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Sm-Nd isotopic systematics of Iherzolitic shergottite Yamato-793605

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Abstract: We have undertaken Sm-Nd isotopic studies on Yamato-793605 Iherzolitic shergottite. The Sm-Nd internal isochron obtained for acid leachates and residues of whole-rock and separated mineral fractions yields an age of 185 ± 16 Ma with an initial ϵ_{Nd} value of $+9.7 \pm 0.2$. The obtained Sm-Nd age is, within analytical errors, identical to the Rb-Sr age of this meteorite as well as to the previous Rb-Sr and Sm-Nd ages of Allan Hills-77005 and Lewis Cliff 88516, although the ϵ_{Nd} values are not identical to each other. Elemental abundances of lithophile trace elements remain nearly unaffected by aqueous alteration on the Martian surface. The isotopic systems of Iherzolitic shergottites, thus, are considered to be indigenous, although disturbances by shock metamorphism are clearly observed. “Young ages of ~ 180 Ma” have been consistently obtained from this and previous Rb-Sr, Sm-Nd and U-Pb isotopic studies and appear to represent crystallization events.

key words: shergottite, Iherzolitic, Sm-Nd, age, Martian meteorites

1. Introduction

Shergottites belong to Martian meteorites and show basaltic, olivine (+orthopyroxene)-phyric or Iherzolitic textures. Up to now eight specimens including Yamato (Y)-793605 are classified as Iherzolitic shergottites (Meyer, 2005; Kojima, 2006). Except Allan Hills (ALH)-77005 and Northwest Africa (NWA) 1950, the sample sizes of Iherzolitic shergottites are small, weighing less than 50 g. The Mg/(Mg+Fe) ratios ($mg^* = Mg/(Mg+Fe) \times 100$ mole%) for Iherzolitic shergottites are fairly constant ($mg^* = 67$ to 74 ; Meyer, 2005). The Iherzolitic shergottites show somewhat higher shock pressure (~ 40 – 55 GPa) than basaltic shergottites (~ 25 – 45 GPa; Fritz *et al.*, 2005).

Nyquist *et al.* (2001) presented “ejection ages” of Martian meteorites using the available their cosmic-ray exposure ages and terrestrial ages of Martian meteorites. The ejection age of Y-793605 (4.70 ± 0.50 Ma) is similar to that of Lewis Cliff (LEW) 88516 (3.94 ± 0.40 Ma), but does not overlap the ejection age of 3.06 ± 0.20 Ma for ALH-77005. The younger ejection age for ALH-77005 is similar to those of basaltic shergottites, Shergotty, Zagami, Los Angeles and Queen Alexandra Range (QUE) 94201. However, the uncertainty in production rates of cosmogenic nuclides prevents precise determination of ejection ages. It is expected that the three lherzolitic shergottites have the same ejection age (Nyquist *et al.*, 2001).

As a part of an earlier consortium study (Kojima *et al.*, 1997) we had undertaken U-Th-Pb and Rb-Sr isotopic studies of Y-793605 (Misawa *et al.*, 1997; Morikawa *et al.*, 2001). Preliminary results of the Sm-Nd isotopic study of Y-793605 were presented as a print-only abstract in the NIPR symposium (Yamada *et al.*, 2003). However, there were systematic errors in the data reduction program for NdO^+ measurements. It turned out that we had underestimated contributions of SmO^+ to NdO^+ signals. Thus, we present here the revised Sm-Nd age, which is 30 Ma older than the age previously reported by Yamada *et al.* (2003) and Misawa *et al.* (2006), and discuss in more detail the crystallization ages of lherzolitic shergottites on the basis of isotopic systematics making a comparison of the Y-793605 data with those of other shergottites.

2. Sample and analytical procedures

The meteorite sample studied, Y-793605,10, consists of several fragments weighing 408 mg and previously allocated for the consortium study (Kojima *et al.*, 1997). The samples used in this study were the same as the ones used earlier for U-Th-Pb and Rb-Sr isotopic studies (Misawa *et al.*, 1997; Morikawa *et al.*, 2001). A whole-rock sample was prepared from the finest fraction ($<63 \mu\text{m}$) before olivine, pyroxene and plagioclase separation. Thus, the sampling was not biased toward interstitial materials such as phosphates or opaque minerals.

