Juvinas	Nakhla	Pasamonte	Zagami	ALHA 78132
Li	2.1	2.7	10.6	13.1	10.5	9.0	4.8	10.1	4.0	8.3
Sc			29.1	29.3	33.7	28.4	54.7	29.3	62.6	26.7
Co	682		9.0	3.7	9.9	7.6	55	7.5	43	7.8
Ni	14,600		5.1	4.7	5.0	4.9	91	22	82	20
Cu	117		3.8	3.7	6.3	4.7	6.6	2.3	15	1.8
Ga	7.5		2.4	3.0	2.1	2.9	4.2	2.9	15	2.5
Rb	1.3		0.40	0.76	1.2	0.33	4.1	0.40	5.7	0.42
Sr	15		78	91	101	78	55	79	35	73
Y	2.7		17	29	21	16	3.7	17	13	16
Zr	16		41	87	49	48	12	48	65	45
Nb	2.3		3.9	7.3	5.1	4.2	1.8	3.9	4.9	3.9
Cs	0.09		0.01	0.03	0.03	0.02	0.53	0.01	0.37	0.01
Ba	5.3		32	57	86	30	26	32	25	31
Hf	0.33		0.95	2.2	1.2	1.2	0.28	1.1	1.7	1.0
Pb	2.1		0.18	0.47	0.26	2.30	0.58	0.31	1.2	0.38
U	0.02		0.11	0.17	0.28	0.09	0.05	0.09	0.07	0.12
La	0.58		3.0	5.7	3.8	2.9	2.0	3.0	1.4	3.0
Ce	1.4		7.6	14.0	9.4	7.1	5.1	7.4	3.3	8.2
Pr	0.23		1.2	2.2	1.5	1.1	0.80	1.2	0.52	1.3
Nd	1.2		5.9	10.7	7.6	5.4	3.7	5.7	2.8	6.2
Sm	0.43		1.9	3.5	2.6	1.7	0.82	0.86	1.1	1.8
Eu	0.12		0.70	0.93	0.75	0.70	0.25	0.66	0.44	0.68
Gd	0.40		2.3	4.3	3.0	2.4	0.77	2.4	1.6	2.3
Tb	0.08		0.48	0.79	0.56	0.43	0.12	0.46	0.35	0.45
Dy	0.47		3.1	5.0	3.6	2.7	0.71	3.0	2.2	2.7
Ho	0.12		0.67	1.1	0.79	0.64	0.15	0.66	0.51	0.64
Er	0.28		1.8	3.0	2.3	1.8	0.43	1.8	1.4	1.8
Tm	0.06		0.29	0.42	0.34	0.28	0.07	0.27	0.22	0.28
Yb	0.35		1.9	3.0	2.3	1.8	0.38	1.8	1.4	1.7
Lu	0.05		0.29	0.41	0.34	0.26	0.07	0.29	0.20	0.26

All trace element data are listed in parts per million (ppm). Precision of the concentration data for Fe-anorthosite 62255 is lowered to 20–40% (2σ) due to very low concentrations of most trace elements.
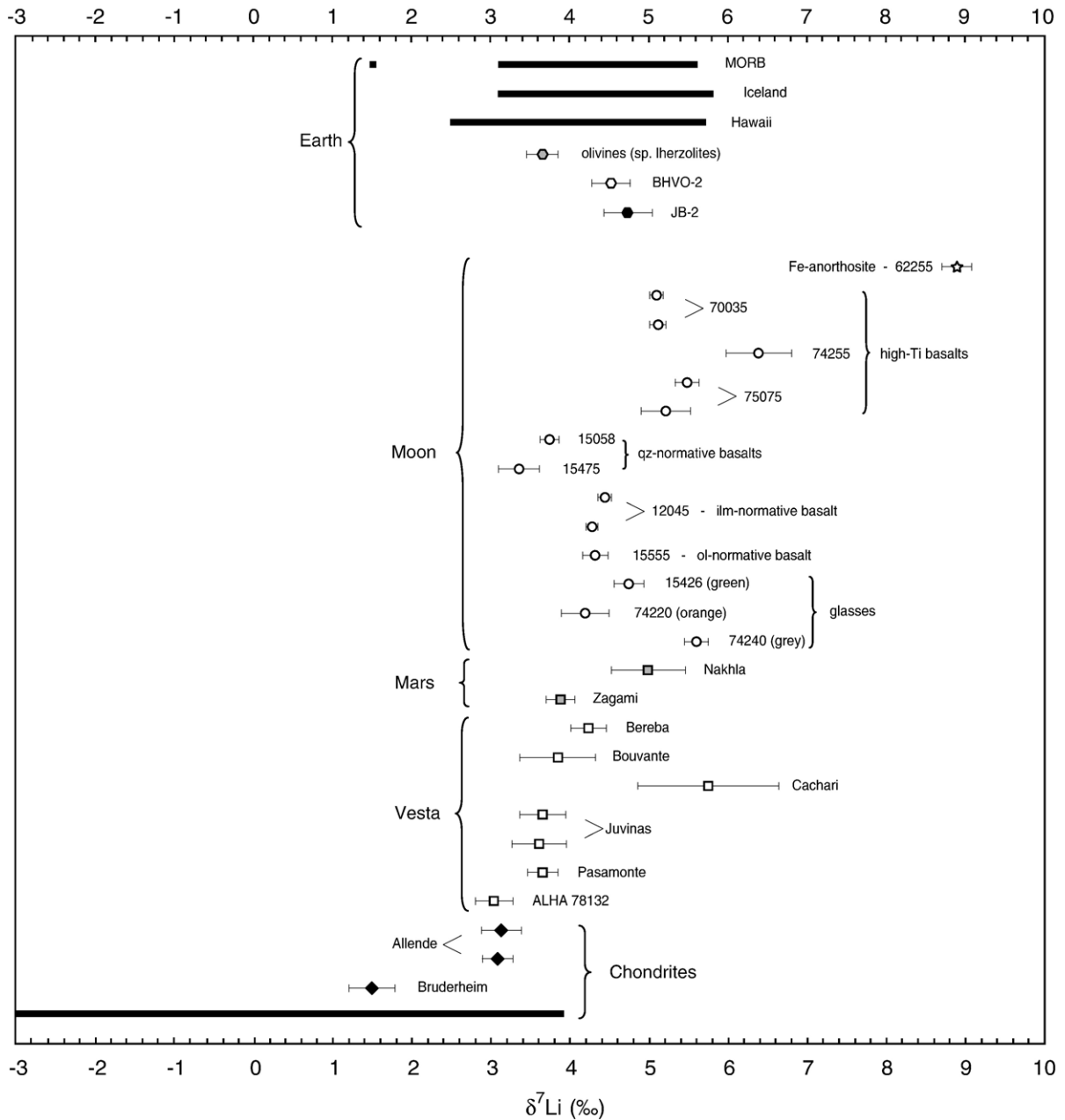
Fig. 2. Lithium isotope composition of terrestrial and extraterrestrial materials. MORB range is from Tomascak [85] and Elliott et al. [22], Iceland range is from Pistiner and Henderson [86], Ryan and Kyle [87] and high-^{3}He/^{4}He samples from Magna et al. [69], Hawaii from Chan and Frey [18], δ^7Li range of chondrites is from McDonough et al. [7] and James and Palmer [83]. Olivines from spinel lherzolites are from this study. BHVO-2 and JB-2 are displayed as long-term reproducibility standards (see Chapter 2 and [23]). Apparent variations of δ^7Li among lunar rocks cannot be related to possible surface exposure to isotopically heavy solar wind particles, even not in case of low-Li ferroan anorthosite 62255 due to its extremely short exposure history <2 Myrs. Grey glass 74240 comes from the same location as orange glass 74220 and is very similar in chemical composition to this spatially related orange glass (apart from slightly elevated Na contents [88,89]). Large proportions of basaltic fragments and grey "ropy" glass spherules cause macroscopically grey colour, orange glass component represents only a very small portion of grey glass. Clinopyroxene is the most abundant mineral phase. It has been suggested that the grey glass is a product of a local large highland impact [90].

