

Comprehensive analysis for major, minor and trace element contents and Sr–Nd–Pb–Hf isotope ratios in sediment reference materials, JSd-1 and MAG-1

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In view of the requirement of a well-characterized and easily available aquatic sediment reference material, a comprehensive analysis comprising of fifty major, minor and trace elements as well as Sr–Nd–Pb–Hf isotopes were carried out in the stream sediment reference material, JSd-1, issued by the Geological Survey of Japan. The data for marine sediment reference material, MAG-1, issued by U.S. Geological Survey is also obtained for comparison. The elements were divided into two groups: Group I and Group II. Elements in Group I form stable soluble ions in HNO₃; and those in Group II form soluble oxo- and fluoro-complexes in HF, such as Zr, Nb, Hf, Ta, etc. For Group I, the sample was decomposed with HF in a tetra fluoro ethylene (TFE) bomb at 245°C for 96 hrs with Mg addition. The elemental concentration was measured by quadrupole type inductively coupled plasma source mass spectrometry (ICP-QMS) and sector field type ICP-MS (ICP-SFMS) using isotope dilution-internal standardization (ID-IS) methods. The aliquot of the sample solution was passed through 3-step column chemistry for isotope ratio determination of Pb by multiple collector (MC) ICP-MS and thermal ionization mass spectrometry (TIMS), and Sr and Nd by TIMS. For Group II elements, the sample was decomposed with HF in a TFE bomb with the same time and temperature settings. Zr, Mo, Sn, Sb and Hf were determined by ID, and Nb and Ta by ID-IS using ICP-QMS. The original JSd-1 powder showed heterogeneity for Group II elements, indicating insufficient pulverization and distribution. Thus, we further pulverized the powder and measured the concentration, which showed improved homogeneity. The aliquot for the re-pulverized powder was passed through 2-step column chemistry, and the Hf isotope ratio was determined by MC-ICP-MS. Thus a new data on the trace elements as well as Sr–Nd–Pb–Hf isotope ratios is provided for JSd-1 and MAG-1 in this paper.

Keywords: sediment standard, JSd-1, MAG-1, trace elements, Sr–Nd–Pb–Hf isotope ratios

INTRODUCTION

In order to assess the global transportation of materials and elements on the earth's surface and oceans, a proper evaluation of the input from the rivers is a prerequisite. Elemental geochemistry of sediments traces the provenance, sedimentary processes and past climatic changes (e.g., Nath *et al.*, 1997, 2000; Nath, 2001). When analyzing the sediments, the geochemical reference material with similar matrix would be preferred to evaluate the analytical method. Therefore, we chose the stream sediment standard reference material, JSd-1, issued by the Geological Survey of Japan (GSJ), and carried out comprehensive major, minor and trace element analysis.

The data presented in this paper would partly fill up the need for a good reference material for studying coastal/aquatic sediments, which will have application both in the field of environmental geochemistry as well as the crustal evolution studies.

As most rivers should pass through the continental crust, they usually contain zircon, which is resistant to usual acid decomposition. For complete decomposition of zircon, we digested samples in a tetra fluoro ethylene (TFE) bomb at 245°C for 96 hrs. However, we found the reproducibility in some elements for JSd-1 to be >10% and large error during the first analyses. Therefore, we re-pulverized JSd-1 and re-measured the powder as we suspected the sample heterogeneity of the original powder. Re-analyses have improved the reproducibility to <10%.

The purpose of this paper is to present a new data set for major, minor and trace element (50 elements) by ICP-MS after bomb digestion as well as the Sr–Nd–Pb–Hf isotope ratios for JSd-1 and MAG-1, for which no data or only uncertain data are available.

