

**NOTE****Precise determination of 14 REEs in GSJ/AIST geochemical reference materials JCp-1 (coral) and JCT-1 (giant clam) using isotope dilution ICP-quadrupole mass spectrometry**

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The concentrations of fourteen rare earth elements (REEs) in GSJ/AIST geochemical reference materials JCp-1 (coral) and JCT-1 (giant clam) were identified by isotope dilution inductively-coupled plasma-mass spectrometry, using a quadrupole mass filter (ID-ICP-QMS). Large samples (2~4.1 g) were used to eliminate inhomogeneities in the sample powders. The sample powders were spiked with enriched isotopes and decomposed using HCl. The REEs were separated from the matrix elements by Fe(OH)<sub>3</sub>-coprecipitation and purified by cation-exchange chromatography. The REEs were further divided into light REE, middle REE, and heavy REE fractions using cation-exchange chromatography, eluted with 2-hydroxyisobutyric acid (HIBA).

The abundances for ten poly-isotopic REEs were obtained using both the isotope dilution method and the conventional peak height comparison method, using a calibration curve. The recovery rates for the ten REEs were then calculated by comparing the values obtained by these two methods. The obtained recovery rates were then interpolated for mono-isotopic REEs, and their concentrations were corrected from their relative peak heights. The obtained values were determined twice, using different spike/sample ratios, and agreed within +/-2%, with the exception of La, Ce, and Ho. The ID gave precise abundances for the fourteen different REEs rapidly and easily.

Keywords: isotope dilution, ICP-MS, JCp-1, JCT-1, REE

**INTRODUCTION**

The recent development and increase in popularity of inductively coupled plasma-mass spectrometry (ICP-MS) has enabled scientists to quickly determine the concentrations of various elements that had previously been difficult to ionize by conventional mass spectrometry. However, the facile ionization of certain elements by ICP has, in some cases, prevented the reliable determination of their concentrations using multiple isotopes. Various polyatomic interferences, corresponding to the oxides and argides of certain elements, are observed in the analyses.

The fine structure of REE abundance patterns, such as the tetrad effect, have become important parameters for studying their geochemical records (e.g., Masuda *et al.*, 1987; Kawabe *et al.*, 1991; Lee *et al.*, 2010). Precise

data are essential to accomplish reliable data analyses. Internal standard methods and chemical purification are used for better reproducibility (e.g., Hirata *et al.*, 1988). Unfortunately, chemical purification methods, such as coprecipitation with Fe(OH)<sub>3</sub>, are efficient but often lead to low recovery rates of target elements. Although isotope dilution using thermal ionization mass spectrometry (TIMS) is the best technique for discriminating and stabilizing the ion beams among REEs (e.g., Masuda *et al.*, 1973), the technique requires robust laboratory methods. Therefore, we have chosen to explore ICP-MS for the determination of REEs using isotope dilution (ID). In this study, fourteen REEs in GSJ/AIST geochemical reference materials JCp-1 (coral) and JCT-1 (giant clam) are determined using ID-ICP-MS with a quadrupole mass filter.

**EXPERIMENTAL***Samples and chemical procedure*

The REE concentrations of two GSJ/AIST

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Table 1. Natural isotope ratios obtained by ICP-QMS used for this study

Element	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu
Spike isotope (Sp)	<sup>138</sup> La	<sup>142</sup> Ce	<sup>145</sup> Nd	<sup>149</sup> Sm	<sup>151</sup> Eu	<sup>157</sup> Gd	<sup>163</sup> Dy	<sup>167</sup> Er	<sup>171</sup> Yb	<sup>176</sup> Lu
Reference isotope (Re)	<sup>139</sup> La	<sup>140</sup> Ce	<sup>146</sup> Nd	<sup>147</sup> Sm	<sup>153</sup> Eu	<sup>155</sup> Gd	<sup>161</sup> Dy	<sup>166</sup> Er	<sup>172</sup> Yb	<sup>175</sup> Lu
Possible interferences	<sup>138</sup> Ba, <sup>138</sup> Ce	<sup>142</sup> Nd								<sup>176</sup> Yb, <sup>176</sup> Hf
Sp/Re ratio measured*	0.000853	0.1248	0.4793	0.9243	0.9111	1.056	1.307	0.6874	0.6539	0.02815
STD deviation (1σ)	0.000016	0.0020	0.0023	0.0024	0.0026	0.0020	0.0020	0.0014	0.0025	0.00102
Literature (AUPAC)**	0.000901	0.1256	0.4828	0.9219	0.9161	1.057	1.318	0.6826	0.6541	0.02659
This study/Literature	0.947	0.993	0.993	1.003	0.995	0.999	0.992	1.007	1.000	1.059

\*Average of six time measurements 20140708.