The whole-rock and mineral concentrate samples were prepared and subjected to three-step acid leaching experiments to remove secondary lead contamination. The acid-leachate and -residue samples were spiked with three mixed tracers (^{233}U - ^{236}U - ^{230}Th - ^{205}Pb , ^{87}Rb - ^{84}Sr , and ^{149}Sm - ^{150}Nd) at the Lead-free Lab., U.S. Geological Survey in Denver. After being completely decomposed, the samples were passed through anion exchange columns for uranium, thorium and lead separation. The eluent before and after the uranium, thorium and lead fractions was recovered, dried down and re-dissolved in 6M hydrochloric acid. This chemical separation was done in Denver. The sample solutions were used for Rb-Sr isotopic analysis at Kobe University. Rubidium and strontium were separated from major elements by cation exchange columns with hydrochloric and nitric acids. The eluent before and after rubidium and strontium fractions was recovered. Rare earth elements were separated from major elements by cation exchange columns (Dowex AG 50W-X12) with hydrochloric and nitric acids. Neodymium and samarium were separated from other REE by cation exchange columns (Dowex AG 50W-X12) with 0.2M α -hydroxy isobutyric acid. Both residue and leachates of the whole-rock sample, WR,R, WR,L1 and WR,L2, plus those samples (PX2,R, OL,R and PX2,L1)

containing enough neodymium (\geq several 10^{-9} g) were analyzed. Unfortunately, isotopic analysis of some leachate and residue samples (PL,L1, PX1,L1 and PX1,R) containing $>1 \times 10^{-9}$ g neodymium failed due to inadequate chemical yields. Samarium and neodymium blanks were lower than 1.2 pg and 6.6 pg, respectively.

All isotopic measurements were made on a Finnigan-MAT 262 multi-collector mass spectrometer at Kobe University. Neodymium was measured as NdO^+ on Re single-filaments using an oxygen leak. The oxygen isotopic composition of our reservoir was measured using a ^{150}Nd tracer. The average value measured for $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ are 0.0003813 and 0.002060, respectively. The average values of $^{143}\text{Nd}/^{144}\text{Nd}$ for JNdi-1 neodymium standard and for the BCR-1 sample during the course of this study were 0.511259 ± 0.000027 ($2\sigma_p$, 29 analyses of NdO^+ runs, σ_p = standard deviation of the population) and 0.511786 ± 0.000007 ($2\sigma_p$, 4 analyses of NdO^+ runs), respectively, normalized to $^{146}\text{Nd}/^{144}\text{Nd} = 0.724140$. Due to the significant interferences of SmO^+ to the NdO^+ signals, we could not obtain a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of the pyroxene residue sample (PX2,R).

A 2.20 mg sub-sample from the $<63 \mu\text{m}$ WR fraction (original weight ~ 105 mg) was analyzed for trace elements without acid leaching. The sample was dissolved with a mixture of $\text{HF} + \text{HClO}_4$ and added potassium, rubidium, strontium, barium and REE spike solutions. Abundances of trace elements were determined by a direct-loading isotope dilution method with a thermal ionization mass spectrometer, model JEOL-05RB (Nakamura *et al.*, 1989).

3. Results and discussion

3.1. Lithophile trace element abundances in Yamato-793605

Trace element abundances including REE in Y-793605 are given in Table 1 along with literature data for ALH-77005, LEW 88516 and NWA 1950. We used a small aliquot of the whole-rock sample, which could be easily affected by REE-rich phases such as phosphates. Nevertheless, Y-793605 shows a light-REE (LREE) depleted pattern ($1.1\text{--}1.5 \times \text{CI}$), having no europium anomaly, and possessing a hump in the dysprosium region ($\sim 4 \times \text{CI}$; Fig. 1a), which is in good agreement with the UCLA data for Y-793605 (Warren and Kallemeyn, 1997; Warren *et al.*, 1999). The Tokyo Metropolitan University (TMU) data (Ebihara *et al.*, 1997; Kong *et al.*, 1999) for the 40–120 mg-sized samples, and the JSC data (Mittlefehldt *et al.*, 1997) calculated for the bulk composition using a 720 mg-sized sample (glass-poor plus glass-rich) are 65% and 30%, respectively, lower than the present results. These discrepancies in bulk trace element abundances are mainly due to the heterogeneous distribution of non-poikilitic lithologies (Kojima *et al.*, 1997) which carry Large Ion Lithophile (LIL) elements. The general REE pattern of Y-793605 is almost identical to those of ALH-77005 (Ma *et al.*, 1981; Shih *et al.*, 1982; Dreibus *et al.*, 1992; Laul, 1987) and LEW 88516 (Dreibus *et al.*, 1992; Treiman *et al.*, 1994; Gleason *et al.*, 1997), but the absolute abundances of REE in NWA 1950 are about twice those of other Antarctic lherzolitic shergottites (Gillet *et al.*, 2005) (Fig. 1b). The characteristic features of lherzolitic shergottites suggest that these rocks were genetically related and experienced similar fractionation processes.

