

## Sm–Nd systematics of zircon

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### Abstract

$^{147}\text{Sm}$ – $^{143}\text{Nd}$  and  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  systems were studied in nineteen 3.32–4.02 Ga zircon grains from Jack Hills metaconglomerate, 12 of which were previously analyzed for Lu–Hf. Nd concentrations in the zircons are 0.9–20 ppm. The amount of Nd recovered was between 13 and 446 pg. The analytical precision of  $^{142}\text{Nd}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios varied between 0.004% and 0.08% ( $2\sigma_m$ ) depending on the sample size. The  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios vary from 0.4 to 1.2.  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios are variably radiogenic, from 0.5125 to 0.5346. Combined interpretation of  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  and U–Pb systems shows that LREE in zircons are a mixture of a primary component with high Sm/Nd ( $>1.6$ – $2.0$ ), and a secondary, younger component with low Sm/Nd. Determination of initial  $\epsilon^{143}\text{Nd}$  of ancient zircons with a precision and accuracy sufficient for petrogenetic interpretations may not be possible because of large errors in the  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio, which propagate to the uncertainty of  $\epsilon^{143}\text{Nd}$ . Additionally, the  $\epsilon^{143}\text{Nd}$  values are biased by the presence of secondary Nd of unknown age and isotopic composition in more altered zircons. The  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  system is more promising as a gauge for this secondary, alteration-related REE component in zircon. Application of the  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  system in zircon to determine the timing of early terrestrial differentiation is promising. It will require advancement of the analytical procedures to achieve the lowest possible blanks and maximum sensitivity. Ion yield as high as 20–30% will be required.

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### 1. Introduction

Zircon is a mineral of exceptional versatility in geology and geochemistry. It is the most widely used mineral in U–Pb geochronology, and a time capsule of outstanding stability for tracer isotopes (Hf, O) and trace elements. Moreover, detrital zircons in Archean metasedimentary rocks represent the only known

material record of the Hadean. The use of zircon as an isotopic time capsule is being developed for additional systems, e.g. the search for extinct terrestrial  $^{244}\text{Pu}$  as recorded in fission xenon (Honda et al., 2003).

Since zircon contains measurable amounts of REE, it may be suitable for Nd isotopic studies (Kinny and Maas, 2003). If zircon preserves Nd isotopic information, these data would help resolve the long-standing conflict between the Nd and Hf isotopes in early Archean (Galer and Goldstein, 1991; Bennett et al., 1993; Gruau et al., 1996; Vervoort et al., 1996;

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Moorbath et al., 1997; Vervoort and Blichert-Toft, 1999), and to get firm constraints on the timing of primary crust–mantle differentiation, chondritic vs. non-chondritic composition of the bulk silicate earth, and the possible existence of a hidden mantle reservoir.

In order to test the potential of the Sm–Nd isotopic system for studies of early terrestrial evolution, this paper presents Sm–Nd and U–Pb data from 3.32–4.02 Ga single detrital zircon grains from the extensively studied Jack Hills metaconglomerate W-74 (Compston and Pidgeon, 1986). U–Pb and Lu–Hf from some of these grains were reported previously (Amelin et al., 1999). Radiogenic isotope effects in both the long-lived  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  system ( $T_{1/2}=106$  b.y., Audi et al., 1997; Begemann et al., 2001), and in the short-lived  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  system ( $T_{1/2}=103$  m.y., Audi et al., 1997), are reported.

$^{147}\text{Sm}$ – $^{143}\text{Nd}$  isotopic systematics of zircon has been studied by several workers (Patterson et al., 1992; von Blanckenburg, 1992; von Quadt, 1992; Stern, 1992; von Quadt and Gebauer, 1993; Paquette et al., 1994, 1995) using milligram-size multi-grain fractions. The range of reported Nd concentrations from these studies is 1–186 ppm. The most important finding of these studies was that xenocrystic zircon in granitoid rocks can preserve Sm–Nd isotopic signatures of the crustal precursor, just as it preserves U–Pb isotopic signatures (Patterson et al., 1992; von Blanckenburg, 1992). Sm–Nd isochrons for igneous zircon fractions from mafic rocks can give ages consistent with the upper intercepts of U–Pb discordia lines (e.g. von Quadt, 1992). These observations suggest considerable robustness of the Sm–Nd system in zircon. The  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  system in zircon has not been previously explored.

## 2. Procedures

Here I report Sm–Nd data for 19 Jack Hills zircon grains and three fractions of the standard zircon 61.308B. Selection and preparation of the Jack Hills zircon grains followed the same procedures described by Amelin et al. (1999). Zircons were spiked with  $^{205}\text{Pb}$ – $^{235}\text{U}$  before dissolution, and with  $^{149}\text{Sm}$ – $^{150}\text{Nd}$  mixed tracers. The grains 1–12 were also spiked with  $^{176}\text{Lu}$ – $^{180}\text{Hf}$  mixed tracer. Mutual contamination of

spikes (e.g., contents of Sm and Nd introduced with  $^{205}\text{Pb}$ – $^{235}\text{U}$  and  $^{176}\text{Lu}$ – $^{180}\text{Hf}$  spikes) was well below 0.1 pg with the exception of Pb contamination from the  $^{176}\text{Lu}$ – $^{180}\text{Hf}$  spike, which contributed 3–10 pg of Pb per analysis. In order to minimize Pb contamination of the grains analyzed for both Sm–Nd and Lu–Hf (grains 1–12), the  $^{149}\text{Sm}$ – $^{150}\text{Nd}$  and  $^{176}\text{Lu}$ – $^{180}\text{Hf}$  solutions were added after anion-exchange separation of U and Pb (Amelin et al., 1999). Zircon grains 32–39 and standard zircon fractions, not analyzed for Lu–Hf, were spiked with  $^{205}\text{Pb}$ – $^{235}\text{U}$  and  $^{149}\text{Sm}$ – $^{150}\text{Nd}$  before dissolution. Spiking either before or after U–Pb separation should not introduce bias in Sm/Nd ratios, because Sm and Nd are not absorbed, and hence not fractionated, during U–Pb separation. Identical results obtained for Lu–Hf in zircon with spiking before and after U–Pb separation (Amelin et al., 2000) confirm that the elements that are not absorbed in the U–Pb separation procedure pass through the anion exchange columns without fractionation. Hf (and Zr), Lu and middle REEs including Sm and Nd were separated using 0.7 cm<sup>3</sup> cation exchange columns in 1 M HCl+0.1 M HF followed by 4 M HCl. Nd and Sm were separated on columns packed with 0.7 cm<sup>3</sup> of Eichrom Ln-Spec resin (HDEHP on polymer support), by sequential elution with 0.23–0.5 M HCl. Ce was removed prior to Nd elution by washing columns with 0.1 M HCl.