\*\*De Laeter *et al.* (2003).

Table 2. Analytical results (ppb) of REE for JCp-1 and JCt-1.

Sample	JCp-1-1	JCp-1-2	Average JCp-1 (% deviation from Av.)	JCt-1-1	JCt-1-2	Average JCt-1 (% deviation from Av.)	JCp-1/JCt-1	Total blank (ng)
La	25.6	23.9	24.8 (3.4)	5.46	5.57	5.52 (1.0)	4.49	0.9
Ce	39.1	36.8	38.0 (3.0)	16.35	16.68	16.52 (1.0)	2.30	1.9
Pr	7.62	7.35	7.49 (1.9)	1.78	1.81	1.80 (1.0)	4.16	—
Nd	31.6	31.2	31.4 (0.6)	6.79	6.83	6.81 (0.3)	4.61	0.4
Sm	6.10	6.03	6.07 (0.6)	1.323	1.339	1.331 (0.3)	4.56	0.05
Eu	1.428	1.381	1.405 (1.7)	0.306	0.311	0.309 (0.8)	4.55	0.01
Gd	7.91	7.92	7.92 (0.1)	1.550	1.531	1.541 (0.6)	5.14	0.07
Tb	1.22	1.23	1.22 (0.4)	0.264	0.270	0.267 (1.1)	4.57	—
Dy	8.82	8.95	8.89 (0.7)	1.933	2.00	1.967 (1.7)	4.52	0.04
Ho	2.20	2.16	2.18 (0.9)	0.475	0.490	0.483 (3.1)	4.51	—
Er	7.07	6.99	7.03 (0.6)	1.643	1.661	1.652 (0.5)	4.26	0.02
Tm	1.08	1.09	1.09 (0.9)	0.289	0.285	0.287 (0.7)	3.80	—
Yb	7.47	7.58	7.53 (0.7)	2.20	2.22	2.21 (0.5)	3.41	0.03
Lu	1.250	1.239	1.245 (0.4)	0.400	0.403	0.402 (0.4)	3.10	0.009
Sample (mg) used for analysis	2035	2203		3834	4143			

geochemical reference materials, JCp-1 and JCt-1, prepared from coral *Porites* sp. (JCp-1) and giant clam *Tridacna gigas* (JCt-1) collected from Okinawa Prefecture (Okai *et al.*, 2004), were analyzed. Okai *et al.* (2004) analyzed nine elements, collaboratively. The reported values for heavy metals agreed well with one another.

ICP-MS is sensitive enough to measure REEs using a few milligrams of geological samples. However, there is rarely a high degree of homogeneity observed in such a small sample size. Sample heterogeneities for Ni, Cr, Dy, and Ho were reported in milligram sized samples of BCR-1 (Filby *et al.*, 1985). Kamioka and Tanaka (1989) analyzed nine aliquots of JB-1 and JG-1 (60~100 mg, each) by INAA with simultaneous neutron irradiation to test the homogeneity of the sample powder. The analytical results of JG-1 revealed the heterogeneity of samples for some elements, including Cr, La, Ce, Nd, Sm, Hf, Th, and U. No significant sample heterogeneity was detected for JB-1 at this sample size. To prevent a heterogeneity bias, we used suitably large quantities of sample powder (2.0~4.1 g) in this study.