Table 1. Trace element abundances in lherzolithic shergottites (in ppm).

Sample	Yamato-793605				ALH-77005	LEW 88516	NWA 1950	
	wt (mg)*	408	209	310	724	n.d.	250	326
K	214	110	204			233	200	< 800
Rb	0.926 (0.966) [†]		< 1.3	0.48		0.783	0.83	0.78
Sr	8.86 (11.8) [†]		< 44			14.1	14.7	21.5
Ba	3.42		< 17			4.53	4.93	9.94
La	0.316	0.0977	0.29	0.201		0.314	0.31	0.586
Ce	0.795	0.221	0.84			0.742	0.87	1.51
Pr		0.0423					0.14	0.240
Nd	0.735	0.249	< 0.12			0.762	0.82	1.34
Sm	0.425	0.167	0.45	0.298		0.450	0.47	0.739
Eu	0.197	0.0715	0.206	0.132		0.224	0.23	0.343
Gd	0.857	0.371					0.78	1.37
Tb		0.0695	0.168	0.11			0.16	0.261
Dy	1.14	0.542	< 1.6			1.16	1.10	1.77
Ho		0.106	0.234				0.24	0.367
Er	0.720	0.312				0.659	0.70	0.984
Tm		0.0428					0.089	0.141
Yb	0.648	0.286	0.56	0.40		0.541	0.57	0.810
Lu	0.0900	0.0420	0.080	0.065		0.0742	0.083	0.120
References	this work [#]	[1]	[2]	[3]		[4]	[5]	[6]
Technique	ID-TIMS	ICP-MS	INAA	INAA-RNAA		ID-TIMS	INAA-RNAA	ICP-AES

*Sample weights represent processed amounts. n.d.=not described in detail (Shih *et al.* processed approximately 2 to 3 g of sample).

[#]A split of 2.20 mg from the whole-rock sample (< 63 μ m, weighing ~105 mg) was used.

[†]Values in parentheses are from the WR sample, weighing 101.99 mg (calculated data from acid leachate and residue samples, Morikawa *et al.*, 2001).

[1] Ebihara *et al.* (1997): Weighted average of two different portions (weighing 31.3 mg and 40.7 mg).

[2] Warren *et al.* (1999): A 208 mg aliquot from a powdered sample (weighing 310 mg) was used.

[3] Mittlefehldt *et al.* (1997): Weighted average of glass-rich and glass-poor samples. A 32.18 mg aliquot for the glass-rich sample and a 77.69 mg aliquot for the glass-poor sample from two original splits, 58 mg and 666 mg, respectively were used.

[4] Shih *et al.* (1982).

[5] Dreibus *et al.* (1992).

[6] Gillet *et al.* (2005).

3.2. Samarium and neodymium abundances of acid leachate and residue samples

The samarium and neodymium analytical results for whole-rock and mineral separate samples of Y-793605 are given in Table 2 and shown in Fig. 1c. As already pointed out, Y-793605 contains calcium-phosphates which are distributed heterogeneously (Nagao *et al.*, 1997; Mittlefehldt *et al.*, 1997; Wadhwa *et al.*, 1999). In lherzolithic shergottites, calcium-phosphates are a sink for REE; thus the bulk REE abundances are governed by phosphates (Laul, 1987; Lundberg *et al.*, 1990; Harvey *et al.*, 1993; Lin *et al.*, 2005). The samarium and neodymium abundances of the leachate samples are high ($3\text{--}24 \times \text{CI}$), relative to those of the untreated whole-rock ($1.5\text{--}2.8 \times \text{CI}$), indicating that phosphates could have been leached out during the acid-leaching experiments (Misawa *et al.*, 1997; Morikawa *et al.*, 2001). The CI-normalized Sm/Nd ($(\text{Sm}/\text{Nd})_{\text{CI}}$) ratios of acid leachates (WR,L1, WR,L2 and PX2,L1) are approximately 1.8, and are identical to those of whitlockite ($(\text{Sm}/\text{Nd})_{\text{CI}}=1.7\text{--}1.9$) in lherzolithic shergottites, ALH-77005,