Procedural blanks, measured repeatedly during this study, averaged  $2 \pm 2$  pg for both Sm and Nd. Although low, these blanks are not negligible for the small amounts of Sm and Nd in the zircons. All reported Sm and Nd concentrations and  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios are corrected for blank. The amount of Nd was too small to measure precisely the isotopic composition of the blank, so its composition was assumed to be equal to the modern chondritic value. Uncertainty in the blank correction is propagated into the error of  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios, and in many cases constitutes the largest source of uncertainty.

Mass spectrometry techniques, the isotopic composition of oxygen used for corrections, and data reduction are identical to those previously used at the Jack Satterly Geochronology Lab (Amelin et al., 1997; Amelin and Rotenberg, 2004). The results of isotopic analyses from “small” (0.3 ng) and “large” (10–15 ng) loads of the La Jolla Nd standard, measured during this study, are shown in Table 1.

Table 1

Nd isotopic composition of the La Jolla standard measured as NdO+ from silica gel loads

Amount, ng	Ion yield% <sup>a</sup>	<sup>142</sup> Nd/ <sup>144</sup> Nd	2σ	<sup>143</sup> Nd/ <sup>144</sup> Nd	2σ	<sup>145</sup> Nd/ <sup>144</sup> Nd	2σ	<sup>148</sup> Nd/ <sup>144</sup> Nd	2σ	<sup>150</sup> Nd/ <sup>144</sup> Nd	2σ
15	4.4	1.141897	0.000016	0.511887	0.000005	0.348411	0.000010	0.241603	0.000009	0.236473	0.000026
15	2.8	1.141874	0.000017	0.511879	0.000004	0.348421	0.000003	0.241597	0.000008	0.236472	0.000018
15	2.6	1.141878	0.000018	0.511875	0.000005	0.348415	0.000004	0.241600	0.000008	0.236487	0.000016
15	3.9	1.141882	0.000015	0.511876	0.000005	0.348411	0.000004	0.241597	0.000008	0.236486	0.000014
15	3.9	1.141887	0.000016	0.511879	0.000004	0.348413	0.000003	0.241592	0.000008	0.236475	0.000015
15	7.6	1.141881	0.000016	0.511870	0.000004	0.348412	0.000003	0.241602	0.000008	0.236485	0.000016
10	9.2	1.141908	0.000015	0.511884	0.000004	0.348415	0.000003	0.241601	0.000008	0.236373	0.000014
0.3	18.7	1.141855	0.000053	0.511847	0.000020	0.348387	0.000016	0.241594	0.000039	0.236425	0.000059
0.3	13.7	1.141858	0.000073	0.511849	0.000026	0.348384	0.000024	0.241613	0.000051	0.236340	0.000110
0.3	6.3	1.141925	0.000093	0.511914	0.000036	0.348416	0.000035	0.241592	0.000065	0.236310	0.000110
0.3	6.1	1.141873	0.000092	0.511872	0.000038	0.348360	0.000034	0.241595	0.000070	0.236326	0.000124
0.3	4.0	1.141903	0.000125	0.511883	0.000046	0.348376	0.000041	0.241544	0.000107	0.236238	0.000152
0.3	6.4	1.141878	0.000078	0.511877	0.000031	0.348406	0.000025	0.241592	0.000050	0.236332	0.000084
10–15 ng loads											
Average	4.9	1.141887		0.511879		0.348414		0.241599		0.236464	
2 sigma pop	4.7	0.000022		0.000011		0.000006		0.000007		0.000076	
2 sigma pop %	95	0.0019		0.0021		0.0019		0.0029		0.0320	
0.3 ng loads											
Average	9.2	1.141882		0.511874		0.348388		0.241588		0.236329	
2 sigma pop	10.4	0.000050		0.000045		0.000037		0.000042		0.000110	
2 sigma pop %	113	0.0043		0.0088		0.0106		0.0175		0.0463	

<sup>a</sup> Number of ions of <sup>144</sup>Nd registered by the collectors divided by the number of atoms of <sup>144</sup>Nd loaded on the filament.

Average values of all isotopic ratios measured from 10 to 15 ng loads and from 0.3 ng loads agree within 2σ error limits, and the <sup>142</sup>Nd/<sup>144</sup>Nd and <sup>143</sup>Nd/<sup>144</sup>Nd are nearly identical, suggesting that the accuracy of isotopic composition measured from sub-nanogram amounts of Nd is not compromised by small sample size. Several Nd loads from zircons yielded very low signals, which were measured using the Daly detector. This procedure provided concentration measurements only, and Nd isotopic compositions for these zircons are not reported. Ion yields (number of ions of <sup>144</sup>Nd registered by the collectors divided by the number of atoms of <sup>144</sup>Nd loaded on the filament) calculated from the La Jolla standard analyses are between 2.8% and 18.6%. The ion yield values do not correlate with the size of the load.

To check the entire procedure including chemical separation, three fractions of the standard zircon 61.308B (Wiedenbeck et al., 1995) were analysed. <sup>142</sup>Nd/<sup>144</sup>Nd and <sup>143</sup>Nd/<sup>144</sup>Nd ratios for all three fractions are reproducible, and the <sup>142</sup>Nd/<sup>144</sup>Nd ratio is coherent with the value obtained from the La Jolla standard (Table 1). The value for <sup>142</sup>Nd/<sup>144</sup>Nd of 1.141872±0.000027, the weighted average of small

La Jolla and standard zircon analyses is used as a terrestrial reference value in discussing the <sup>146</sup>Sm–<sup>142</sup>Nd systematics. The difference between the lowest and the highest <sup>147</sup>Sm/<sup>144</sup>Nd ratio measured in three fractions of standard zircon is 3%, well outside of analytical error. These variations are interpreted to reflect primary heterogeneity of the standard zircon.

Isochron regressions, weighted averages and median values with their error limits were calculated using Isoplot-Ex version 2.49 (Ludwig, 2001). Error limits are 95% confidence intervals for isochrons and weighted averages. Errors of the isotopic ratios and of other values mentioned in the text, are 2σ of the mean, unless indicated otherwise. Correlations are calculated using the “correlation analysis tool” of Microsoft Excel 2000.