Carbonate rocks may contain organic matter and a small amount of silicate. Kawabe *et al.* (1991) analyzed the REEs present in two limestone samples and one geologically-aged calcareous gneiss. They were decomposed by two different methods: 1) simple dissolution by HCl, alone, and; 2) complex decomposition methods, including HF+HNO<sub>3</sub>+HClO<sub>4</sub> digestion and a further fusion process with Na<sub>2</sub>CO<sub>3</sub> and H<sub>3</sub>BO<sub>3</sub> in a Pt-crucible. No significant differences in REE and yttrium results were found between the two decomposition methods, even in the case of the calcareous gneiss (Kawabe *et al.*, 1991).

In the current study, samples were spiked with enriched isotopes of <sup>138</sup>La, <sup>142</sup>Ce, <sup>145</sup>Nd, <sup>149</sup>Sm, <sup>151</sup>Eu, <sup>157</sup>Gd, <sup>163</sup>Dy, <sup>167</sup>Er, <sup>171</sup>Yb, and <sup>176</sup>Lu and then decomposed gently overnight on a hot plate using 2 and 6 M HCl. The Fe co-precipitation of the REEs was performed at a pH of 6.5, by adding 5 mg Fe<sup>3+</sup> and an ammonia solution. The precipitates were re-dissolved in 2 M HCl, and the REEs were separated by cation-exchange chromatography (AG50W-X8 200–400 mesh; 0.5 cm × 17 cm column) to separate out the Fe and other matrix elements. The ob-

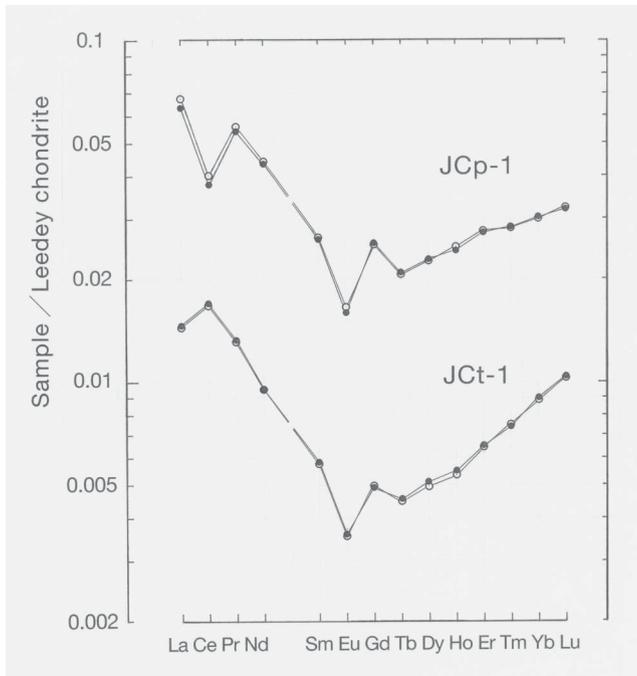


Fig. 1. Leedeey chondrite-normalized REE abundance patterns for GSJ/AIST geochemical reference materials JCp-1 (coral) and JCt-1 (giant clam).

tained REE fraction was separated further to HREEs (Ho, Er, Tm, Yb, Lu), MREEs (Sm, Eu, Gd, Tb, Dy), and LREEs (La, Ce, Pr, Nd). This was done using a cation exchange column (AG50W-X8 200–400 mesh; 0.3 cm × 9.8 cm), eluted with 0.09 M, 0.2 M, and 0.3 M 2-hydroxyisobutyric acid (HIBA), with the pH adjusted to 4.60. The separation among the three fractions was clear and very little tailing was observed in the neighboring fractions. The fractions were then evaporated until dry and re-dissolved using 1% HNO<sub>3</sub>.

#### Mass spectrometry

The determination of REEs with ID-ICP-MS was previously demonstrated in Denmark by Baker *et al.* (2002) and Kent *et al.* (2004), using magnetic sector instruments equipped with multiple collectors (MC). They measured ten polyisotopic REEs and praseodymium using this method. While the data obtained by the MC-ICP-MS technique were of high quality, few laboratories have access to MC-ICP-MS systems that are able to detect enriched isotopes.