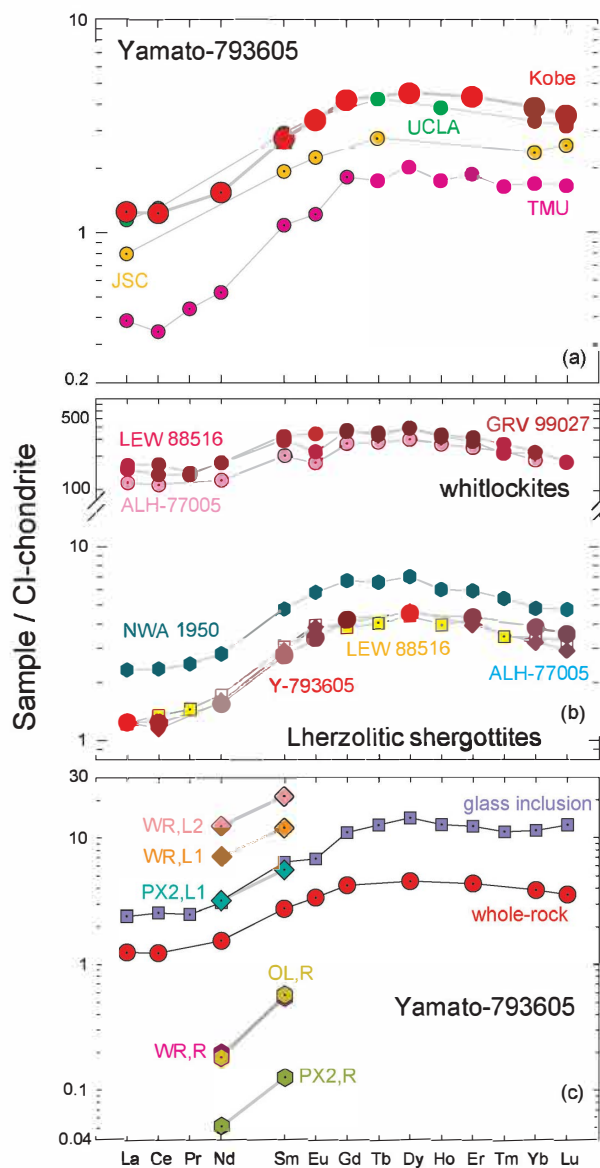


Fig. 1. CI-normalized REE abundance patterns. (a) Yamato-793605 whole-rock samples: Kobe=(this work), TMU=Ebihara et al. (1997) and Kong et al. (1999), UCLA=Warren and Kallemeyne (1997) and Warren et al. (1999), JSC=Mittlefehldt et al. (1997). (b) Whole-rock samples of ALH-77005 (Shih et al., 1982), Y-793605 (this work), LEW 88516 (Dreibus et al., 1992) and NWA 1950 (Gillet et al., 2005), and whitlockite in ALH-77005 (Lundberg et al., 1990), LEW 88516 (Harvey et al., 1993) and GRV 99027 (Lin et al., 2005). (c) Acid leachate and residue samples of Yamato-793605 (this study) and a silicate inclusion in olivine (Wadhwa et al., 1999).

Table 2. Samarium and neodymium analytical results for lherzolitic shergottite Yamato-793605.

Sample*	Weight (mg)	¹⁴⁷ Sm (nmol/g)	Sm (ppm)	¹⁴⁴ Nd (nmol/g)	Nd (ppm)	¹⁴⁷ Sm/ ¹⁴⁴ Nd [§]	¹⁴³ Nd/ ¹⁴⁴ Nd [¶]
WR,L1	7.75	1.90	1.90	5.53	3.35	0.343 ± 7	0.512526 ± 27 [§]
WR,L2	7.75	3.41	3.42	9.74	5.91	0.350 ± 22	0.512536 ± 27
WR,R	94.24	0.0843	0.0846	0.152	0.0922	0.555 ± 3	0.512768 ± 27
OL,R	110.47	0.0887	0.0890	0.140	0.0846	0.636 ± 7	0.512881 ± 27
PX2,L1	6.83	0.863	0.865	2.49	0.151	0.347 ± 2	0.512517 ± 27
PX2,R	62.27	0.0192	0.0193	0.0406	0.0246	0.472 ± 15	failed
JNdi-1 Nd standard			(NdO ⁺ runs, n = 29)				0.511259 ± 27 ^{**}
BCR-1			(NdO ⁺ runs, n = 4)				0.511786 ± 7
			(Nd ⁺ runs, n = 2)				0.511788 ± 10

Samarium and neodymium concentrations of acid leachates are calculated against the dissolved weight during a three-step leaching treatment. Thus, the abundances of samarium and neodymium in these samples represent minimum values.

*WR=whole-rock, OL=olivine, PX2=pyroxene, L1=0.01M hydrobromic acid leachate, L2=0.1M hydrobromic acid leachate, R=acid residue.

[§]Uncertainties correspond to last figures.

[¶]Normalized to ¹⁴⁶Nd/¹⁴⁴Nd=0.724140.

[§]Uncertainties correspond to last figures and represent ± 2σ_m error limits. σ_m=standard deviation of the mean.