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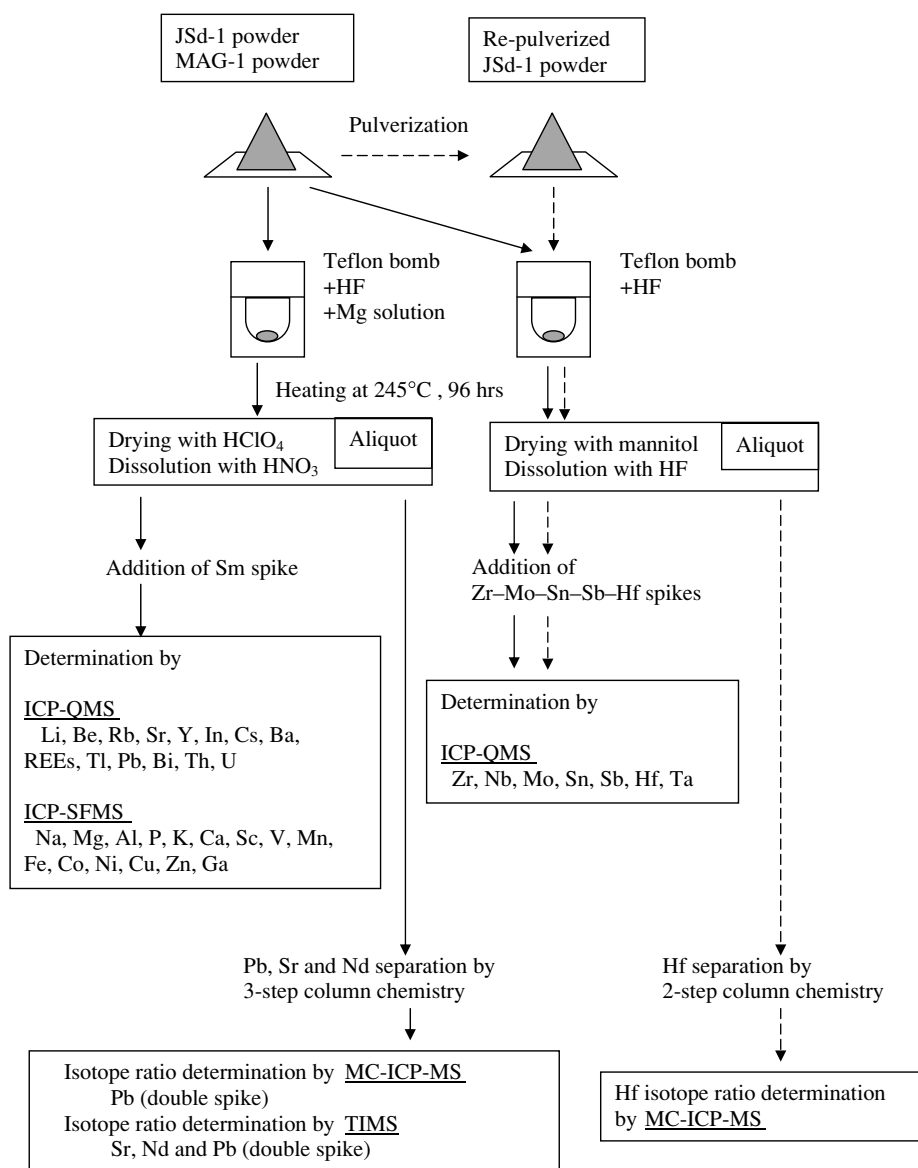


Fig. 1. Schematic diagram for elemental analysis procedure by acid digestion. The dotted line shows the flow of the re-pulverized powder.

EXPERIMENTAL

Classification of elements into two groups

In solution analysis such as inductively coupled plasma source mass spectrometry (ICP-MS), the elements must be perfectly dissolved in solution during the acid decomposition. For this purpose, we divided elements into two groups: Group I and Group II. Elements in Group I (Li, Be, Na, Mg, Al, P, K, Ca, Sc, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, In, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Tl, Pb, Bi, Th and U) form stable soluble ions in HNO_3 ; and those in Group II (Zr,

Nb, Mo, Sn, Sb, Hf and Ta) form soluble oxo- and fluoro-complexes in HF.

Reagents and silicate reference materials

Water, HF, HCl and HNO_3 were purified as described elsewhere (Nakamura *et al.*, 2003). EL-grade HCl and HNO_3 from Kanto Chemical Co. Inc. (Japan) and HClO_4 (TAMAPURE-AA-100) from Tama Chemicals Co. Ltd. (Japan) were directly used in sample digestion and column chemistry. The purified HCl by sub-boiling (denoted as 1D HCl) was used in the final elution of Pb. The Mg solution was purified by passing through AG 1X8 to re-

Table 1. Major element composition of JSd-1 by XRF

(a) Loss of ignition (%)

	#1	#2	#3	Average	RSD %
	2.45	2.45	2.48	2.46	0.6

(b) Major element composition

	#1	#2	#3	#4	#5	Average	RSD %	Reference**
SiO ₂ (%)	67.14	67.39	67.23	67.56	67.33	67.33	0.2	66.55
TiO ₂ (%)	0.64	0.64	0.64	0.65	0.65	0.64	0.1	0.64
Al ₂ O ₃ (%)	14.55	14.54	14.54	14.59	14.55	14.55	0.1	14.65
Fe ₂ O ₃ ^T (%)	4.95	4.96	4.96	4.98	4.96	4.96	0.2	5.06
MnO (%)	0.09	0.09	0.09	0.09	0.09	0.09	0.0	0.09
MgO (%)	1.75	1.76	1.75	1.76	1.76	1.76	0.4	1.81
CaO (%)	3.04	3.05	3.04	3.05	3.04	3.04	0.2	3.03
Na ₂ O (%)	2.73	2.72	2.73	2.71	2.75	2.73	0.5	2.73
K ₂ O (%)	2.17	2.18	2.17	2.18	2.18	2.18	0.3	2.18
P ₂ O ₅ (%)	0.12	0.12	0.12	0.12	0.12	0.12	0.7	0.12
LOI* (%)	2.46	2.46	2.46	2.46	2.46			
Total (%)	99.64	99.92	99.73	100.15	99.88	99.86	0.2	
NiO (μg g ⁻¹)	10.5	9.0	9.7	8.5	9.1	9.4	8.3	9.0

*The average of (a) is used.