Table 3
Lithium concentrations and isotope compositions of terrestrial samples

	Li (ppm)	δ^7Li (‰)	2σ
Peridotites — minerals			
San Carlos ol	1.6	3.64	0.15
San Carlos opx	0.52	3.32	0.35
Vitim 314-58 ol	1.9	3.76	0.05
Vitim 314-58 opx	0.39	3.78	0.15
Vitim 314-58 cpx	1.4	5.21	0.23
Atsagin-Dush 8520-09 ol	1.5	3.55	0.15
Atsagin-Dush 8520-09 cpx	0.82	5.96	0.26
Tariat MPH 79/1 ol	2.0	3.75	0.04
Tariat MHP 79/1 cpx	1.4	2.57	0.32
Kilbourne Hole 96-2 ol	1.7	3.56	0.39
Peridotites — whole rocks			
Atsagin-Dush 8520-12 wr	1.6	4.11	0.50
Atsagin-Dush 8520-19 wr	1.7	4.23	0.25
Atsagin-Dush 8520-20 wr	1.6	4.27	0.07
Atsagin-Dush 8520-30 wr	1.4	3.77	0.40
Peridotites — standards			
PCC-1 (USGS)	1.1	8.85	0.41
JP-1 (GSJ)	1.8	3.97	0.41

ol — olivine; opx — orthopyroxene; cpx — clinopyroxene; wr — whole rock.

similar to the best estimate for the Earth's mantle (δ^7Li~+4‰). In fact lunar basalts might offer greater insights into the Li isotope composition of terrestrial planetary mantles because of the anticipated absence of large fractionations.

The overall range of Li isotope composition among lunar samples is, however, surprisingly broad. The most extreme composition found among the various lunar samples is for the lunar highlands anorthosite 62255 (δ^7Li=+8.9‰). The issue arises as to whether this spread might be caused by secondary irradiation/implantation. Solar wind (SW) and galactic cosmic rays (GCR) may alter those rocks at the lunar surface not protected by a magnetic field. The bulk Sun has ^{7}Li/^{6}Li ~ 10^6 [36] and solar wind has a ^{7}Li/^{6}Li ~ 31 [37]. ^{7}Li/^{6}Li~2 have been reported in galactic cosmic ray-induced spallation reactions [38], and the interstellar medium ^{7}Li/^{6}Li has been estimated at ~12 [39], and ~2 [40].

Cosmogenic effects would produce roughly equal amounts of ^{6}Li and ^{7}Li by fission of heavy nuclides because spallation production ^{7}Li/^{6}Li ratio can be as low as ~1.0 (e.g. [41]). Rather higher values of ~2 were measured for low-energy galactic cosmic rays [42]. Spallogenic Li has been detected in lunar soils yielding values of ^{7}Li/^{6}Li~2 [38]. Therefore, Li of purely spallogenic origin is extremely light δ^7Li ≈ −850‰ [9]. This component has been detected in small quantities in refractory inclusions from several meteorites [9,43] and in four lunar soils studied with depth profiling [37].

It is impossible that spallogenic effects are responsible for ^{7}Li enrichment as detected in lunar samples.