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

LEW 88516 and Grove Mountains (GRV) 99027 (Lundberg *et al.*, 1990; Harvey *et al.*, 1993; Lin *et al.*, 2005). We can estimate REE dissolution during acid treatment on the basis of the unleached sample and the acid residue of the WR sample. About 88% of neodymium and 82% of samarium were dissolved during a three-step acid leaching. This is consistent with an earlier leaching experiment using 1M hydrochloric acid for 15 min in which phosphates carry 80–90% of total LREE in ALH-77005 (Laul, 1987).

Samarium and neodymium abundances of the whole-rock and olivine residue samples (WR,R and OL,R) are not much different; the (Sm/Nd)_{CI} ratios of WR,R and OL,R are 2.8 and 3.3, respectively. Enrichments of trace elements in the olivine residue (Sr=0.17×CI, Nd=0.18×CI, Sm=0.58×CI) are too large to account for by igneous fractionation (Fig. 1c), suggesting a contribution from the trapped melts enriched in LIL elements, although the Sm/Nd ratio of OL,R is somewhat higher than that of melt inclusion ((Sm/Nd)_{CI}=2.1) measured by ion microprobe (Wadhwa *et al.*, 1999). In lherzolitic shergottites, melt inclusions which carry LIL elements exist in olivine but are almost absent in pyroxene (Mikouchi and Miyamoto, 1997; Ikeda, 1997; Wadhwa *et al.*, 1999). It is worth noting that the Sm/Nd ratios of WR,R, PX2,R and OL,R ((Sm/Nd)_{CI}=2.4–3.3) are systematically high compared to those of acid leachates for Y-793605 and those of whitlockite ((Sm/Nd)_{CI}=1.7–1.9) in lherzolitic shergottites, suggesting that contributions of phosphates carrying REE to the residue samples are, if any, negligible.

3.3. Sm-Nd age of Yamato-793605 and isotopic signatures of source material

Figure 2 shows a ¹⁴⁷Sm/¹⁴⁴Nd and ¹⁴³Nd/¹⁴⁴Nd diagram for Y-793605. Two acid-

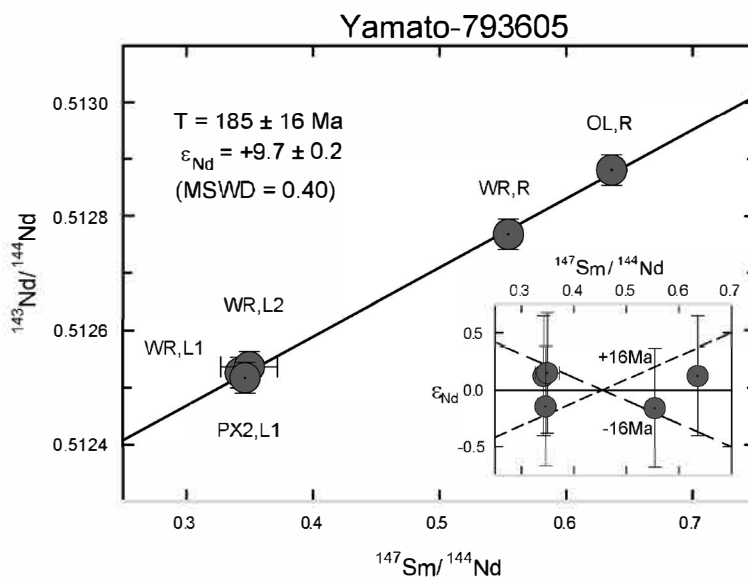


Fig. 2. Sm-Nd isotopic data for Yamato-793605. Two acid-washed (WR,R and OL,R) and three acid leachate (WR,L1, WR,L2 and PX2,L1) samples define a linear array corresponding to a Sm-Nd age of $185 \pm 16 \text{ Ma}$ (MSWD=0.40) for $\lambda (^{147}\text{Sm}) = 0.00654 \text{ Ga}^{-1}$, and an initial ϵ_{Nd} value of $+9.7 \pm 0.2$ using the ISOPLOT/Ex regression program (Ludwig, 2003). Inset depicts deviation of an individual point from the isochron as represented by ϵ_{Nd} .

washed (WR,R and OL,R) and three acid leachate (WR,L1, WR,L2 and PX2,L1) samples define a linear array corresponding to an Sm-Nd age of $185 \pm 16 \text{ Ma}$ (MSWD = 0.41) for $\lambda (^{147}\text{Sm}) = 0.00654 \text{ Ga}^{-1}$, and an initial ϵ_{Nd} value of $+9.7 \pm 0.2$ using the ISOPLOT/Ex regression program (Ludwig, 2003). The obtained Sm-Nd age is, within analytical errors, almost identical to the Sm-Nd ages of ALH-77005 and LEW 88516 (Borg *et al.*, 2002), although the ϵ_{Nd} values are not identical to each other (Fig. 3).