### 3. Results

#### 3.1. Sm and Nd concentration

Sm–Nd data for 19 Jack Hills zircon grains are shown in Table 2. Nd concentrations vary from 0.9 to

Table 2  
Zircon Sm–Nd and U–Pb data

Frac. #	Sample <sup>a</sup>	Sample wt, mg	<sup>207</sup> Pb/ <sup>206</sup> Pb	2σ error	U–Pb discord. <sup>b</sup>	[Nd], ppm <sup>c</sup>	[Sm], ppm <sup>d</sup>	Amount Nd, ng <sup>d</sup>	<sup>147</sup> Sm/ <sup>144</sup> Nd	2σ error <sup>d</sup>	<sup>142</sup> Nd/ <sup>144</sup> Nd <sup>d</sup>	2σ error <sup>e</sup>	<sup>142</sup> Nd/ <sup>144</sup> Nd corr. <sup>e,f</sup>	<sup>143</sup> Nd/ <sup>144</sup> Nd	2σ error	<sup>143</sup> Nd/ <sup>144</sup> Nd initial <sup>g</sup>	$\epsilon^{143}\text{Nd}$ (T) <sup>h</sup>	2σ error	T_Nd CHUR, Ga <sup>i</sup>	Pb–Nd discord <sup>j</sup>
1	61.308B	0.247	0.0025	0.0002		4.00	5.72	0.988	0.865	0.003	1.141860	0.000099	1.141860	0.512927	0.000031	0.51291	5.5	0.6	0.067	
2	61.308B	0.252	0.0025	0.0002		4.16	5.78	1.047	0.840	0.003	1.141858	0.000073	1.141858	0.512920	0.000031	0.51291	5.3	0.6	0.067	
3	61.308B	0.238	0.0025	0.0002		4.07	5.81	0.969	0.862	0.006	1.142030	0.000230	1.142030	0.512916	0.000084	0.51290	5.2	1.6	0.064	
4	W74 Gr1	0.042	3.868	0.001	0.021	1.34	2.33	0.056	1.050	0.042	1.141900	0.000350	1.141887	0.529900	0.000130	0.50300	−91	21	3.063	0.208
5	W74 Gr2	0.043	3.516	0.001	0.071	3.43	4.69	0.148	0.826	0.014	1.141950	0.000110	1.141949	0.524038	0.000071	0.50482	−64	7	2.745	0.219
6	W74 Gr3	0.024	3.824	0.001	0.249	18.6	17.2	0.446	0.560	0.004	1.141957	0.000089	1.141953	0.515707	0.000026	0.50152	−121	2	1.286	0.664
7	W74 Gr4	0.027	3.353	0.002	0.172	2.15	3.32	0.058	0.933	0.037	1.141290	0.000510	1.141290	0.523770	0.000210	0.50309	−102	17	2.296	0.315
8	W74 Gr5	0.025	4.022	0.001	0.070	5.02	7.54	0.126	0.908	0.018	1.141900	0.000250	1.141869	0.526210	0.000100	0.50202	−106	9	2.891	0.281
9	W74 Gr6	0.021	3.328	0.003	0.753	20.7	30.1	0.435	0.880	0.006	1.141927	0.000066	1.141927	0.521584	0.000023	0.50221	−120	2	1.988	0.403
10	W74 Gr7	0.044	4.004	0.001	0.137	3.73	4.64	0.164	0.753	0.012	1.141920	0.000120	1.141898	0.521792	0.000043	0.50182	−110	6	2.497	0.376
11	W74 Gr8	0.025	3.384	0.002	0.017	1.36	2.72	0.034	1.207	0.076	1.141380	0.000930	1.141379	0.532670	0.000230	0.50566	−51	34	3.003	0.113
12	W74 Gr9	0.022	4.022	0.001	0.033	1.84	2.35	0.040	0.772	0.047	1.141690	0.000520	1.141665	0.525380	0.000200	0.50480	−51	25	3.350	0.167
13	W74 Gr10	0.020	3.388	0.001	0.047	2.67	4.36	0.053	0.987	0.042	1.142160	0.000360	1.142160	0.528220	0.000110	0.50610	−42	19	2.984	0.119
14	W74 Gr11	0.012	3.982	0.001	0.013	2.67	4.71	0.032	1.065	0.073	1.141230	0.000790	1.141201	0.534640	0.000330	0.50654	−18	38	3.826	0.039
15	W74 Gr12	0.018	3.380	0.001	0.010	1.52	2.74	0.027	1.090	0.086	1.141920	0.000630	1.141919	0.531470	0.000240	0.50711	−22	38	3.190	0.056
16	W74 Gr32	0.031	4.003	0.001	0.097	2.21	2.74	0.069	0.748	0.028	1.141660	0.000520	1.141639	0.520510	0.000200	0.50068	−133	15	2.169	0.458
17	W74 Gr34	0.028	3.375	0.001	0.044	4.80	3.21	0.134	0.404	0.011	1.141900	0.000420	1.141900	0.512500	0.000140	0.50349	−94	5	−0.100	1.030
18	W74 Gr35	0.013	3.382	0.001	0.009	3.27	3.02	0.043	0.557	0.037										
19	W74 Gr36	0.026	3.500	0.002	0.053	1.81	2.61	0.047	0.869	0.044										
20	W74 Gr37	0.010	3.449	0.001	0.032	3.06	4.25	0.031	0.838	0.064										
21	W74 Gr38	0.015	4.002	0.001	0.024	0.99	1.77	0.015	1.081	0.149										
22	W74 Gr39	0.014	3.511	0.001	0.026	0.94	1.36	0.013	0.875	0.143										

<sup>a</sup> Standard zircon 61.308B fractions are multiple fragments; Jack Hills zircons (W74) are single grains.

<sup>b</sup> U–Pb data for W74 grains 1 to 12 are from Amelin (1998).

<sup>c</sup> The U–Pb discordance is the deviation of a U–Pb analytical point from concordia, defined as  $100 \times ((\text{Exp}(\lambda^{238}\text{U} \times \text{Age}_{207/206}) - 1) - ^{238}\text{U}/^{206}\text{Pb}) / (\text{Exp}(\lambda^{238}\text{U} \times \text{Age}_{207/206}) - 1)$ .

<sup>d</sup> Sm and Nd concentrations and <sup>147</sup>Sm/<sup>144</sup>Nd ratios are corrected for blank of  $2 \pm 2$  pg for both Sm and Nd. The uncertainty is propagated into the error of <sup>147</sup>Sm/<sup>144</sup>Nd ratio.

<sup>e</sup> Nd isotopic ratios are corrected for fractionation using exponential law and the ratio of <sup>146</sup>Nd/<sup>144</sup>Nd=0.7219.

<sup>f</sup> Corrected for in situ decay of <sup>146</sup>Sm assuming <sup>146</sup>Sm/<sup>144</sup>Sm=0.008 at 4.56 Ga, and evolution in a chondritic reservoir between 4.56 Ga and the <sup>207</sup>Pb/<sup>206</sup>Pb age of the zircon.

<sup>g</sup> Calculated using the measured <sup>143</sup>Nd/<sup>144</sup>Nd and <sup>147</sup>Sm/<sup>144</sup>Nd, and the <sup>207</sup>Pb/<sup>206</sup>Pb date.

<sup>h</sup>  $\epsilon^{143}\text{Nd}$  is calculated using the CHUR parameters <sup>143</sup>Nd/<sup>144</sup>Nd=0.512636 and <sup>147</sup>Sm/<sup>144</sup>Nd=0.1966 and the <sup>207</sup>Pb/<sup>206</sup>Pb age of the zircon.

<sup>i</sup> Nd model dates are relative to CHUR.

<sup>j</sup> The Pb–Nd discordance is defined here as the difference between <sup>207</sup>Pb/<sup>206</sup>Pb age and Nd model age, divided by <sup>207</sup>Pb/<sup>206</sup>Pb age.