**Imai *et al.* (1996).

move Pb. The ¹⁴⁹Sm and the ⁹¹Zr–⁹⁷Mo–¹²¹Sb–¹¹⁹Sn–¹⁷⁹Hf spikes were prepared after Makishima and Nakamura (2006) and Lu *et al.* (2007a), respectively. An in-house Nd standard solution for thermal ionization mass spectrometry (TIMS), PML-Nd was prepared from 10000 μg ml⁻¹ Nd plasma standard solution (Spex Inc., USA).

JSd-1 from GSJ and MAG-1 from USGS were used. JSd-1 was further pulverized to enhance homogeneity by the alumina swing mill (Makishima and Nakamura, 1997) to be <400 mesh for determination of major elements by X-ray fluorescence analysis (XRF), Group II elements and the Hf isotope ratio, and the original powder of JSd-1 was used in quantifying Group I elements and for Sr–Nd–Pb isotope analysis. MAG-1 was used directly, but number of repetitions was limited because of paucity of the powder in our laboratory. JB-3 from GSJ was used in tests of reproducibility in isotope analysis.

Determination of major elements by XRF

Major elements and Ni were determined by XRF, PW2400 (Philips Analytical, The Netherlands). Loss on ignition (LOI) was determined by igniting the sample at 1000°C. The sample of 0.5 g was fused using lithium metaborate flux at 1050°C. The determination of major elements and Ni were carried out based on a calibration curve method using 14 silicate standard materials from

GSJ (JA-2, JA-3, JB-1b, JB-2, JB-3, JG-1a, JG-2, JGb-1, JGb-2, JH-1, JP-1, JR-1, JR-2, and JR-3). Reference values of Imai *et al.* (1995, 1999) and Terashima *et al.* (1998) were used.

Sample decomposition and determination of Group I elements

The comprehensive elemental and isotope analytical scheme is shown in Fig. 1. All experiments were carried out in a clean room (Nakamura *et al.*, 2003). JSd-1 (29–35 mg) and MAG-1 (46 mg) were weighed, mixed together with the Mg solution after Takei *et al.* (2001) to prevent stable AlF₃ from forming, heated in a TFE bomb with HF at 245°C for 96 hrs. Then the decomposed sample was stepwise dried with HClO₄ twice after Yokoyama *et al.* (1999) to decompose fluorides. The sample was finally dissolved with 0.5 mol L⁻¹ HNO₃. The sample solution aliquot was taken, mixed with the Sm spike, diluted and measured.

Twenty-seven trace elements in Group I were analyzed by quadrupole type inductively coupled plasma mass spectrometer (ICP-QMS), Agilent 7500cs (Yokogawa Analytical Systems, Inc., Japan) in PML. Samarium concentration was determined by isotope dilution (ID), while other Group I elements were determined by using the ¹⁴⁹Sm intensity as an internal standard (an ID-IS method).