On a concordia diagram only the PX2 leachates and residue define a chord which corresponds to an upper intercept of $\sim 4.4 \text{ Ga}$ and a lower intercept of $\sim 210 \text{ Ma}$ (Misawa *et al.*, 1997). We first interpreted the U-Pb age of $\sim 210 \text{ Ma}$ possibly representing a disturbance due to the intense shock metamorphism. On a $^{204}\text{Pb}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ diagram, on the other hand, a tie-line connecting WR,R and PX1,R gives a negative Pb-Pb age (Fig. 4). Old ages (3.8–4.4 Ga) are calculated from the pairs PL,R and WR,R or PL,R and PX1,R. As a result, we could not obtain internally consistent U-Pb or Pb-Pb ages. The Sm-Nd age obtained in this study ($185 \pm 16 \text{ Ma}$) and the Rb-Sr age of $174 \pm 17 \text{ Ma}$ (calculated using combined data; Morikawa *et al.*, 2001) are internally consistent within analytical uncertainties. These facts suggest that Y-793605 crystallized $\sim 180 \text{ Ma}$ ago from LREE-depleted source regions. On the age versus ϵ_{Nd} and age versus initial $^{87}\text{Sr}/^{86}\text{Sr}$ diagrams, the error parallelograms for Y-793605 do not overlap those of ALH-77005 or LEW 88516 (Borg *et al.*, 2002; see Fig. 3), suggesting that the three meteorites are derived from slightly different sources.

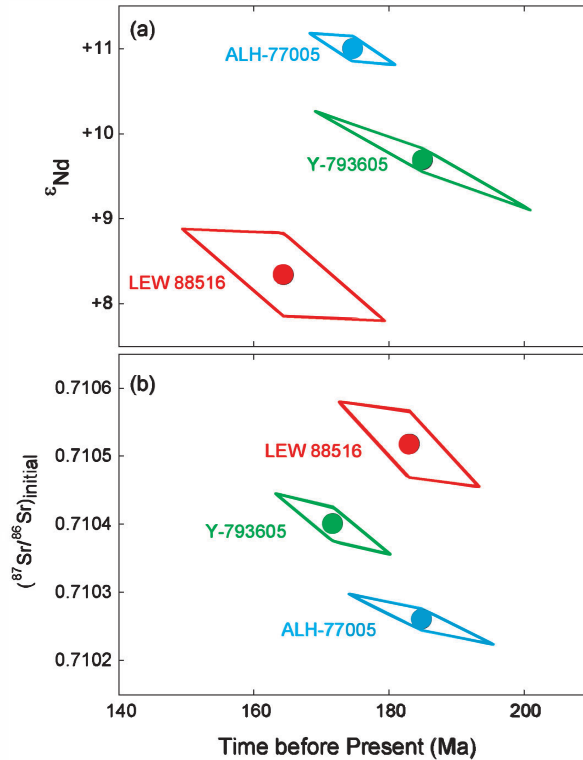


Fig. 3. T (age) versus $^{143}Nd/^{144}Nd$ evolution (a) and initial $^{87}Sr/^{86}Sr$ (b) diagrams for Iherzolitic shergottites. Data are from Morikawa *et al.* (2001), Borg *et al.* (2002) and this study. Ages and initial isotopic ratios are re-calculated using ISOPLOT/Ex (Ludwig, 2003). Strontium isotopic ratios are adjusted to $^{87}Sr/^{86}Sr=0.710250$ of the NBS 987 standard.

3.4. Isotopic disturbance during alteration/metasomatism?

Bouvier *et al.* (2005) argued that most Rb-Sr and Sm-Nd mineral isochron ages of shergottites, including Iherzolitic shergottites, were reset recently (*i.e.*, ~180 Ma ago) by acidic aqueous solutions percolating throughout the Martian surface. Similar arguments were made earlier by Jagoutz and Wänke (1986) and Blichert-Toft *et al.* (1999). Thus, the question arises whether ~180 Ma ages observed in shergottites represent crystallization of basaltic magmas, or resetting events by aqueous alteration or metasomatism? Bouvier *et al.* (2005) suggested that the carrier phases of uranium, thorium, REE and strontium are phosphates, and that U-Pb, Sm-Nd, Rb-Sr and Lu-Hf isotopic systems were disturbed during acid leaching on the Martian surface. Their conclusion is that only the Pb-Pb ages should be considered as the crystallization events. For Y-793605, the second and third leachates and the acid residues define a linear array corresponding to a 4.2 Ga “old Pb-Pb age” (Fig. 4). However, this correlation is here interpreted as a mixing between terrestrial (plus Martian?) lead and indigenous lead in the acid residue sample. The situations are almost identical for the whole-rock samples of ALH-77005 and LEW 88516.