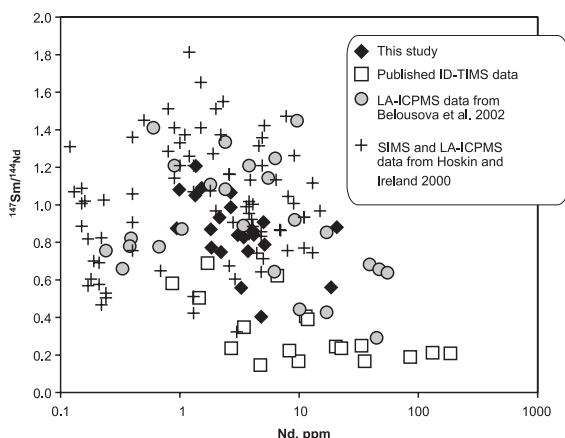


Fig. 1. Correlation between Nd concentration and  $^{147}\text{Sm}/^{144}\text{Nd}$  in zircon. Jack Hills single zircon analyses are those studied in this paper. Published data obtained with isotope dilution analyses are from Patterson et al. (1992), von Blanckenburg (1992), von Quadt (1992), Stern (1992), von Quadt and Gebauer (1993), Paquette et al. (1994), Paquette et al. (1995). SIMS and laser ablation ICP-MS data are from Belousova et al. (2002) (first quartile, median and third quartile of the data set for each rock type; minimum and maximum values are not included), and from Hoskin and Ireland (2000). The  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios for SIMS and laser ablation ICP-MS data are calculated from Sm/Nd ratios assuming modern chondritic  $^{143}\text{Nd}/^{144}\text{Nd}$ .

20 ppm (Fig. 1), and overlap with the lower part of the range of published data (Fig. 1).  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios in the Jack Hills zircons vary from 0.4 to 1.2. These ratios are similar to those measured with high spatial resolution (SIMS and LA-ICP-MS) methods in zircon from various rock types (e.g. Hoskin and Ireland, 2000; Belousova et al., 2002). They are typically higher than published zircon ID-TIMS analyses of large multi-grain fractions (the range of 0.14–0.62). The Nd concentration and  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio in the Jack Hills zircons are slightly negatively correlated (correlation coefficient  $r^2=0.12$ ). Excluding two analyses with high Nd concentrations (Grains 3 and 6) makes the correlation stronger ( $r^2=0.37$ ). Most published multi-grain ID-TIMS zircon analyses show low  $^{147}\text{Sm}/^{144}\text{Nd}$  and high Nd concentrations. All zircons with Nd concentration higher than 30 ppm have low  $^{147}\text{Sm}/^{144}\text{Nd}$ .

The amount of Nd in the analyzed zircons varies between 13 and 446 pg. The precision of Nd isotopic analyses declines with the amount of Nd in the analyzed fractions (Fig. 2). Fractions containing less than 50 pg of Nd yielded errors of  $^{142}\text{Nd}/^{144}\text{Nd}$  and

$^{143}\text{Nd}/^{144}\text{Nd}$  between 0.03% and 0.08%. Precision of the Nd isotopic analyses from larger Nd fractions is greater, approaching 0.004% for fractions over 400 pg.

### 3.2. $^{147}\text{Sm}-^{143}\text{Nd}$ systematics

The  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios vary from unradiogenic (0.5125) to highly radiogenic (0.5346) and are broadly correlated with the  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios (Fig. 3). This correlation suggests that a large fraction of radiogenic Nd present in the zircons was accumulated in situ.

Initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios and  $\epsilon^{143}\text{Nd}$  values, calculated using the measured  $^{207}\text{Pb}/^{206}\text{Pb}$  dates, are presented in Table 2. The main component in the error of the initial  $^{143}\text{Nd}/^{144}\text{Nd}$  value comes from uncertainty in  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios due to Sm and Nd blank correction. Since the estimates of the blank uncertainty propagated into the  $\epsilon^{143}\text{Nd}$  values encompass the entire range of the measured blanks, the errors of  $\epsilon^{143}\text{Nd}$  values can be considered the maximum estimates. Most of the initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios in the Jack Hills zircons, between 0.50068 and 0.50711, are lower than the initial value for the solar system of  $0.50671 \pm 0.00015$  (Amelin and Rotenberg, 2004).

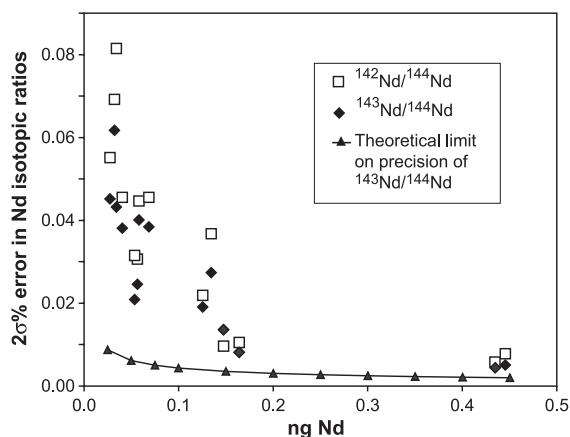


Fig. 2. Analytical errors in Nd isotopic ratios measured from the Jack Hills zircons vs. amount of Nd in the analyzed fractions. The curve shows the limit on precision for measured  $^{143}\text{Nd}/^{144}\text{Nd}$ . The limit is estimated on the basis of counting statistics alone, using the average ion yield value of 6.9%. The procedure-specific factors that influence the precision limit such as the error magnification of demagnification due to normalization, and instrument-specific parameters such as amplifier noise, are not included in the precision estimate.

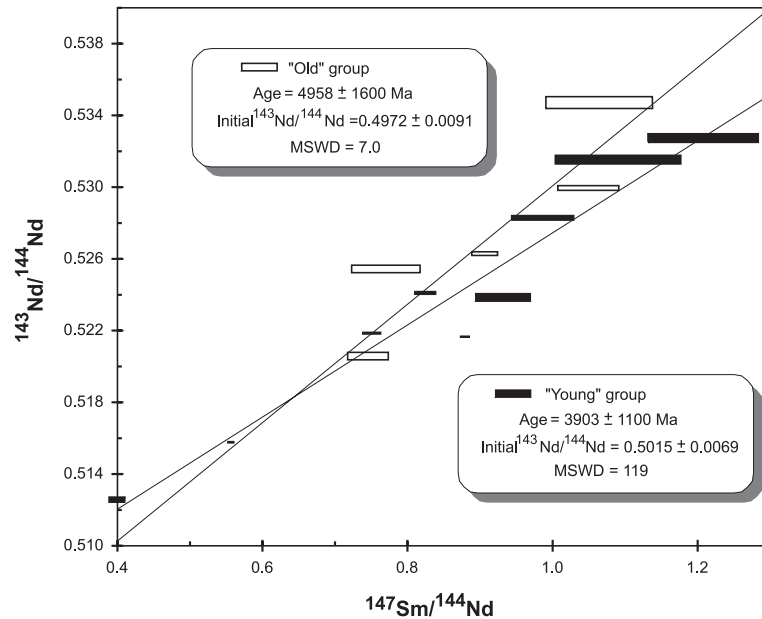


Fig. 3.  $^{147}\text{Sm}/^{144}\text{Nd}$  vs.  $^{143}\text{Nd}/^{144}\text{Nd}$  isochron plot for the Jack Hills zircons. Error bars are  $2\sigma$  of the mean. The data are regressed separately for the “young” group of grains ( $^{207}\text{Pb}/^{206}\text{Pb}$  dates between 3328 and 3516 Ma), and the “old” group ( $^{207}\text{Pb}/^{206}\text{Pb}$  dates between 3824 and 4022 Ma), using Model 2 of the Isoplot (Ludwig, 2001).