Table 2. Concentration of Group I elements in Jsdl-1 and MAG-1 by ICP-MS

Li ($\mu\text{g g}^{-1}$)	Method ¹⁾		Jsdl-1								Average	RSD %	Reference ³⁾	MAG-1	Reference ⁴⁾	Blank (ng)
	ICP-MS ²⁾		#1	#2	#3	#4	#5	#6	#6							
Li	ID-IS	Q	22.7	21.1	22.5	22.0	22.5	21.6	22.1	22.1	3	22.8			3	
Be	ID-IS	Q	1.19	1.19	1.22	1.17	1.24	1.23	1.21	1.21	2	1.4	2.56	3.2	0.02	
Sc	ID-IS	SF (HR)	8.9	9.5	11.3	9.7	8.4	10.6	9.7	9.7	11	10.9	16.1	17.2	<0.2	
V	ID-IS	SF (MR)	64	68	66	51	52	64	61.2	61.2	12	76	144	140	3.5	
Co	ID-IS	SF (MR)	11.5	10.0	11.2	10.5	10.5	10.4	10.7	10.7	5	11.2	3.59	20.4	0.05	
Ni	ID-IS	SF (HR)	10	7	6	8	9	10	8.29	8.29	21	7.04	48.8	53	18	
Cu	ID-IS	SF (HR)	19.9	18.0	20.8	21.9	19.1	19.2	19.8	19.8	7	22	12.5	30	12	
Zn	ID-IS	SF (HR)	106	92	99	112	101	107	103	103	7	96.5	168	130	82	
Ga	ID-IS	SF (HR)	17.8	16.3	15.0	15.8	15.4	15.7	16.0	16.0	6	17.2	24.3	20.4	5	
Rb	ID-IS	Q	63.1	63.6	62.6	60.7	64.6	62.7	62.9	62.9	2	67.4	138	149	0.3	
Sr	ID-IS	Q	326	347	349	331	342	346	340	340	3	340	138	146	0.1	
Y	ID-IS	Q	12.6	12.5	13.1	12.7	12.8	12.7	12.7	12.7	2	14.8	22.82	28	0.06	
In	ID-IS	Q	0.0422	0.0437	0.0438	0.0430	0.0433	0.0437	0.0433	0.0433	1		0.07		0.06	
Cs	ID-IS	Q	1.95	1.94	1.97	1.89	1.97	1.98	1.95	1.95	2	1.89	8.23	8.6	0.004	
Ba	ID-IS	Q	492	508	500	490	511	505	501	501	2	520	405	479	3	
La	ID-IS	Q	16.2	16.1	16.9	15.1	15.7	15.5	15.9	15.9	4	18.1, 16.4 ⁵⁾	38.0	43	0.2	
Ce	ID-IS	Q	31.9	32.2	34.0	31.0	32.0	31.4	32.1	32.1	3	34.4, 32.7 ⁵⁾	79.7	88	0.3	
Pr	ID-IS	Q	4.05	3.98	4.17	3.88	4.03	3.99	4.02	4.02	2	4.05, 4.16 ⁵⁾	9.50	9.3	0.04	
Nd	ID-IS	Q	16.7	16.5	17.6	16.3	16.7	16.7	16.8	16.8	3	17.6, 17.3 ⁵⁾	37.0	38	0.1	
Sm	ID	Q	3.45	3.33	3.42	3.30	3.44	3.40	3.39	3.39	2	3.48, 3.52 ⁵⁾	6.95	7.5	0.3	
Eu	ID-IS	Q	0.964	0.957	0.992	0.942	0.947	0.945	0.955	0.955	2	0.925, 0.93 ⁵⁾	1.40	1.55	0.02	
Gd	ID-IS	Q	3.38	3.28	3.52	3.26	3.40	3.39	3.37	3.37	3	2.71, 3.18 ⁵⁾	6.57	5.8	0.03	
Tb	ID-IS	Q	0.478	0.453	0.470	0.445	0.461	0.471	0.463	0.463	3	0.431, 0.446 ⁵⁾	0.913	0.96	0.005	
Dy	ID-IS	Q	2.71	2.61	2.65	2.58	2.60	2.68	2.64	2.64	2	2.23, 2.66 ⁵⁾	5.18	5.2	0.05	
Ho	ID-IS	Q	0.511	0.486	0.511	0.493	0.496	0.518	0.503	0.503	2	0.318, 0.504 ⁵⁾	0.979	1.02	0.1	
Er	ID-IS	Q	1.41	1.37	1.37	1.36	1.38	1.39	1.38	1.38	1	0.906, 1.44 ⁵⁾	2.70	3	0.02	
Tm	ID-IS	Q	0.197	0.192	0.196	0.193	0.188	0.200	0.194	0.194	2	0.13, 0.201 ⁵⁾	0.387	0.43	0.004	
Yb	ID-IS	Q	1.31	1.26	1.29	1.28	1.28	1.28	1.28	1.28	1	1.18, 1.33 ⁵⁾	2.51	2.6	0.01	
Lu	ID-IS	Q	0.196	0.189	0.195	0.192	0.190	0.196	0.193	0.193	2	0.186, 0.191 ⁵⁾	0.375	0.40	0.003	
Tl	ID-IS	Q	0.321	0.339	0.338	0.324	0.336	0.339	0.333	0.333	2	0.407	0.657	0.13		
Pb	ID-IS	Q	12.6	12.2	12.7	12.3	12.8	12.6	12.5	12.5	2	12.9	15.0	24	0.7	
Bi	ID-IS	Q	0.101	0.096	0.098	0.097	0.098	0.097	0.098	0.098	2		0.337	0.34	0.02	
Th	ID-IS	Q	4.40	4.42	4.55	4.21	4.36	4.36	4.38	4.38	3	4.44	12.0	11.9	0.006	
U	ID-IS	Q	0.967	0.977	0.999	1.011	0.975	1.004	0.989	0.989	2	1	2.80	2.7	0.02	
Na ₂ O (%)	ID-IS	SF (MR)	2.73	2.80	2.82	2.73	2.83	2.85	2.79	2.79	2	2.727	3.94	3.83	<2	
Al ₂ O ₃	ID-IS	SF (MR)	14.9	15.3	15.4	14.9	15.1	14.9	15.1	15.1	2	14.65	16.3	16.37	<2	
P ₂ O ₅	ID-IS	SF (MR)	0.106	0.112	0.117	0.104	0.108	0.114	0.110	0.110	4	0.122	0.610	0.163	<1	
K ₂ O	ID-IS	SF (HR)	2.43	2.37	2.32	2.41	2.41	2.77	2.45	2.45	7	2.183	4.33	3.55	<2	
CaO	ID-IS	SF (MR)	3.03	3.34	3.20	3.11	2.75	2.73	3.03	3.03	8	3.034	1.41	1.37	<2	
MnO	ID-IS	SF (MR)	0.103	0.096	0.096	0.092	0.094	0.095	0.096	0.096	4	0.0924	0.106	0.098	<0.4	
Fe ₂ O ₃ ^T	ID-IS	SF (MR)	5.06	5.14	5.12	4.87	4.98	5.02	5.03	5.03	2	5.059	6.74	6.80	<26	

¹⁾ID, isotope dilution; ID-IS, isotope dilution-internal standardization. ²⁾Q, quadrupole type ICP-MS; SF (MR), sector field type ICP-MS (ICP-SFMS) at middle resolution; SF (HR), ICP-SFMS at high resolution. ³⁾Imai et al. (1996). ⁴⁾Govindaraju (1994). ⁵⁾Yamamoto et al. (2005).