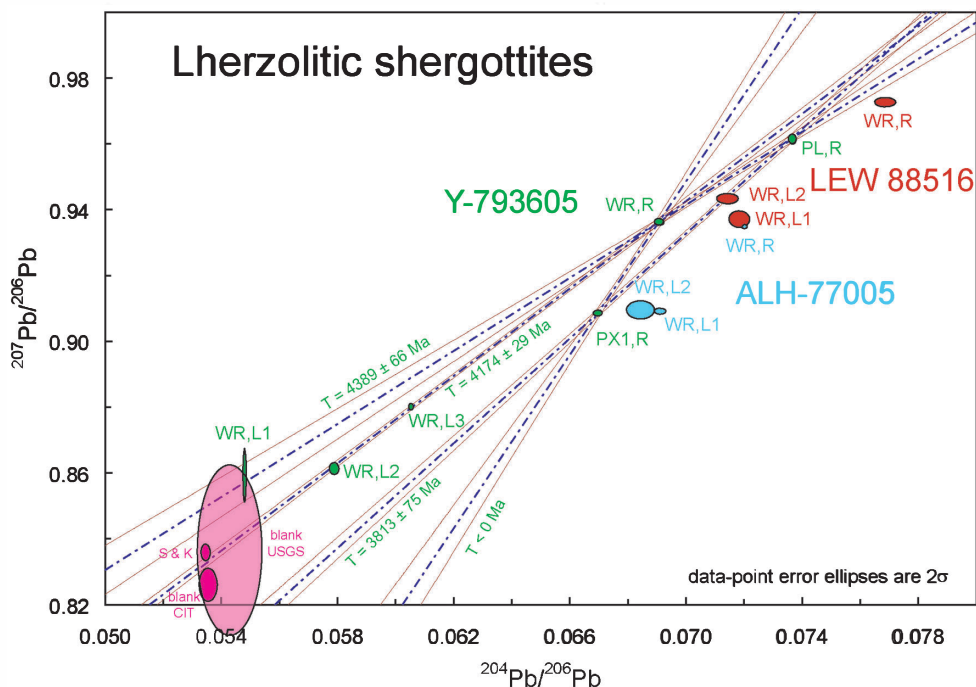


Fig. 4. $^{207}\text{Pb}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{204}\text{Pb}$ diagram for whole-rock samples of Antarctic lherzolitic shergottites (Chen and Wasserburg, 1987, 1993; Misawa *et al.*, 1997). Pyroxene and plagioclase residue samples (PX1,R and PL,R) of Y-793605 are also plotted. Terrestrial lead isotopic compositions (S & K) are from Stacey and Kramers (1975).

The detailed mechanisms of aqueous alteration on the Martian surface are still not well-understood. Grady *et al.* (2005) suggested different flows of water. Surface water in contact with Martian atmosphere might be percolating downward from above and precipitation of salts could have occurred. On the other hand, groundwater from melted ice could be circulating from below and alteration of silicates could have occurred. We consider the elemental fractionations of uranium and thorium which could have occurred during aqueous alteration on the Martian surface. Uranium and thorium have similar chemical properties and tetravalent oxidation states with similar ionic radii ($\text{U}^{4+} = 100$ pm, $\text{Th}^{4+} = 109$ pm). Under oxidizing conditions, uranium forms the uranyl ion (UO_2^{2+} ; $\text{U}^{6+} = 73$ pm) which forms compounds easily soluble in water. Therefore, uranium becomes a mobile element and could be separated from thorium, which exists only in the tetravalent state and whose compounds are generally insoluble in water. The $^{232}\text{Th}/^{238}\text{U}$ ($\equiv \kappa$) ratios of whole-rock samples of lherzolitic shergottites determined by isotope dilution mass spectrometry are relatively constant (Table 3). The μ values of ALH-77005 leachate and residue samples are much higher than those of Y-793605 and LEW 88516.

In order to remove terrestrial lead contamination for whole-rock samples of lherzolitic shergottites, several experiments involving steps of acid leaching have been conducted

Table 3. U-Th-Pb fractionations of lherzolitic shergottites (whole-rock samples) during acid leaching.