This is a clear proof that the Sm–Nd system in the zircons is disturbed.

$^{147}\text{Sm}$ – $^{143}\text{Nd}$  data for individual grains can also be expressed as model dates (i.e. two-point isochron dates relative to the assumed source reservoir).  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios in most analyzed zircons are sufficiently high to make the model dates rather insensitive to the choice of the reference reservoir (the exception is grain 34, which contains unradiogenic Nd, therefore its model date is unreliable and is not considered further). For simplicity the model dates are calculated relative to the chondritic uniform reservoir (CHUR, Jacobsen and Wasserburg, 1980) using a single-stage model. If both Sm–Nd and U–Pb systems remained closed since the time of formation of the zircon approximated by the  $^{207}\text{Pb}/^{206}\text{Pb}$  date, then the  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  model date can be expected to be consistent with the  $^{207}\text{Pb}/^{206}\text{Pb}$  date, with possible small deviations to either higher or lower value due to non-chondritic isotopic composition of Nd in the source rock of the zircon. The relationship between  $^{207}\text{Pb}/^{206}\text{Pb}$  dates and  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  model dates for the Jack Hills zircons (Fig. 4) shows no correlation between these dates. Furthermore, all Sm–Nd model

dates are younger, and most of them are much younger, than the  $^{207}\text{Pb}/^{206}\text{Pb}$  dates. Young  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  model dates can be explained if Sm and Nd in zircons are mixtures of a primary or “old” component (initial Sm and Nd, and in situ grown  $^{143}\text{Nd}$ ) and one or more secondary or “young”

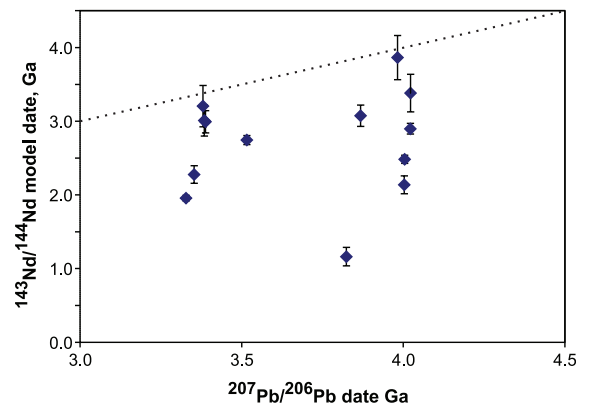


Fig. 4.  $^{207}\text{Pb}/^{206}\text{Pb}$  dates and  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  model dates (Table 2) for the Jack Hills zircons. The Pb–Nd concordia (the locus of consistent dates) is shown with a thick dotted line. Error bars are  $2\sigma$  of the mean.



components (presumably alteration-related). In this case,  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  model date may be anywhere between the time of the zircon formation and the time of the most recent alteration.

The relationship between  $^{207}\text{Pb}/^{206}\text{Pb}$  dates and  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  model dates can be further expressed as Pb–Nd discordance (Table 2). This is an age-independent parameter defined here as the difference between  $^{207}\text{Pb}/^{206}\text{Pb}$  date and Nd model date, divided by  $^{207}\text{Pb}/^{206}\text{Pb}$  date (similar to the definition of U–Pb discordance). Pb–Nd discordance is a composite measure of the proportion of primary and secondary components in Sm–Nd system of zircon, and the age difference between the components. The Pb–Nd discordance approaches zero when the contribution of the secondary component is small, or when the age of the secondary component is close to the time of the zircon crystallization. Large values of Pb–Nd discordance in many zircons (Table 2) show that the secondary Sm–Nd component is both abundant (comprises a large fraction in the Nd budget of zircon) and young (has a late Archean or post-Archean crustal residence age). Sm–Nd and U–Pb systematics of zircon alone are not sufficient for independent determination of the age and abundance of this secondary component.

$^{147}\text{Sm}$ – $^{143}\text{Nd}$  model dates  $T_{\text{Nd}}(\text{CHUR})$  are positively correlated ( $R^2=0.47$ ) with  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio (Fig. 5a). Pb–Nd discordance has negative correlation ( $R^2=0.68$ ) with  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio (Fig. 5b). These relationships demonstrate that the primary REE component in zircon has high  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio of 1.0–1.2, which corresponds to Sm/Nd ratio of 1.6–2.0. If similar relationships hold for zircons in general, they may be used to evaluate the contribution of a secondary component to the REE budget of zircons on the basis of Sm and Nd concentrations alone.

To obtain further constraints on the nature of the Sm–Nd disturbance, Pb–Nd discordance is compared to the discordance in the U–Pb systems. U–Pb discordance results from the loss of radiogenic Pb, and in some cases from new zircon growth on an older grain. Strong positive correlation between these parameters (Fig. 6a) holds for all but one zircon (grain 6). A broad positive correlation also exists between Pb–Nd discordance and alpha dose, calculated from U and Th concentrations and  $^{207}\text{Pb}/^{206}\text{Pb}$  age (Fig. 6b). These correlations suggest that both Pb–

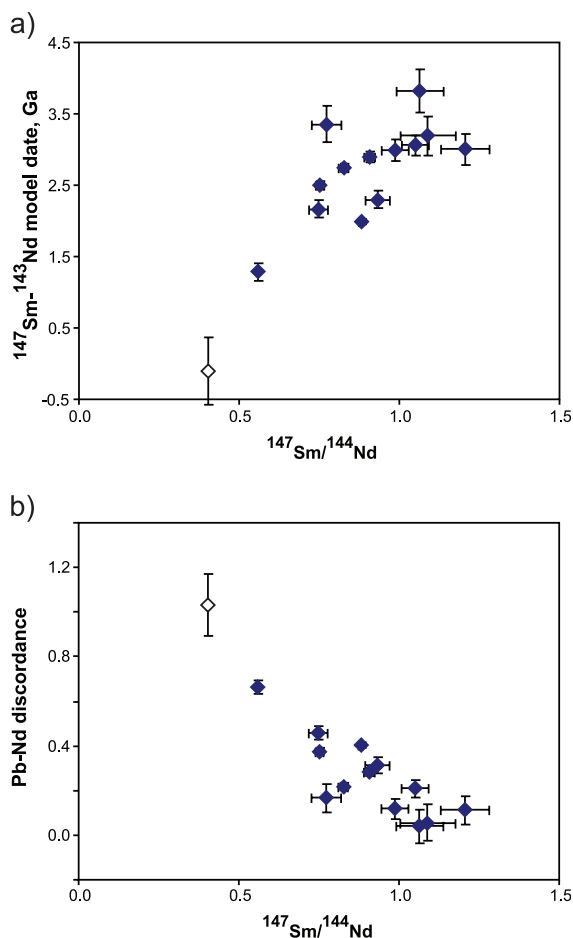


Fig. 5.  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  model dates (a) and Pb–Nd discordance (b) plotted against the measured  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios in the zircons. The data point of the Grain 34 is shown with an open symbol. Error bars are  $2\sigma$  of the mean.