In this study, mass spectrometry was performed on an Elan 6100 (Perkin Elmer) in the Korea Polar Research Institute. The degrees of oxide and hydroxide interferences on REEs were examined by Kim *et al.* (2014) and corrected. The natural isotope ratios used for the current isotope dilution were measured from solutions with the

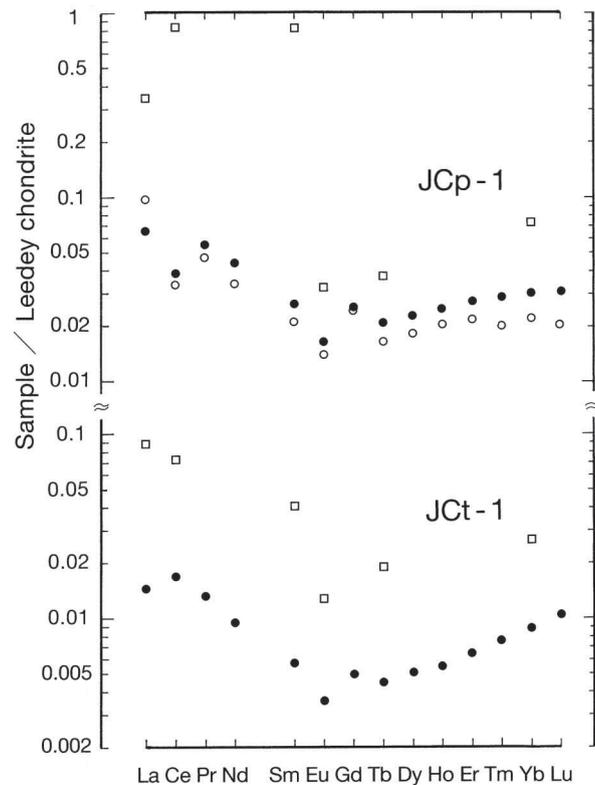


Fig. 2. Leedeey chondrite-normalized REE abundance patterns for JCp-1 and JCt-1, obtained in this study (solid circle), compared with data obtained by Aizawa (2008) (open square) and Jupiter (2008) (open circle).

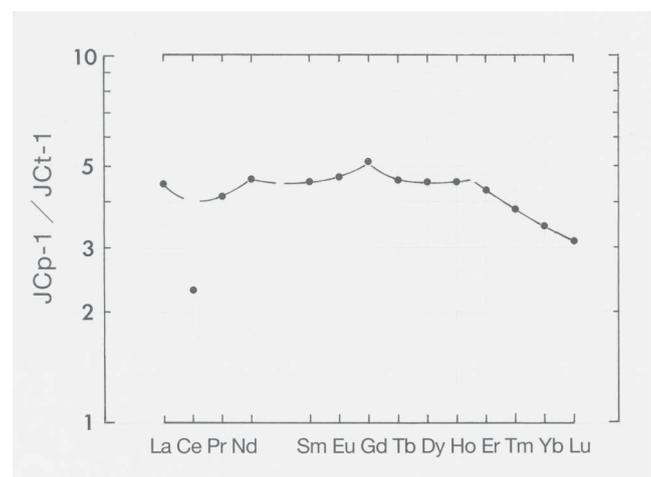


Fig. 3. Relative REE abundance patterns of GSJ/AIST geochemical reference materials JCp-1 (coral) and JCt-1 (giant clam).

same REE composite combination, namely, LREEs, MREEs, and HREEs, as mentioned above. The results are shown in Table 1, along with the IUPAC values (De Laeter *et al.*, 2003). The obtained isotope ratios agreed well with the IUPAC values, with the exception of La and Lu. The natural ratios of  $^{138}\text{La}/^{139}\text{La}$  and  $^{176}\text{Lu}/^{175}\text{Lu}$  are 0.000901 and 0.02659, respectively. The large differences in isotopic abundances may make it difficult to measure such isotope ratios accurately with a quadrupole mass filter. However, the ICP-QMS gave accurate isotope ratios within  $\pm 1\%$  of the IUPAC values for isotope ratios with similar peak heights, as shown in Table 1. The spiked, enriched isotopes for La and Lu are  $^{138}\text{La}$  and  $^{176}\text{Lu}$ , respectively, and the isotope ratios of  $^{138}\text{La}/^{139}\text{La}$  and  $^{176}\text{Lu}/^{175}\text{Lu}$  are 0.0756 and 2.43, respectively. The spiking of these enriched isotopes facilitates the measurement of accurate isotope ratios.