Sample	$^{232}\text{Th}/^{238}\text{U}$ (κ)	$^{238}\text{U}/^{204}\text{Pb}$ (μ)
Yamato-793605 (Misawa <i>et al.</i>, 1997)		
0.01M hydrobromic acid leachate	1.21	2.92
0.1M hydrobromic acid leachate	4.16	6.69
1M nitric acid leachate	19.5	1.26
Residue	1.64	1.43
Calculated Total	3.93	3.06
Allan Hills-77005 (Chen and Wasserburg, 1987)		
1M hydrobromic acid + 2M hydrochloric acid leachate [§]	3.87	37.8
1M nitric acid leachate [¶]	5.26	42.3
Residue	3.83	10.3
Calculated Total	4.02	15.1
Lewis Cliff 88516 (Chen and Wasserburg, 1993)		
1M hydrobromic acid + 2M hydrochloric acid leachate [§]	4.08	6.55
1M nitric acid leachate [¶]	3.97	5.84
Residue	2.77	2.41
Calculated Total	3.82	4.91
Northwest Africa 1950 (Gillet <i>et al.</i>, 2005)		
Total [*]	4.5	

[§]2 ml 1M hydrobromic acid and 2 ml 2M hydrochloric acid at 75°C for 1 hour.

[¶]2 ml 1M nitric acid at ~75°C for 1 hour.

^{*}Calculated from uranium and thorium concentrations.

(Chen and Wasserburg, 1987, 1993; Misawa *et al.*, 1997). As a result, large elemental fractionations between uranium and thorium sometimes occurred. The κ value of 0.01M hydrobromic acid leachate of Y-793605 is 1.21, which is more than one order of magnitude smaller than the κ value of 0.1M nitric acid leachate ($\kappa=19.5$). Some of the trace elements in lherzolitic shergottites may have been mobilized to grain boundaries due to brecciation (only for Y-793605) and/or shock metamorphisms, making them more susceptible to leaching by weak acids. Less pronounced, but up to 40% fractionations of Th/U are observed in acid leachate and residue samples of ALH-77005 and LEW 88516 (Chen and Wasserburg, 1987, 1993). However, as mentioned above, the κ values of whole-rock samples of lherzolitic shergottites ("Total" in Table 3) are fairly constant. These facts suggest that there is negligible elemental fractionation, if any, between uranium and thorium during aqueous alteration.

Rare earth element abundances in the parent melts of lherzolitic shergottites equilibrated with their various minerals were determined using the REE concentrations in various phases and their solid-liquid partitioning coefficients (Lundberg *et al.*, 1990; Harvey *et al.*, 1993; Wadhwa *et al.*, 1994). Calculated REE compositions of the melt in equilibrium with low-Ca pyroxene agree with the whole-rock REE patterns. The REE patterns for whitlockites are parallel in ALH-77005, LEW 88516 and GRV 99027, and also parallel to those of whole-rock samples (Fig. 1c). Harvey *et al.* (1993) concluded that only a small fraction of the REE was removed from the melt prior to whitlockite crystallization. This is conflict with the suggestion by Blichert-Toft *et al.*

(1999) that leaching agents such as pressurized groundwater, carbon dioxide or hydrothermal fluids remobilize incompatible trace elements existing in grain boundaries without disturbing the igneous textures, and that the phosphates in shergottites are not primary, but could have been precipitated from leachates. These facts suggest that each shergottite crystallized as a closed-system (Lundberg *et al.*, 1990; Harvey *et al.*, 1993; Wadhwa *et al.*, 1994), and that the abundances of LIL elements remain nearly unaffected by aqueous alteration on the Martian surface.

The isotopic systems of lherzolitic shergottites including phosphates, thus, are considered to be indigenous, although disturbances by shock metamorphism are clearly observed. The “young ages of ~180 Ma” obtained by this and previous studies for Rb-Sr, Sm-Nd and U-Pb systems represent crystallization events.

4. Conclusions

The Sm-Nd internal isochron obtained for acid leachates and residues of whole-rock and separated mineral fractions yields an age of 185 ± 16 Ma with an initial ϵ_{Nd} value of $+9.7 \pm 0.2$. The obtained Sm-Nd age is, within analytical errors, identical to the Rb-Sr age of this meteorite as well as to the previous Rb-Sr and Sm-Nd ages of ALH-77005 and LEW 88516, although the ϵ_{Nd} values are not identical to each other. The elemental abundances of lithophile trace elements remained nearly unaffected by aqueous alteration on the Martian surface. The isotopic systems of lherzolitic shergottites, thus, are considered to be indigenous, although disturbances by shock metamorphism are clearly observed. “Young ages of ~180 Ma” have been consistently obtained from this and previous Rb-Sr, Sm-Nd and U-Pb isotopic studies for lherzolitic shergottites appear to represent crystallization events.

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