Nd and U–Pb discordance are related to radiation-induced partial metamictization, rather than to diffusion of REE, U and Pb, which is very slow in crystalline zircon (Cherniak et al., 1997a,b; Cherniak et al., 2001). Most zircons analyzed in this study have accumulated dose greater than  $3 \times 10^{15}$   $\alpha$ -decays/mg, which corresponds to transition from individual point defects to distorted crystalline domains (Murakami et al., 1991). Distortion of the crystal lattice can make zircon more susceptible to fluid exchange with the host rock. This exchange results in extraction of radiogenic Pb from zircon, and addition of REE with low Sm/Nd ratio and unradiogenic Nd from a fluid

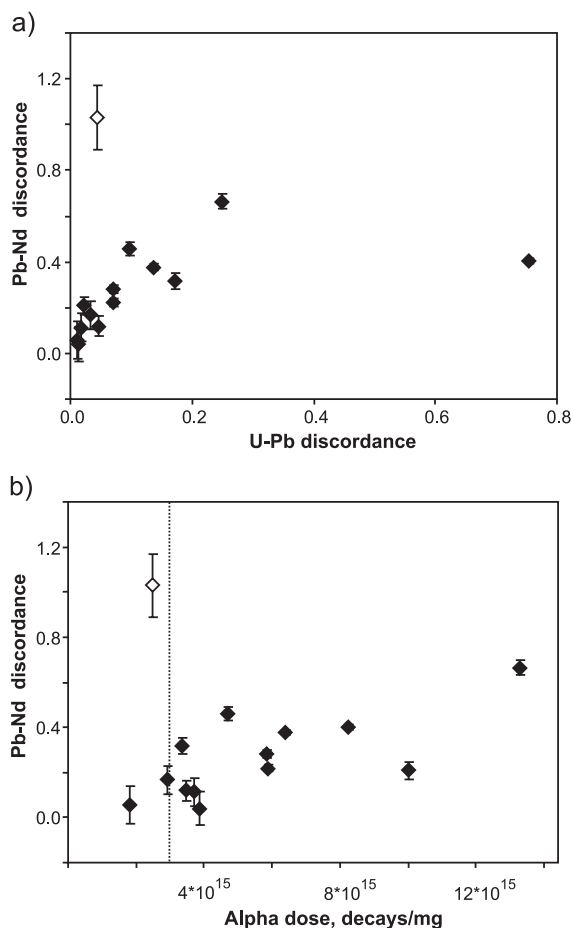


Fig. 6. (a) Discordance between Pb isotopic and  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  model dates vs. discordance in the U–Pb system. (b) Discordance between Pb isotopic and  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  model dates vs. alpha dose accumulated by the zircons. Vertical thick dotted line marks the dose of  $3 \times 10^{15}$   $\alpha$ -decays/mg, which corresponds to transition from individual point defects to distorted crystalline domains (Murakami et al., 1991). The data point of the grain 34 is shown with an open symbol. Error bars are  $2\sigma$  of the mean.

equilibrated with a crustal rock, to the metamict parts of the zircon grains. This was probably the most common mechanism of generating discordance in zircon. The grain 6 (fraction 9) does not follow the main trend. A very high degree of U–Pb discordance combined with moderate Pb–Nd discordance in this grain may be a result of Pb loss related to fracturing (this is one of the two fractured grains analyzed in this study, see Amelin, 1998 for grain descriptions and detailed U–Pb data).

### 3.3. $^{146}\text{Sm}$ – $^{142}\text{Nd}$ systematics

$^{142}\text{Nd}/^{144}\text{Nd}$  ratios in the Jack Hills zircons are presented in Table 2, and are summarized in Table 3. It is possible that grains older than 3.9–4.0 Ga contained a small amount of  $^{146}\text{Sm}$  at the time of formation. This can be estimated from the  $^{207}\text{Pb}/^{206}\text{Pb}$  age and  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio of the zircon, assuming initial  $^{146}\text{Sm}/^{144}\text{Sm}=0.008$  at 4.56 Ga (Lugmair and Galer, 1992; Prinzhofer et al., 1992; Stewart et al., 1994; Amelin and Rotenberg, 2004). Correction for in situ decay of  $^{146}\text{Sm}$  is complicated by the presence of an unknown amount of the “young”, alteration-related Nd component with low  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio. Correction for in situ growth of  $^{142}\text{Nd}$  was applied to all zircon analyses (Table 2). The correction is small compared to the analytical error (3–18% of the analytical error for 3.8–4.02 Ga zircons), and is negligible for younger zircons.

Measured  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios in all grains of old and young groups define a single population with the weighted average of  $1.141927 \pm 0.000041$  (Table 3). This value is marginally higher than the terrestrial reference value of  $1.141872 \pm 0.000027$ . The weighted average  $^{142}\text{Nd}/^{144}\text{Nd}$  for the grains of the older group is indistinguishable from the average of all analyses. Correction for in situ decay of  $^{146}\text{Sm}$  slightly reduces the  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios.

The weighted average of  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios obtained for the entire zircon population is the most precise and therefore gives better constraints on the protolith evolution. The weighted average  $^{142}\text{Nd}/^{144}\text{Nd}$  corresponds to  $\epsilon^{142}\text{Nd}$  between 0 and 90 ppm in the source rocks of the zircons. This range accommodates a wide range of scenarios in which the parent rocks of the zircons were derived from an early depleted mantle (Fig. 7). The Jack Hills zircon  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios are, however, incompatible with the origin from a very early crust produced directly from chondritic bulk earth reservoir.