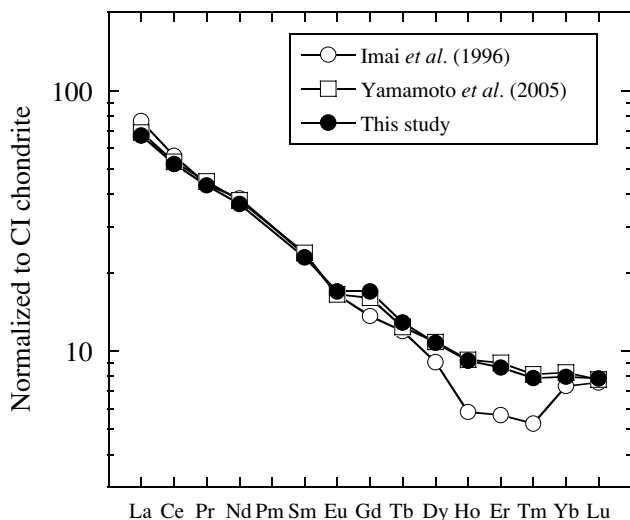


Fig. 2. Chondrite normalized REE patterns of JSd-1. CI chondrite values are from McDonough and Sun (1995).

Na, Mg, Al, P, Ca, V, Mn, Fe and Co were measured by sector field type ICP-MS (ICP-SFMS), ELEMENT (Finnigan, Germany) in PML at middle resolution ($M/\Delta M = \sim 3000$). K, Sc, Ni, Cu, Zn and Ga were measured at high resolution ($M/\Delta M = \sim 7500$). The solution prepared by dissolution of JB-3 was used as the standard solution. Details of the mass spectrometry are described in Makishima and Nakamura (2006).

Sample decomposition and determination of Group II element

The original JSd-1 (25–48 mg) and MAG-1 (35–40 mg), and the re-pulverized JSd-1 (45–61 mg) were weighed and heated in a TFE bomb with HF at 245°C for 96 hrs. The decomposed sample added with mannitol was dried at 70°C. The sample was then dissolved with 0.5 mol L⁻¹ HF, and centrifuged to remove insoluble fluorides. Then the supernatant sample solution aliquot was taken, mixed with the spikes, diluted and measured.

Zr, Mo, Sn, Sb, Hf and Ta were measured by ID using ICP-QMS, Agilent 7500cs. Nb and Ta were measured by the ID-IS method, based on Nb/Zr and Ta/Hf ratios. Details of the mass spectrometry are described in Lu *et al.* (2007a).

Separation and mass spectrometry for Pb, Sr and Nd

Pb, Sr and Nd were purified employing 3-step column separation procedure, which are described in Makishima *et al.* (2007) for Pb and Makishima *et al.* (2008) for Sr and Nd (Case 1 in Fig. 1). All resins were discarded after separation. Recovery yields for Sr, Nd and Pb were ~ 90 , ~ 75 and $\sim 99\%$, and total blanks were ~ 6 pg, ~ 20 pg and ~ 0.7 ng, respectively.

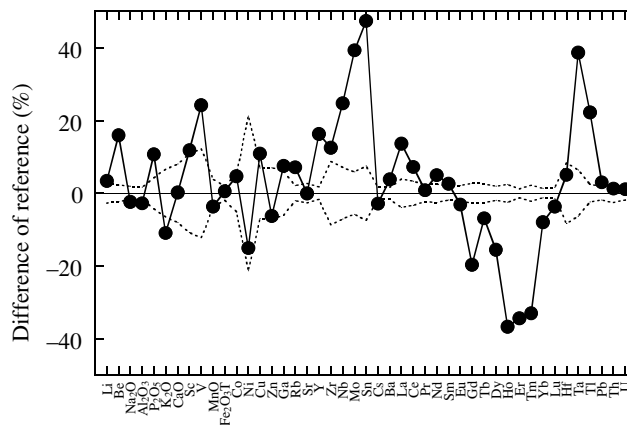


Fig. 3. Difference (%) of the reference value of Imai *et al.* (1996) from this study. The dotted lines indicate RSD % in each element determination in this study as shown in Tables 2 and 3.

The two aliquots of the solution, containing 20 and 5 ng of Pb in 0.5 mol L⁻¹ HNO₃ were prepared after the column separation, and the latter was added with ²⁰⁴Pb–²⁰⁷Pb double spike (DS), and its Pb isotope ratios were determined by the simple double spike multiple collector ICP-MS (DS-MC-ICP-MS) without TI addition. MC-ICP-MS, Neptune, (Thermo Electron Corp., Germany) in PML, was used. Details of the DS-MC-ICP-MS technique are shown in Makishima *et al.* (2007).

TIMS, a modified MAT 261 (Finnigan, Germany) nicknamed as “KIJI” in PML, was also used for the Pb isotope analysis of JSd-1. The Pb sample solution aliquots containing ~ 12 ng and ~ 3 ng were taken and dried, with addition of DS into the latter. The two Pb samples were separately loaded on the single Re filament with silicic activator and measured after Kuritani and Nakamura (2002, 2003).