An effect from exposure to heavy solar wind [37] would of course generate higher ^{7}Li/^{6}Li. However, the depth of SW penetration into regolith particles is on the order of just tenths of microns [37]. Therefore, this effect is generally expected to be very small. More accurately and independently from grain size and solar flux one can calculate the proportion of solar wind-derived Li using ^{36}Ar abundances. Elevated ^{36}Ar abundances are usually found in fine-grained fractions of lunar soils with up to 5-fold ^{36}Ar enrichment in the finest fractions relative to coarser-grained fractions [44]. An abundance of 0.32×10^{16} atoms/g was reported for the 25–42 µm fraction of the lunar soil 67601 [45]. By applying the enrichment factor of 5 to the <25 µm fraction we obtain [^{36}Ar] of 1.6×10^{16} atoms/g. The lunar soil 67601 <25 µm fraction does in fact yield an ^{36}Ar concentration of $60,000 \times 10^{-8}$ cc/g or 1.6×10^{16} atoms/g, in excellent agreement with this prediction (R. Wieler, personal communication to TM and UW, 2005). The solar abundances of ^{7}Li and ^{36}Ar normalized to 10^6 silicon atoms [46] are 52.8 and 8.5×10^4, respectively. From these a solar ^{7}Li/^{36}Ar of 6.2×10^4 can be calculated. Using the measured ^{36}Ar abundances and solar ^{7}Li/^{36}Ar one obtains 9.9×10^{12} of ^{7}Li atoms/g derived from the solar wind in the <25 µm fraction. This number has been multiplied by a factor of 3 in order to account for lower ionization energy of Li compared with argon (FIP factor). This gives 3×10^{13} of ^{7}Li atoms per gram that is the expected portion implanted by the solar wind (fraction <25 µm of sample 67601). An average of 5.2 ppm Li of the 3 coarse fractions of 67601 is used to calculate the number of lunar 2×10^{16} Li atoms/g in the <25 µm grain size fraction. The solar wind portion of Li corresponds only to about 0.15% of the Li in fraction <25 µm. On the basis of a solar wind composition of ^{7}Li/^{6}Li=31 and assuming no fractionation by the implantation process a δ^7Li=+7.6‰ is calculated for the <25 µm fraction based solely on measured ^{36}Ar abundances and the lunar lithium concentration. This calculation provides strong evidence that solar wind is detectable in grain size fractions <25 µm of lunar soil using MC-ICPMS.

To test this theoretical approach we have conducted independent studies of the extent of the effects of solar wind implantation on lunar soils. The Li abundances and isotope compositions have been measured for size fractions from immature lunar soil 67601 (Table 4), which has an exposure age of ~55 Myrs, and in bulk soil 64421 with a higher exposure age of ~210 Myrs [47]. We find clear ^{7}Li enrichment in soil 64421 (δ^7Li=8.3‰) and in the finer-grained fractions of 67601 (Fig. 3 and Table 4)

Table 4
Lithium concentrations and isotope compositions of lunar soils

Sample	Split	Fraction (μm)	Li (ppm)	δ^7Li (‰)
67601	7	<25	5.4	8.44
		25–42	5.6	7.03
		42–90	5.2	5.35
		90–250	5.2	4.93
		>250	4.7	5.31
64421	5		7.4	8.26

but this effect diminishes rapidly with increasing grain size. The three coarser fractions (>42 μm) of soil 67601 have uniform δ^7Li~+5‰. The measured δ^7Li=8.4‰ for the fraction <25 μm is in good agreement with predicted value in the above calculations, given the range of uncertainties. This provides strong evidence for solar wind-derived Li in lunar soils. The explanation for such trend toward heavy δ^7Li values could be a large proportion of abraded surface layers of soil particles that are enriched in ^{7}Li. This effect is insignificant in coarse-grained fractions with volumetrically negligible quantities of such eroded material. Therefore, bulk rock samples of igneous material, even with long exposure age should show no significant effects and the two components (solar wind, spallogenic reactions) can be neglected when interpreting the data set of lunar rocks from this study.

This is confirmed by the observation that the Li isotope compositions of the bulk rocks studied here display no correlation with exposure age (Fig. 4). In particular the very heavy δ^7Li measured in ferroan anorthosite 62255 is accompanied by an extremely short exposure on the lunar surface with Kr exposure age of <2 Myrs [48]. In some respects this is not surprising since neither implantation of solar wind nor spallogenic effects can account for the apparent relationships between Li isotope composition and rock type (Table 1). Similarly, it would be hard to explain the correlations with trace element indices of magmatic differentiation, discussed in the next section.

4.2. Lithium isotope composition of the Moon

A thorough model and review of geochemical and magmatic evolution of the lunar magmasphere have been given elsewhere [49,50]. Lithium isotope variation among lunar basalts most likely reflects heterogeneity in the source. The mare basalts analysed have primitive major element compositions and probably segregated only relatively small amounts of olivine and/or pyroxene. This is unlikely to have caused a detectable change in δ^7Li [13]. The mare basalts are the products of melting of cumulate sources that crystallised from the Lunar

Magma Ocean (LMO) at distinct stages. All investigated mare basalts show a negative Eu anomaly (Fig. 5) providing evidence that the cumulate sources were formed after significant crystallisation of plagioclase in the LMO. It is believed that floating plagioclase formed the early lunar crust [49]. The Eu_N/Eu^* value provides a monitor of how much plagioclase crystallised from the magma ocean. Early cumulates have REE patterns with virtually no Eu anomaly [51]. Later cumulates should develop a REE pattern with negative Eu anomalies and be systematically depleted in Ni and Co and enriched in incompatible elements. The inverse trend of Eu_N/Eu^* vs. δ^7Li for lunar mare basalts (Fig. 6) provides evidence of a relation between magmatic differentiation of the LMO and Li isotope fractionation. However, the trend is scattered and cannot be explained by feldspar fractionation alone. Because the Li content of an anorthosite mainly composed of calcic plagioclase is very low (see Table 1), the overall contribution of the lunar crust to the Li budget of the Moon is particularly limited. Therefore, plagioclase segregation is an unlikely mechanism for generating a significant Li isotope effect.

The sources of the low-Ti mare basalts were composed of early-formed ultramafic cumulates (predominantly olivine and low-Ca orthopyroxene). Flotation of plagioclase imposes a negative Eu anomaly on the crystallising mafic cumulates and produces a complementary positive Eu anomaly in the feldspathic lunar crust. Most of the models for the generation of primary high-Ti basalts require the melting of source rock types consisting of olivine, clinopyroxene, ilmenite, ±plagioclase, ±orthopyroxene [52,53]. Accurate data of relevant mineral-melt fractionation factors ($\alpha_{min-melt}$) are currently unavailable for Li isotopes but the data on
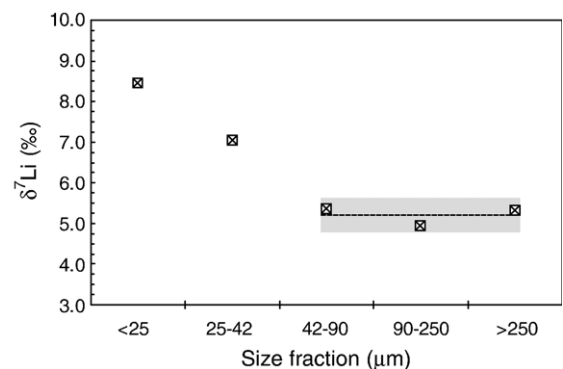