### 3.4. $\text{Sm}$ – $\text{Nd}$ vs. $\text{Lu}$ – $\text{Hf}$

Twelve of the zircon grains analyzed for Sm–Nd in this study were previously analyzed for Lu–Hf (Amelin et al., 1999). Neither the Nd, Lu and Hf concentrations, nor the Sm/Nd and Lu/Hf ratios are correlated. The lack of correlation between



Table 3  
Summary of  $^{142}\text{Nd}/^{144}\text{Nd}$  data

Sample set	Correction for in situ decay of $^{146}\text{Sm}$	$^{142}\text{Nd}/^{144}\text{Nd}$	$2\sigma$ error	MSWD	$\varepsilon^{142}\text{Nd}$ ppm <sup>a</sup>	$2\sigma$ error ppm <sup>b</sup>	$\varepsilon^{142}\text{Nd}$ lower limit, ppm <sup>c</sup>	$\varepsilon^{142}\text{Nd}$ upper limit, ppm <sup>d</sup>
All grains	No	1.141927	0.000041	1.16	48	43	5	91
	Yes	1.141922	0.000050	1.20	44	50	−6	94
3.82–4.02 Ga	No	1.141926	0.000065	0.92	47	62	−14	109
	Yes	1.141913	0.000065	1.05	36	62	−26	98
4.00–4.02Ga	No	1.141900	0.000100	0.54	25	91	−66	115
	Yes	1.141870	0.000100	0.54	−2	91	−92	89

<sup>a</sup> A difference between  $^{142}\text{Nd}/^{144}\text{Nd}$  in the zircons and the mean value of  $1.141872 \pm 0.000027$ , measured in the 0.3 ng load of the La Jolla standard and in the standard zircon 61.308B.

<sup>b</sup> A quadratic sum of errors in  $^{142}\text{Nd}/^{144}\text{Nd}$  in zircons and in the standards.

<sup>c</sup> The sum of  $\varepsilon^{142}\text{Nd}$  and its  $2\sigma$  error.

<sup>d</sup> The difference between  $\varepsilon^{142}\text{Nd}$  and its  $2\sigma$  error.

$^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{147}\text{Sm}/^{144}\text{Nd}$ , considered together with the strong correlation between  $^{147}\text{Sm}/^{144}\text{Nd}$  and Pb–Nd discordance (Fig. 5b), suggests that the presence of the secondary REE component recorded in Sm–Nd systematics has no measurable effect on the

Lu–Hf systematics of zircon. The difference in behaviour between the Sm–Nd and Lu–Hf systems in zircon is probably related to the higher primary concentrations of Lu and Hf compared to Sm and Nd concentrations.

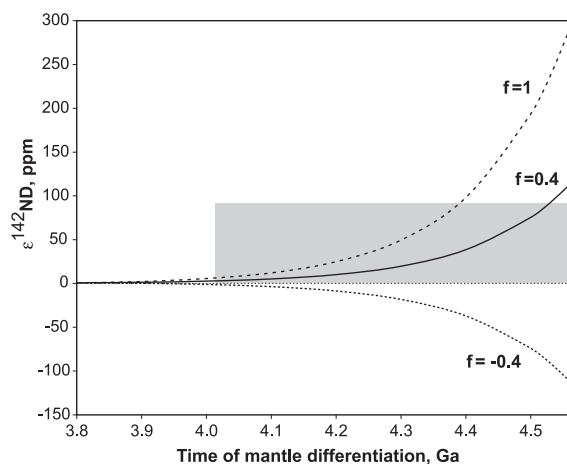


Fig. 7.  $\varepsilon^{142}\text{Nd}$  vs. time of mantle differentiation from a chondritic reservoir (CHUR) with  $^{146}\text{Sm}/^{144}\text{Sm}=0.008$  at 4.56 Ga. Fractionation of Sm/Nd ratio during the mantle differentiation episode is expressed with  $f=[(\text{Sm}/\text{Nd})_{\text{RES}}/(\text{Sm}/\text{Nd})_{\text{CHUR}}]-1$ , where RES is a secondary reservoir (depleted mantle or enriched crust). Grey rectangle shows the range of possible  $\varepsilon^{142}\text{Nd}$  values in the source rocks of the Jack Hills zircons (0–90 ppm) and the timing of the mantle differentiation event (4.02–4.56 Ga). The three curves show the  $\varepsilon^{142}\text{Nd}$  values produced by various degrees of differentiation from the chondritic reservoir:  $f_{\text{Sm}/\text{Nd}}=0.4$  ( $^{147}\text{Sm}/^{144}\text{Nd}=0.275$ , “normal” depleted mantle),  $f_{\text{Sm}/\text{Nd}}=1$  ( $^{147}\text{Sm}/^{144}\text{Nd}=0.394$ , “extreme” depleted mantle), and  $f_{\text{Sm}/\text{Nd}}=-0.4$  ( $^{147}\text{Sm}/^{144}\text{Nd}=0.118$ , average upper continental crust).

## 4. Discussion

### 4.1. Technical limitations on Nd isotopic analysis in zircon

The amount of Nd in the zircon grains analyzed in this study is small, between 13 and 446 pg. This places a serious constraint on the precision of Nd isotopic analysis. The theoretical limit on precision (Fig. 2) is set by the number of ions that are registered by collectors, which in turn depends on the sample size (number of atoms of the analyzed element), ion yield (a product of ionization efficiency and mass-spectrometer transmission), and atomic abundances of the studied isotopes (e.g., Birck, 2001). Errors of  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios, normalized to  $^{146}\text{Nd}/^{144}\text{Nd}$ , are 1.5–3.0 times larger than the theoretical values for both 0.3 ng and 10–15 ng loads. Additional sources of errors responsible for the difference between theoretical and experimental precision are amplifier noise, error magnification on  $^{144}\text{Nd}$  involved in normalization, deviation from exponential fractionation behaviour combined with fractionation drift during measurement (hence drifting normalized  $^{143}\text{Nd}/^{144}\text{Nd}$ ), and loss of ion beam integration time

due to baseline measurements and magnet switching. The experimental errors are 1.5–3.0 times higher than the theoretical limit (Fig. 2). The precision of  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of 46–109 ppm obtained from 0.3 ng loads is however acceptable for producing meaningful Nd isotopic data. If the analytical procedure can be modified to increase the ion yield from 6% (the average for standard analyses in this study) to 30% (close to the maximum values achieved with TIMS for any element; Birck, 2001), then similar precision of analysis can be obtained from 50 pg Nd.

Measured errors in the analyses of 150–450 pg loads are two to three times higher than the theoretical limits based on counting statistics, i.e. the excess errors are of the same magnitude as in the 0.3–15 ng La Jolla Nd analyses. Smaller Nd fractions gave much larger analytical errors, 5–10 times larger than the theoretical limits. This may be related, in part, to the larger contribution of the amplifier noise (the other additional sources of error are likely to be independent of the sample size and the ion beam intensity). It is more likely, however, that larger errors are related to lower ionization efficiency for Nd from zircons. Estimates of ion yields for two zircon standards (fractions 1 and 2, Table 2) and two Jack Hills zircon grains (fractions 16 and 17, Table 2) gave ion yields between 1.3% and 2.8%, significantly lower than for the La Jolla standard. Lower ion yields are probably related to the presence of impurities, such as organics from the resin used for Sm and Nd separation, that suppress ionisation. Development of Sm–Nd in zircon for potential routine use will require careful optimization of the Nd separation procedure.