TIMS, MAT 262 (Finnigan, Germany) nicknamed as “SARU” in PML, was used for the Sr isotope ratio measurement. Sr of ~ 50 ng was loaded on the single W filament with Ta activator, and the ⁸⁸Sr signal intensity was kept to be $\sim 3 \times 10^{-11}$ A. ⁸⁶Sr/⁸⁸Sr = 0.1194 was used for normalization, assuming the power law. 110 ratios were obtained in 10 blocks.

TIMS, Triton TI (Thermo Electron Corp., Germany) housed in PML, was used for the Nd isotope ratio analysis. The Nd fraction was dried with HClO₄ to decompose organic materials before loading. The Re double filament technique was employed using ~ 60 ng of Nd, and the ¹⁴⁶Nd signal intensity was kept to $\sim 4 \times 10^{-12}$ A. 112 ratios were obtained in 8 blocks with alternately changing amplifiers (virtual amplifier). ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 was used for normalization employing the exponential law. The repeated analysis of the in-house Nd standard, PML-Nd gave an average of 0.511704 ± 0.000008 (2SD, $n = 8$)

Table 3. Concentration for Group II elements in JSd-1 and MAG-1 by ICP-MS

(a) Original JSd-1 powder

	#1	#2	#3	#4	#5	Average	RSD %	Blank (ng)
Zr ($\mu\text{g g}^{-1}$)	139	111	114	168	121	131	18	0.6
Nb ($\mu\text{g g}^{-1}$)	8.54	9.80	8.42	10.79	9.74	9.46	10	0.2
Mo ($\mu\text{g g}^{-1}$)	0.355	0.495	0.471	1.040	0.660	0.604	44	1
Sn ($\mu\text{g g}^{-1}$)	1.73	2.11	1.76	2.10	2.15	1.97	10	0.9
Sb ($\mu\text{g g}^{-1}$)	0.232	0.268	0.249	0.296	0.273	0.264	9	0.2
Hf ($\mu\text{g g}^{-1}$)	3.42	2.75	2.68	4.10	3.03	3.20	18	0.06
Ta ($\mu\text{g g}^{-1}$)	0.539	0.588	0.521	0.672	0.622	0.588	10	0.02

(b) Re-pulverized JSd-1 powder

	#1	#2	#3	#4	#5	#6	Average	RSD %	Reference*
Zr ($\mu\text{g g}^{-1}$)	129	118	105	123	105	124	117	9	132
Nb ($\mu\text{g g}^{-1}$)	9.65	8.84	8.07	9.44	8.25	9.11	8.89	7	11.10
Mo ($\mu\text{g g}^{-1}$)	0.507	0.489	0.462	0.509	0.436	0.477	0.480	6	0.67
Sn ($\mu\text{g g}^{-1}$)	1.96	1.84	1.73	2.06	1.71	1.97	1.88	7	2.77
Sb ($\mu\text{g g}^{-1}$)	0.289	0.289	0.276	0.296	0.265	0.283	0.283	4	—
Hf ($\mu\text{g g}^{-1}$)	3.56	3.44	3.07	3.55	3.00	3.66	3.38	8	3.55
Ta ($\mu\text{g g}^{-1}$)	0.678	0.650	0.596	0.675	0.589	0.675	0.644	6	0.89

(c) Original MAG-1 powder

	#1	#2	Average	Reference**
Zr ($\mu\text{g g}^{-1}$)	126	109	117	126
Nb ($\mu\text{g g}^{-1}$)	14.0	12.2	13.1	12.0
Mo ($\mu\text{g g}^{-1}$)	1.08	0.882	0.979	1.6
Sn ($\mu\text{g g}^{-1}$)	3.77	3.17	3.47	3.6
Sb ($\mu\text{g g}^{-1}$)	0.919	0.798	0.859	1.0
Hf ($\mu\text{g g}^{-1}$)	3.48	2.95	3.21	3.7
Ta ($\mu\text{g g}^{-1}$)	0.917	0.801	0.859	1.1

*Imai *et al.* (1996).

**Govindaraju (1994).

with La Jolla Nd of 0.511840 ± 0.000010 (2SD, $n = 8$) during the course of this study. Details of Sr and Nd analysis by TIMS are described in Makishima *et al.* (2008).

Separation and mass spectrometry for Hf

A two-step column chemistry for Hf was employed. In the first column, Hf, Zr and Ti were collected using an anion-exchange resin, AG1X8. Then Hf was purified in the second column using UTEVA resin. The recovery yield of Hf was ~88% and total blank was ~4 pg.

MC-ICP-MS, Neptune, (Thermo Electron Corp., Germany) in PML, was used for the Hf isotope analysis. $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ was used for normalization, assuming the

exponential law. The correction factor for normalizing our results to the commonly accepted value of JMC 475 of 0.282160 was multiplied to all $^{176}\text{Hf}/^{177}\text{Hf}$ ratios presented in this study. Details of the Hf separation and the mass spectrometry are shown in Lu *et al.* (2007b).

RESULTS AND DISCUSSION

Analytical results for major elements in JSd-1 by XRF

XRF analytical results for major elements in JSd-1 are shown in Table 1. The reproducibility is <0.7%, and the results are consistent with the reference values of Imai *et al.* (1996).