Fig. 3. Size fractions vs. δ^7Li in Apollo 16 soil 67601. Apparent trend toward heavier δ^7Li values with finer fractions of the North Ray crater soil reflects most probably implantation of isotopically heavy solar wind [37]. Dashed line is the average of three coarse-grained fractions with δ^7Li=5.20±0.46‰ (2σ; grey bar) that may reflect the starting isotope composition.
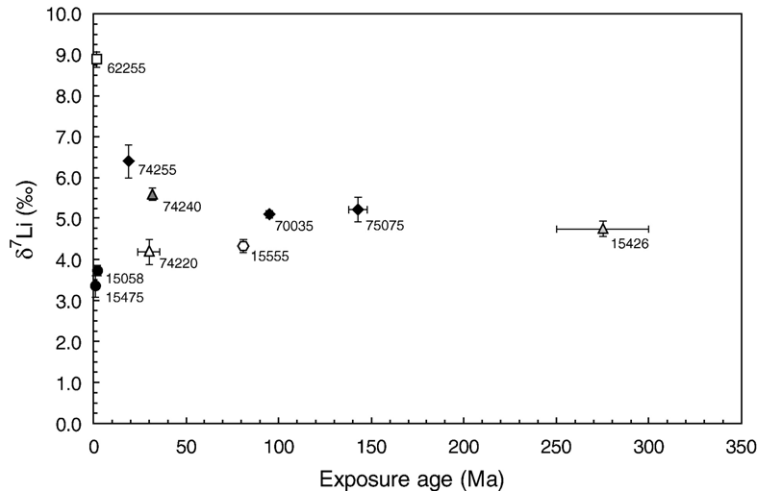
Fig. 4. Exposure ages vs. δ^7Li for lunar samples. Closed diamonds — high-Ti mare basalts; triangles — volcanic glasses (open — orange glass 74220, dark grey — grey glass 74240, light grey — green glass 15426); polygon — olivine-normative basalt 15555; closed circles — quartz-normative basalts; open square — ferroan anorthosite 62255. No systematic trend is observed among the data. Exposure ages are taken from Drozd et al. [48], Eugster et al. [91], Hörz et al. [92], Huneke et al. [93], Stettler et al. [94] and Yokoyama et al. [95].
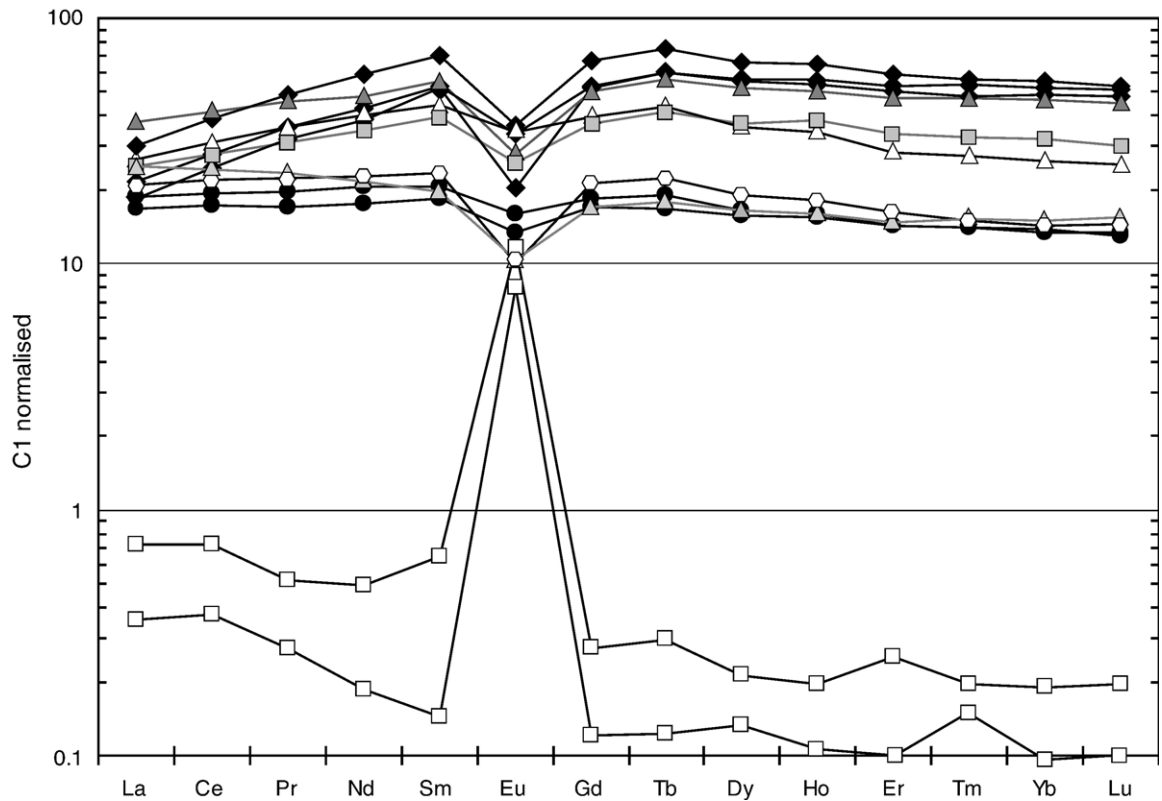
Fig. 5. C1-normalised REE patterns of lunar rocks. Symbols are the same as in Fig. 4. Grey squares — ilmenite-normative basalt 12045. Also REE pattern for Fe-anorthosite 65315 is plotted. Note apparent scatter in trace element data for both anorthosites caused by larger analytical uncertainties. Bottom pattern of Fe-anorthosite 65315 is approximate only due to analytical uncertainties for most elements exceeding 50% (2σ).
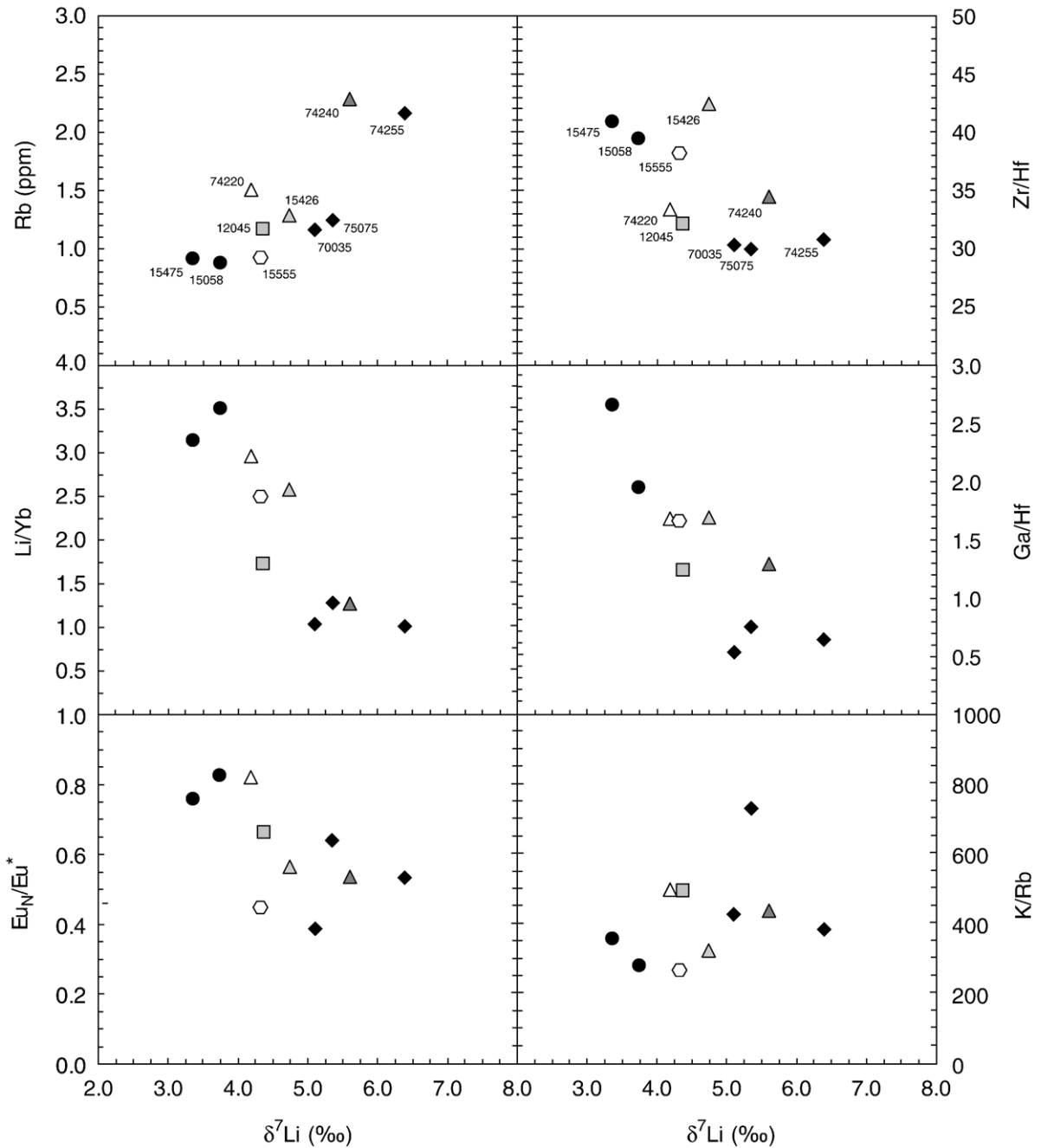
Fig. 6. Indices of magmatic fractionation vs. δ^7Li in lunar basalts and glasses. Symbols are the same as in Fig. 4. Ferroan anorthosite 62255 is not plotted. Variations in Rb abundances, Li/Yb, Eu_N/Eu^*, Ga/Hf and Zr/Hf ratios are related to precipitation of clinopyroxene, ilmenite, armalcolite, spinel and titanite and possibly anorthite from the LMO. Excess Eu in 62255 ($Eu_N/Eu^* > 25$) relative to other rocks is caused by Eu substitution for Ca in anorthosite that is nearly pure anorthite (>97%). K abundance data are from Papike et al. [96], Rhodes and Hubbard [97], Rhodes et al. [88], Rose et al. [98,99] and Taylor et al. [100].