Zircon grains analyzed in this study are relatively large, about 10–40  $\mu\text{g}$ . This is about 10 times larger than most zircons analyzed for U–Pb in provenance studies. If Nd concentrations found here are typical for zircons in general, then both refinements to the separation procedure and maximizing ion yields are necessary for any future use of the Sm–Nd method for this mineral.

The main source of uncertainty of the  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio is blank correction. The errors associated with correction to the average blanks of  $2 \pm 2$  pg are 1–13% for both Sm and Nd, and these errors are directly propagated into the error of the Sm/Nd ratio. In order to reduce the contribution of the blank correction to the level of combined other sources of uncertainty

(spike calibration and errors in measured isotopic ratios, which amount to 0.3–1.0%), at least a ten-fold reduction of blank will be necessary, if the relative errors of the blanks remain unchanged. It will take a major effort to achieve the intended total procedure blanks of 0.2 pg or lower.

#### 4.2. Sm–Nd chronometry of zircon

Despite high parent to daughter ratios, the  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  system as a chronometer for zircon formation cannot match the precision, accuracy and versatility of the U–Pb system. The use of the  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  system in single zircon grains limited by large analytical errors, especially for low-Nd, relatively alteration-free zircons. It is also limited by the presence of an unknown amount of secondary, alteration-related Sm and Nd.

The  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  system is used to study the timing, extent and possible heterogeneity of early planetary differentiation (e.g. Goldstein and Galer, 1992; Harper and Jacobsen, 1992). This system is practically free of limitations related to the errors in  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios (the  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios are only involved in correction for in situ decay of  $^{146}\text{Sm}$ , which is small for 4.0–4.1 Ga zircons, and is negligible for zircons younger than 3.8–3.9 Ga). The presence of a young secondary component with presumably average terrestrial  $^{142}\text{Nd}/^{144}\text{Nd}$  can be a problem, because this secondary isotopically normal Nd dilutes isotopically anomalous primary Nd and thus obscures the signal.

For the zircons analyzed in this study, the main limitation on getting useful information from the  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  system is the analytical precision of  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios. It is therefore essential to study only the best-preserved zircon grains, using improved procedures optimized for sensitivity.

#### 4.3. Zircon as a time capsule for the $^{147}\text{Sm}$ – $^{143}\text{Nd}$ system

Straightforward use of  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  system in zircon as a time capsule (i.e. calculation of  $\epsilon^{143}\text{Nd}$ ) is unlikely to be successful for the same reasons that hinder its use as a chronometer: large errors in  $^{147}\text{Sm}/^{144}\text{Nd}$  ratios, which propagate to the uncertainty of  $\epsilon^{143}\text{Nd}$ , in the best preserved, alteration-free zircons, and the presence of secondary Nd of unknown

age and isotopic composition in more altered zircons. In the studies using REE distribution in zircon as a petrogenetic indicator, the  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  system can be promising as a gauge for the secondary REE component. Although with Sm/Nd system alone it is impossible to determine independently the age of the secondary component and the fraction of this component in Nd budget of zircon, this may be done by comparative study of U–Pb and Pb–Nd discordance patterns in initially homogeneous zircon populations of meta-igneous rocks.

Although the details of primary vs. secondary Sm–Nd systematics of zircon are not yet completely understood, the results of this study provide clear evidence that relative LREE enrichment (as shown by Sm/Nd lower than 1.6–2.0) observed in many zircons is likely to be secondary. They corroborate the need for caution in interpretation of LREE systematics of ancient zircons expressed by Whitehouse and Kamber (2002).

#### 4.4. Analytical advancements required for obtaining high-precision Sm–Nd data from single grains of zircon

The results of this study suggest that the Sm–Nd system in zircon may become a widely applicable tool in geochemistry, if the analytical parameters, most importantly sensitivity, are substantially improved. These goals are within reach of modern isotope geochemistry using current instrumentation.

*Procedure blanks.* The separation procedure used in this study has been designed for analysis of nanogram amounts of Nd and Sm from rocks and minerals with low REE concentration (peridotites and chondrites). The columns used for group REE separation, and for Nd and Sm separation, contain ca. 0.7 ml of resin each. The mass of zircons analyzed here would allow reducing the sizes of the columns to 0.05 ml or less. Without any other changes in the procedure, the separation blank will be reduced proportionally to the sizes of the columns. Furthermore, the simple chemical composition of zircon may permit a simpler procedure for group REE separation, for example a modification of the batch separation in dilute HCl+HF on an anionite resin developed for Hf isotope geochemistry (e.g. Patchett and Tatsumoto, 1980; Corfu and Noble, 1992). Combined with using the purest

available reagents, these measures should reduce the procedure blank for Nd and Sm to ca. 0.1 pg.

*Ionization efficiency.* The highest ion yield obtained in this study for a 0.3 ng load of Nd standard is 18%, or about 40–60% of the mass spectrometer transmission (Birck, 2001). However, most of the sample and standard loads gave ion yields about 3–10 times lower. These results show that ionization of Nd from silica gel can be extremely efficient, but it can be strongly suppressed by unknown factors. A systematic study is required to understand the role of the analytical conditions that influence ionization efficiency: impurities in the separated Nd and Sm; structure of silica gel; proportion of silica gel, sample and phosphoric acid, area and thickness of the load; the rate of heating during sample loading and conditioning before analysis; and pressure and composition of residual gas in the ion source. Such a study can be a part of a larger project aimed at understanding of properties of silica gel as ion emitter.

*Electrometer noise.* Even with optimized ionization efficiency, the intensity of an ion beam produced by a sub-picomole amount of Nd would be relatively small. Precision for low intensity ion beams can be improved by using charge collection (a technique based on using a capacitor in the feedback loop of an electrometer; Esat, 1995). This technique reduces the electrometer noise by a factor of up to 500, and, if used in a multicollector mass spectrometer, preserves the advantage of simultaneous collection (insensitivity of results to the ion beam fluctuations). This technique has been successfully used for high-precision analyses of picogram amounts of Th (Stirling et al., 1995) and Os (Bennett et al., 1996).

## 5. Conclusions

Zircon is an imperfect Sm–Nd chronometer and time capsule. Initial  $\varepsilon^{143}\text{Nd}$  of the source rocks of ancient zircons, or the timing of the zircon crystallization may be difficult, and in some cases impossible, to determine using the  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  system. Application of the  $^{147}\text{Sm}$ – $^{143}\text{Nd}$  system to detect the secondary REE component in zircon, and of the  $^{146}\text{Sm}$ – $^{142}\text{Nd}$  system to study the timing of early planetary differentiation are more promising, but will require advance-

ment of the analytical procedures to achieve Sm and Nd blanks of 0.1–0.2 pg or lower, and ion yields of 20–30% in isotopic analyses. These goals are within reach of modern isotope geochemistry.

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