Table 4. Pb isotope ratios of JSd-1 and MAG-1

	$^{206}\text{Pb}/^{204}\text{Pb}$		$^{207}\text{Pb}/^{204}\text{Pb}$		$^{208}\text{Pb}/^{204}\text{Pb}$	
JSd-1						
DS-MC-ICP-MS		SE		SE		SE
#1	18.4858	0.0004	15.6177	0.0005	38.5980	0.0013
#2	18.4826	0.0004	15.6168	0.0005	38.5941	0.0013
#3	18.4829	0.0005	15.6160	0.0005	38.6168	0.0014
#4	18.4766	0.0005	15.6161	0.0005	38.5914	0.0014
#5	18.4799	0.0005	15.6176	0.0004	38.5894	0.0014
		RSD (%)		RSD (%)		RSD (%)
average	18.4816	0.019	15.6168	0.005	38.5979	0.029
DS-TIMS						
#1	18.4840		15.6164		38.5979	
#2	18.4777		15.6123		38.5910	
#3	18.4809		15.6153		38.6186	
#4	18.4741		15.6139		38.5896	
#5	18.4808		15.6181		38.5986	
		RSD (%)		RSD (%)		RSD (%)
average	18.4795	0.020	15.6152	0.014	38.5991	0.030
MAG-1						
DS-MC-ICP-MS	18.8648	SE	15.6539	SE	38.7920	SE
		0.0007		0.0008		0.0022
Standards (DS-MC-ICP-MS; Makishima <i>et al.</i> , 2007)						
		RSD (%)		RSD (%)		RSD (%)
NIST 981 (<i>n</i> = 35)	16.9417	0.007	15.4988	0.008	36.7196	0.009
JB-3 (<i>n</i> = 6)	18.2964	0.004	15.5380	0.006	38.2494	0.007

Analytical results for Group I elements in JSd-1 and MAG-1 by ICP-MS

The analytical results for Group I elements of JSd-1 and MAG-1 by ICP-MS are shown in Table 2. The reproducibility for most of the elements was between 2 and 4% (with an average of 2%) except for Co, Cu, Zn, Ga, K₂O, CaO (5–8%), Sc and V (11 and 12%) and Ni (21%). The larger reproducibility for transition metals is caused by relatively larger error in ICP-SFMS at middle/high resolution and their low concentration in JSd-1. Although the sample powder is not re-pulverized for the Group I element analysis, the heterogeneous distribution of accessory minerals such as zircon, which is observed in the next section, does not affect reproducibility of the HREE analysis. For example, RSD % of heavy rare earth elements (HREE) is 1–3% (Gd–Lu), which is similar to that of light rare earth elements (LREE) (3–4%) for La–Nd. Therefore, the homogeneity of the original powder is sufficient to be used as the standard for Group I elements. Although the MAG-1 was only analyzed once, most analytical results are consistent with those of Govindaraju (1994), except Co, Cu, Pb and P₂O₅, which require future investigations. The procedural total blanks in the bomb digestion are shown in Table 2. Most blanks in Table 2 are higher than the procedural blank obtained in the ultrasonic digestion used in Makishima and Nakamura

(2006), which are considered to come from the Mg solution and the bomb.

Chondrite-normalized REE pattern of JSd-1 of this study are shown in Fig. 2 and compared to that of reference values of Imai *et al.* (1996) (the values are also shown in Table 2). While the patterns at LREE portion show a good similarity with the pattern of Imai *et al.* (1996), large negative differences for HREE (Gd–Yb), especially over –30% for Ho, Er and Tm are found in the data of Imai *et al.* (1996). We have also presented the patterns based on the data published by Yamamoto *et al.* (2005) in Fig. 2. Our values are similar to Yamamoto *et al.* (2005), in which acid digestion in open beaker is combined with carbonate fusion. This indicates possible effects of insufficient digestion of zircon in the previous analysis, which contains large portion of HREE in the sample. Thus it is suggested that the recommended values of Imai *et al.* (1996) for these elements need to be revised.

Analytical results for Group II elements in JSd-1 and MAG-1 and effectiveness of re-pulverization

The concentration for Group II elements in the original and re-pulverized JSd-1 powders, and MAG-1 are shown in Table 3. The procedural total blanks in the bomb digestion are also shown in Table 3. The reproducibility for the original JSd-1 is 9–44% and unacceptably larger

Table 5. Sr isotope ratios of JSd-1 and MAG-1 by TIMS

		$^{87}\text{Sr}/^{86}\text{Sr}$	2SE
JSd-1	#1	0.705743	11
	#2	0.705725	10
	#3	0.705746	12
	#4	0.705736	10
	#5	0.705725	14
	average	0.705735	20
			2SD
			2SE
MAG-1		0.722739	14
			2SD
Standards			2SD
JB-3 ($n = 5$)	average	0.703449	11
NIST 987 ($n = 8$)	average	0.710241	28

All 2SE and 2SD correspond to the last digit of each isotope ratio.

than those of JB-3 in Lu *et al.* (2007a). However, the reproducibility for the re-pulverized JSd-1 became significantly better to 4–9%. The reproducibility of Zr, Hf and Mo improved far larger than that of Nb, Sb and Ta. Both averages are similar within analytical errors except for Mo. The improvement for Zr and Hf can be explained by better homogenization of zircon by further powdering. The reason for large error of Mo might be heterogeneous distribution of some phase enriched in Mo. For MAG-1, the analysis was repeated only twice. The difference between two measurements was relatively large, indicating sample heterogeneity partly because of no re-pulverization. However, the average of the two measurements was similar to the reference of Govindaraju (1994).