mantle minerals reported in this study provide evidence of ~2‰ equilibrium fractionation between olivine and clinopyroxene at magmatic temperatures. The dominance of clinopyroxene in the source of high-Ti mare

basalts and the ultramafic olivine-dominated cumulates of the low-Ti mare basalts could already account for most of the δ^7Li range detected in mare basalts. This is fully consistent with trends between δ^7Li and REE ratios or

Zr/Hf (Fig. 6) because clinopyroxene and to a lesser extent titanite are the major Zr/Hf-fractionating phases [54,55].

Strong correlations between Li isotopes and trace elements are found for indices that span a greater relative range of variability in basalts. For example Li/Yb and Ga/Hf vary widely in the basalts and clearly correlate inversely with δ^7Li (Fig. 6). Gallium and lithium are considered to be at most only slightly incompatible and no phase fractionates them strongly. This is endorsed by the basalts, which yield Ga and Li concentrations that vary by a factor of two at most (Tables 1 and 2). In contrast the REEs and high field strength elements (HFSEs) vary in concentration by more than a factor of four. Therefore, the variation in Ga/Hf and Li/Yb is actually dominated by a large degree of variability in HFSEs and REEs. The samples with lowest Ga/Hf and Li/Yb are the Apollo 17 glasses and high-Ti mare basalts. This is fully in line with a source consisting mainly of late clinopyroxene-rich cumulates. These samples are also more enriched in alkalis leading to a positive correlation between Rb concentration and δ^7Li (Fig. 6) and therefore, clearly more evolved than low-Ti basalts. On the basis of a study of a terrestrial volcanic rock sequence it has been stated earlier that magmatic differentiation has no effect on δ^7Li [13]. However, Tomascak et al. [13] explored only some 10% segregation of olivine±pyroxene±plagioclase whereas the sources of high-Ti basalts are thought being formed after >95% of the LMO had been crystallised. That such extensive magmatic differentiation can fractionate stable isotopes has been shown with oxygen isotopes. For example, a significant shift has been produced by olivine segregation in highly evolved melts ($MgO_{melt}<2\%$; [56]). Assuming a fractionation factor $\alpha_{olivine-melt}=0.999$ between olivine and silicate melt (as inferred from olivine measurements in this study) a simple Rayleigh fractionation model produces significant Li isotope fractionation. If 95% of the LMO is crystallised, the δ^7Li value of the residual melt increases by more than 2.5‰ compared with the starting composition. This may in addition contribute to the δ^7Li range observed for the lunar basalts.