Quantification was accomplished by both isotope dilution and conventional peak-height comparison, using non-spiked isotopes, measured simultaneously. The two sets of data were compared, and the recovery rates were calculated for ten poly-isotopic REEs to correct the concentrations of the mono-isotopic REEs. The recovery rates were 1.2 and 0.9 for the LREEs and HREEs, respectively, and varied gradually by atomic number. The HIBA was found to be a weak sensitizer for REEs in ICP-MS, and rates larger than unity were found to be caused by REE sensitization using HIBA. These recovery rates are not only simply the recovery rates produced by chemical treatments, but they are values representing a combination of the recovery rates (by chemical treatments) and the REE sensitization effect by HIBA. The recovery rates for the mono-isotopic REEs, i.e., Pr, Tb, Ho, and Tm, were then estimated from the recovery rates of the neighboring two poly-isotopic REEs.

## RESULTS AND DISCUSSIONS

The results obtained with different ratios of sample and spike solutions are listed in Table 2 ( $N = 2$ ). The blank contributions for JcT-1 and JcP-1 were less than 5% and 1%, respectively, and were subtracted. The obtained values and average of the duplicate analyses are shown in Table 2. The Leedey chondrite (Masuda, 1975; Masuda *et al.*, 1973) normalized REE patterns are shown in Fig. 1. The values obtained from different spike/sample ratios agreed within  $\pm 2\%$ , with the exception of La and Ce, for JcP-1, and Ho for JcT-1. The recovery rate of Ho was estimated from the recovery rates of neighboring elements Dy and Er. Though Ho and Er were recovered as HREEs, Dy was recovered as an MREE, as mentioned earlier. The difficulty of the ion-exchange at the boundary reduced the accurate estimation of the recovery rate. Interference corrections for  $^{138}\text{La}$  and  $^{142}\text{Ce}$  from  $^{138}\text{Ba}$ ,  $^{138}\text{Ce}$ , and

$^{142}\text{Nd}$  were necessary, as indicated in Table 1. The JcP-1 contained more REEs than JcT-1, and the spiked isotopes,  $^{138}\text{La}$  and  $^{142}\text{Ce}$ , were relatively less abundant than  $^{139}\text{La}$  and  $^{140}\text{Ce}$ .  $^{138}\text{La}$  and  $^{142}\text{Ce}$  suffered from a larger interference correction from  $^{138}\text{Ce}$  and  $^{142}\text{Nd}$ , and the reproducibility was reduced.

Rare earth elements in JcP-1 and JcT-1 had been previously analyzed by INAA (Aizawa, 2008), and REEs in JcP-1 have previously been analyzed by conventional ICP-MS (Jupiter, 2008). A V-shape chondrite-normalized pattern is common for results determined by ICP-MS (Fig. 2). The results determined by INAA show much higher values than those by ICP-MS. The JcP-1 contained a relatively high level of uranium, at 2.7 ppm (Aizawa, 2008), and the fission and spectral interferences in the INAA determination of REEs in the geochemical samples with high U/REE ratios were reported using a comparison of GSJ carbonate reference rocks between ICP-AES and INAA (Kawabe *et al.*, 1994).

Lanthanide tetrad effects were found in the marine environment by Masuda and Ikeuchi (1979) and in leucogranite by Masuda *et al.* (1987). The tetrad effect is expected to be maintained in all REEs, shown by W- or M-shapes. Although the zigzag pattern is clear for the HREEs found in nature, the pattern is not clear in the LREEs. This depends on the inclination of the chondrite-normalized REE pattern. The fine structures of the REE pattern are easier to identify in a flat pattern than in a steep pattern. As shown in Fig. 1, the tetrad effect is not obvious in the LREE region for either JcP-1 or JcT-1. However, the mutually normalized REE pattern shows a clear W-shaped tetrad effect (Fig. 3). This indicates that the 14 REE data for both JcP-1 and JcT-1 are of sufficient quality to reveal the fine tetrad structure. This result confirms that the isotope dilution technique using the ICP quadrupole mass spectrometer is an excellent and more accessible technique to obtain precise REE data for samples with low REE concentrations.

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