The difference of the reference value for JSd-1 (Imai *et al.*, 1996) from that obtained by ICP-MS in this study is plotted in Fig. 3. The difference for V, Nb, Mo, Sn, Ta, Tl and HREE (discussed above) are >20% and large. We propose new data sets as candidates for the recommended values.

Analytical results for Pb isotope ratios for JSd-1 and MAG-1

Pb isotope ratios of JSd-1 and MAG-1 measured by DS-MC-ICP-MS, and those of JSd-1 by DS-TIMS are shown in Table 4. As shown in the table, both methods gave similar results and reproducibility (RSD %) for JSd-1 indicating the accuracy of MC-ICP-MS. The reproducibility of JSd-1 (0.005–0.030%) in both DS-MC-ICP-MS and DS-TIMS is larger than that for NIST 981 (0.007–0.009%) by MC-ICP-MS. This could be attributed to small heterogeneity of the sample. It is also confirmed that the Pb–Sr column chemistry used in this study is applicable to Pb analysis by TIMS. The bomb digestion with the Sm spike for the Group I element analysis gave Pb blank of

Table 6. Nd isotope ratios of JSd-1 and MAG-1 by TIMS

		$^{143}\text{Nd}/^{144}\text{Nd}$	2SE
JSd-1	#1	0.512570	13
	#2	0.512577	11
	#3	0.512560	16
	#4	0.512580	13
	average	0.512571	18
	2SD		
MAG-1		0.512046	10
			2SD
Standards			2SD
JB-3 ($n = 5$)	average	0.513049	18
PML-Nd ($n = 8$)	average	0.511704*	8

All 2SE and 2SD errors correspond to the last digit of each isotope ratio.

*This value corresponds to 0.511840 of La Jolla Nd (see text).

Table 7. Hf isotope ratios of JSd-1 and MAG-1 by MC-ICP-MS

		$^{176}\text{Hf}/^{177}\text{Hf}$	2SE
JSd-1	#1	0.282787	3
	#2	0.282803	2
	#3	0.282802	3
	#4	0.282796	3
	#5	0.282791	3
	#6	0.282803	3
	average	0.282797	14
			2SD
			2SE
MAG-1		0.282542	5
			2SD
Standards			2SD
JB-3 ($n = 3$)	average	0.283230	5
JMC14374 ($n = 6$)	average	0.282185*	3

All 2SE and 2SD correspond to the last digit of each isotope ratio.

*This value is the original value without correction and used for correction.

0.7 ng. However, the blank effect is ~0.02%, similar to analytical uncertainty, thus negligible, because difference of the Pb isotope ratios between the blank and sample should be <10% and the total sample Pb is ~400 ng compared to the blank of 0.7 ng.

Aung *et al.* (2004) measured the Pb isotope ratio of JSd-1 by ICP-QMS. Although there is no ^{204}Pb data and errors are large in their study, their $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of 0.843 ± 0.001 and 2.088 ± 0.001 , and are consistent with our values of 0.8450 and 2.0888, respectively.

Analytical results of Sr and Nd isotope ratios for JSd-1 and MAG-1

Analytical results of Sr for JSd-1 and MAG-1 together with those of JB-3 and NIST 987 obtained in this study from different sample decomposition and column chemistry are shown in Table 5. The reproducibility of JSd-1 is comparable to that of the NIST 987 Sr standard, 0.000028.

Analytical results of the Nd isotope ratio for JSd-1 and MAG-1 as well as JB-3 and the in-house Nd standard, PML-Nd by TIMS are shown in Table 6. The reproducibility for JSd-1 of 0.000018 is larger than that of the Nd standard, 0.000008, however, similar to that of JB-3 (Table 6). The better reproducibility for the Nd standard is due to the higher intensity of $>1 \times 10^{-11}$ A for ^{146}Nd . As there are no reliable data for Sr and Nd isotope ratios of JSd-1, these data can be used as the reference values.

Hf isotope ratios of JSd-1 and MAG-1

Hf isotope ratios of JSd-1 and MAG-1, together with those of the Hf in-house standard, JMC 14374 and JB-3 obtained in this study are shown in Table 7. The values of JB-3 solution are consistent with 0.283223 ± 0.000007 (2SD, $n = 8$) by Lu *et al.* (2007b). The mean precision and reproducibility for JSd-1 are 0.000003 (2SE) and 0.000014 (2SD, $n = 6$), respectively. The larger reproducibility of JSd-1 compared to those of JB-3 and JMC 14374 should be caused by the heterogeneity of JSd-1 powder, although it is re-pulverized. However, the reproducibility is small enough for the JSd-1 powder to be used as the Hf standard. No Hf isotope ratios are reported so far for JSd-1, thus this value could be the reference value.

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