The lunar crust is about ~60 km thick and consists mainly of anorthosite that is complementary to the source of mare basalts. This is also reflected in the REE pattern (Fig. 3 in [49]). Lithium concentration of 0.8 ppm for the studied anorthosite implies a Li concentration of about 4 ppm for the magma ocean assuming an element partition coefficient for plagioclase and basaltic melt $D_{plag-melt}$ of ~0.2 [57]. The δ^7Li value of 8.9‰ for the lunar anorthosite is somewhat surprising. This gives a fractionation factor between plagioclase and basaltic

melt $\alpha_{plag-melt}$ of 1.0049 (assuming a δ^7Li value of 4.0‰ for the lunar magma ocean) and represents an extreme value for equilibrium fractionation at temperatures ≥1150 °C. Whether the high δ^7Li of the lunar crust reflects equilibrium fractionation by plagioclase crystallisation is unclear.

It is possible that the Li isotope composition of 62255 is not in equilibrium with the LMO. The Li concentration of 0.8 ppm measured for this sample is much higher than the 0.14 ppm obtained for a second Fe-anorthosite 65315 which is believed to be one of the most pristine lunar highland crust samples available as deduced also from low C1-normalised REE patterns (Fig. 3 and [58]). Such low Li abundances as in 65315 would mean approximately 0.8 ppm Li for the LMO if $D_{plag-melt}$ ~0.2 but such a low Li content of the LMO is highly unlikely. The possibility that the high δ^7Li value of 62255 reflects Li derived from late fluids or melts that percolated through the lunar crust cannot be excluded. Unfortunately, the amount of Li extracted from 65315 was too small for an isotope ratio measurement. However, the extremely low Li abundances are hard to reconcile with the conclusions of Dreibus et al. [59] who suggest preferential Li incorporation into a plagioclase crystallising very early from the LMO.

The δ^7Li value of the bulk Moon can be estimated from basaltic lavas thought to be derived early from the LMO crystallised cumulates. Among the first reservoirs that separated from the LMO are the sources of two quartz-normative basalts (15058, 15475) and an orange glass (74220) with Eu_N/Eu^* as high as ~0.8. These three samples have δ^7Li values of 3.7±0.1‰, 3.4±0.3‰ and 4.2±0.3‰, respectively. One of the most primitive and little fractionated material available from the Moon is often considered to be the green picritic glass 15426 released from depths >700 km [60]. However, relatively high Ti content of this glass provides evidence for late stage mixing with magmas derived from clinopyroxene- and ilmenite-rich cumulates. This is consistent with a slightly elevated δ^7Li (4.7±0.2‰) compared with the former samples. Finally, olivine basalt 15555 is viewed by some as being representative of the Nd and W isotope composition of pristine, unfractionated lunar mantle [61,62]. But the large negative Eu anomaly indicates equilibration with a more evolved lunar magma ocean and its Li isotope composition ($\delta^7Li=4.3±0.2‰$) may be slightly affected by magmatic segregation of olivine. Therefore the mean of the two quartz-normative basalts and one orange glass sample, taken as providing the most reliable estimate of the bulk composition of the Moon, is $\delta^7Li=+3.8±0.4‰$ (1σ).

4.3. Lithium isotope composition of the terrestrial mantle

In order to constrain the Li isotope composition of the Earth's mantle, we studied mineral separates of spinel lherzolites and whole-rock peridotites. Spinel lherzolites probably best represent the Li isotope composition of the upper mantle. Modal proportions of olivines in spinel lherzolites from this study range from 47 to 62 modal% (San Carlos: 47.2% [63], Vitim: 62.3% [64], Atsagin-Dush: 60.6% [26], Tariat: 57.1% [27], Kilbourne Hole: 57%). Therefore, olivine contains between 80% and 90% of bulk sample Li and is a good approximation for the Li isotope composition of peridotitic mantle rocks. The average δ^7Li of olivines from spinel lherzolites is $3.65 \pm 0.20‰$. Whole-rock analyses of three spinel lherzolites (8520-12, 8520-19, 8520-20) and one harzburgite (8520-30) are also consistent with a δ^7Li value of the terrestrial mantle close to +4‰ (see Fig. 7). These values are similar to the calculated bulk δ^7Li of +3.8‰ for fertile Vitim garnet lherzolite [14]. This is also similar to data for peridotites from Zabargad Island (Egypt), which yield $\delta^7Li \approx 4–5‰$ for the terrestrial mantle [19,21]. All these results are consistent with the predicted upper mantle value close to +4‰ [20].

In contrast, a whole-rock analysis of a fertile San Carlos spinel lherzolite given by Seitz et al. [14] gave light $\delta^7Li = -1.1‰$. The whole-rock data for this San Carlos sample appear inconsistent with the Li concentration and isotope composition determined from mass

balance of the three major minerals analysed. Therefore, it would appear that some poorly understood effect is biasing the result from the whole rock. Our Li isotope data for mineral separates provide some evidence of heavier δ^7Li in clinopyroxene although more data are needed to place better constraints on inter-mineral fractionation. The extensive study of Seitz et al. [14] yielded different results for reasons that are presently unclear. Olivines from their study are heavier in terms of Li isotope compositions than co-existing clinopyroxene and orthopyroxene but span a substantial range of δ^7Li from 1.4‰ to 4.5‰. Co-existing orthopyroxenes were isotopically lighter and clinopyroxenes were in most cases isotopically the lightest major mineral. Although this could reflect variously depleted and metasomatised mantle as suggested by Seitz et al. [14], a more likely explanation for the observed light Li isotope signatures in pyroxenes would encompass late stage diffusion. That such a process can lead to significant shifts in δ^7Li has been shown for silicate melts [65] as well as for solid–liquid systems, as documented in peridotitic lithologies where δ^7Li variations as large as 10‰ were observed [66]. The latter study also proved experimentally that Li isotope fractionation on the order of tens of per mil is readily achievable in a very short-term timescale by diffusion and showed that scatter in δ^7Li data for clinopyroxenes is more pronounced than for olivines. This is consistent with fast Li diffusion in clinopyroxene as recently observed [67].
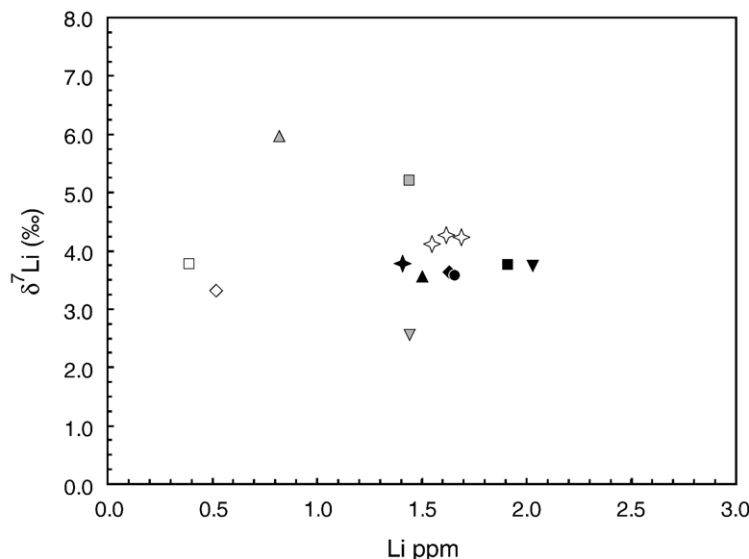

Fig. 7. Li abundances vs. δ^7Li of peridotitic rocks and mineral separates. Closed symbols — olivines; grey symbols — clinopyroxenes; open symbols — orthopyroxenes. Diamonds — San Carlos; squares — Vitim; triangles — Atsagin-Dush; reversed triangles — Tariat; circle — Kilbourne Hole. Solid star represents one harzburgite (8520-30), open stars display spinel lherzolites (8520-12, 8520-19, 8520-20); all are from Atsagin-Dush, Mongolia.

Elliott et al. [22] sketched a possibility that heavy mantle Li may be caused by viscous coupling of hydrated isotopically heavy mantle with complementary dehydrated subducted slab. Some heterogeneity in the mantle does indeed exist as sampled by MORBs and OIBs at various locations. Fresh MORB analyses are sparse but show significant heterogeneity in δ^7Li from +1.5‰ to 5.6‰ [15,17,68] — even greater than for OIB with δ^7Li values from +2.5‰ to 5.8‰ [13,18,69]. OIBs may be derived as unrepresentative small-volume melts from plumes rising from the core–mantle boundary, ultimately fed by subducted slabs [70]. Thus, they may not represent typical upper mantle compositions [22]. MORBs represent shallow mantle melting of depleted lherzolites with interspersed mafic veins [71]. As large volume melts they should be more representative than OIB. However, the question arises of how much variably fractionated Li resulting from recycling is affecting the compositions if metasomatism from recycled components is selectively affecting the compositions of pyroxene, a phase that is preferentially melted during basalt production.

To summarise, the existing data for the Earth's upper mantle are consistent with a $\delta^7Li \sim +4‰$. Non-metasomatised peridotites appear to be strikingly uniform in their Li isotope composition. Four such whole-rock peridotites as well as one peridotitic standard from this study are extremely homogeneous in their δ^7Li (~4.1‰) varying at ±0.4‰ (2σ), consistent with the upper mantle δ^7Li at 4.2‰ defined by Chan [20]. Similar results are found for olivines of spinel lherzolites that average at +3.6‰ and are identical with the mantle value. We therefore suggest that the Earth's upper mantle has $\delta^7Li \sim +4‰$ as inferred from our olivine and whole-rock peridotite data. The Li content of the upper mantle as inferred from non-metasomatised spinel lherzolites of this study is ~1.6 ppm and is in excellent agreement with the estimate of Ryan and Langmuir [33] and Sun and McDonough [72].

Whether the upper mantle is also representative of the lower mantle is less clear. The deep mantle may differ in δ^7Li as inferred from the slab dehydration and Li isotope fractionation model of Zack et al. [12]. Therefore, the possibility exists that the mantle is stratified with respect to Li isotopes. This would be caused by progressive ^7Li depletion in the deep mantle due to its loss from the dehydrated subducted slab. A metasomatic overprint in clinopyroxenes has been shown in some mantle xenoliths from the Far East Russia and Japan [11] which carry extremely negative δ^7Li values inherited from metasomatism by eclogitic melts. The existence of light domains in the mantle is

consistent with data for clinopyroxenes from ultramafic xenoliths. Nishio et al. [11] explained this feature by metasomatic overprint with Li from subducted highly altered basalts that yielded extremely negative values. Similarly, a relationship between light Li and assimilation of subducted crust has been assumed on the basis of glass inclusions analysis in olivines and orthopyroxenes from Iblean plateau tholeiites [73]. Recently, extremely negative δ^7Li values have been found in glass inclusions of olivines from Hawaiian lavas [16]. Kobayashi et al. [16] have attributed these light values to a recycled component, supported also by B and Pb isotopes. Therefore, recycling does appear to transfer a fractionated Li component into the mantle. What its average composition is remains unclear. How different the bulk upper mantle and bulk lower mantle are as a result of recycling is under-constrained.

4.4. Lithium isotope composition of Mars and Vesta

Two martian meteorites give distinct δ^7Li of 3.9‰ (Zagami) and 5.0‰ (Nakhla). Zagami is a basaltic martian meteorite and most likely reflects the composition of the source material within the martian mantle, whereas Nakhla is a clinopyroxenite cumulate that closely resembles shallow ultramafic intrusives [74]. Study of light lithophile elements (Li, B) performed on pyroxenes from martian basalts (Zagami, Shergotty) provided evidence for incompatibility of Li in major mineral phases of martian basalts which has been explained by fluid degassing [75]. The parental melt of Shergotty is supposed to have high Li abundances >20 ppm based on recent mineral-melt partitioning data estimated for martian pyroxenes [76]. A similar study of light lithophile elements distribution (Li, Be, B) in pyroxenes from nakhlites and shergottites led Lentz et al. [77] to conclude that the parental magmas of shergottites had significant water contents whereas the parental magmas of Nakhla were rather dry. Core-to-rim decreases in Li abundances in pyroxenes of Zagami have been explained by possible involvement of late stage fluids [77] that could also potentially fractionate Li isotopes. Indeed, low-temperature alteration hydrous phases, e.g. "iddingsite" (a mixture of smectites and ferrihydrites), gypsum, calcite and halite have been found in nakhlites [78]. The high δ^7Li of Nakhla may therefore be related to the former presence of water on Mars. Significant changes in δ^7Li between pyroxene cores and rims could be caused by the presence of water during petrogenesis of martian basalts [79]. However, a recent detailed ion-microprobe study of distribution of Li and its isotopes in olivine and pyroxene phenocrysts

in lunar meteorite NWA 479 revealed large variations of δ^7Li within single crystals [80]. It has been concluded that diffusive isotope fractionation is responsible for observed Li isotope patterns. By analogy, martian meteorite NWA 480 studied previously [79] could also reflect a similar process rather than degassing. However, further work is necessary to verify this.

Eucrites are thought to be excavated from asteroid 4 Vesta by an impact [81]. Eucrites have high Li abundances compared to martian and terrestrial basalts. Basaltic eucrites possibly represent large-degree melts from chondritic source [82]. Given its incompatibility, the high Li content is therefore surprising (Table 1). An unlikely explanation is that the terrestrial and martian mantles are relatively depleted in Li because of crust formation. This would require that about half of the terrestrial lithium resides in the crust. Although Li is enriched in crust there is little evidence that Li in the crust can account for half the abundance of the terrestrial mantle. There is also no evidence that Li is lost to the core. The most likely explanation might be that the asteroid 4 Vesta is internally heterogeneous. The Li abundances of eucrites are in fact very similar to high-Ti mare basalts of the Moon. The δ^7Li value of studied eucrites (see Table 1) averages at +3.7‰, identical within error to Mars (Zagami), the Moon and the Earth's upper mantle (see above). This provides strong evidence that whatever the reason for the high Li abundance of eucrites, it does not relate to a process that produces large isotope fractionation.

4.5. Lithium isotope compositions of chondrites

Two chondrites have also been measured (see Fig. 2 and Table 1). The carbonaceous CV3 chondrite Allende gives δ^7Li=+3.1‰ whereas a lower δ^7Li=+1.5‰ has been obtained for the L6 chondrite Bruderheim. These results are in accord with a more comprehensive study of chondrites, which reports a range from −4‰ to +3‰ [7]. Recently, Zack et al. [12] demonstrated that metamorphic dehydration at slightly higher temperatures will shift the Li isotope composition of rocks toward negative values, as low as −11‰. The variation among chondrites may reflect aqueous alteration on parent bodies with isotopically light Li in the residual metamorphosed chondrites (e.g. Bruderheim) and isotopically heavy Li related to chondrites with high aqueous alteration index (Orgueil, Allende; [7,83]). The isotopically light Li of chondrites may reflect the bulk solar system δ^7Li, assuming that if anything aqueous processing has shifted some samples to heavier com-

positions. The bulk silicate Earth is expected to have an average δ^7Li value of +4‰, estimated from MORB, e.g. Chan et al. [17]. A solar system with δ^7Li∼0‰ [7] or δ^7Li∼2‰ (W. McDonough, personal communication to ANH, 2005) would imply either that the planet formation process involves some small but significant Li isotope fractionation or there is a currently unidentified isotopically light reservoir within the Earth.

5. Conclusions — inner solar system Li isotope compositions

From these preliminary studies some very clear basic conclusions can be drawn.

(1) Basaltic and ultramafic rocks from the Earth, Moon, Mars and Vesta yield broadly similar Li isotope compositions consistent with a mantle source composition of δ^7Li∼+4‰. There is no reason why each upper mantle should appear to be the same in its Li isotope composition unless each entire terrestrial planetary object is also identical with δ^7Li∼+4‰. Therefore, a first-order conclusion is that the Earth's lower mantle is unlikely to be different in composition from its upper mantle given the similarity between this and other inner solar system upper mantles.

(2) The terrestrial, martian and some low-Ti lunar mare basalts have very similar Li abundances whereas eucrites have high Li abundances similar to high-Ti basalts. This indicates a heterogeneous interior of Vesta. The reason for this is unclear at present but may be related to differentiation during a magma ocean stage.

(3) The Earth, Moon, Mars and Vesta have different structure and composition of their respective crusts and cores. They also have dramatically different geology that includes a long history of subduction of isotopically fractionated Li into the Earth's mantle. However, none of these differences appear to have resulted in major changes in the Li isotope composition of the bulk planetary mantles.

(4) The Li isotope variation among lunar rocks reflects magmatic differentiation during the lunar magma ocean stage. Lithium isotope fractionation is likely caused by crystallisation of olivine, pyroxene and feldspar from the magma ocean and produces a relatively large isotope effect.

(5) There is no evidence for lithium isotope fractionation related to the depletion of volatiles in the inner solar system. This is similar to the result obtained for K [84].

(6) There is also no indication that the Moon-forming Giant Impact resulted in Li isotope fractionation. Therefore, the effects found for Fe [5] may be caused by fractionation during vaporisation of iron metal.

(7) Chondrites, as indicated by the results of this and an earlier study, are isotopically light compared with differentiated planetary bodies of the inner solar system. This is consistent with the results of a more comprehensive study on chondrites [7]. Therefore, there appears to be an important fractionation that takes place in the accretionary disc or in chondrite parent bodies during their thermal metamorphism and aqueous alteration.

Acknowledgements

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