Determination of rare earth element in carbonate using laser-ablation ICP-MS: An examination of the influence of the matrix on LA-ICP-MS analysis

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Abstract

In this study, we examined the influence of the matrix on rare earth element (REE) analyses of carbonate with LA-ICP-MS using carbonate and NIST glass standards. A UV 213 nm Nd:YAG laser system was coupled to an ICP-MS. Laser ablation was carried out in both He and Ar atmospheres to investigate the influence of ablation gas on the analytical results. A small amount of N_2 gas was added to the carrier gas to enhance the signal intensities. Synthetic $CaCO_3$ standards, doped with REEs, as well as NIST glasses (NIST SRM 610 and 612) were used as calibration standards. Carbonatite, which is composed of pure calcite, was analyzed as carbonate samples. The degree of the influence of the matrix on the results was evaluated by comparing with the results which were calibrated by the synthetic $CaCO_3$ and NIST glass standards. With laser ablation in a He atmosphere, the differences between the results calibrated by the synthetic $CaCO_3$ and NIST glass standards were less than 10% across the REE series, except for those of La which were 25%. In contrast, for the measurements made in an Ar atmosphere, the results calibrated by the synthetic $CaCO_3$ and NIST glass standards differed by 25–40%. It was demonstrated that the LA-ICP-MS system can provide quantitative analysis of REE concentrations in carbonate samples using non-matrix matched standards of NIST glasses.

Keywords: LA-ICP-MS, carbonate, rare earth element, matrix effect

1. Introduction

Carbonates have received considerable attention from geochemists and have contributed to geochemical studies of marine and magmatic systems (e.g. coral, limestone and carbonatite). Laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) is a powerful tool for obtaining high spatial resolution data from carbonate samples. It has several advantages over other analytical methods, including the ability to perform rapid and direct analysis of solid-state samples [1-5]. Rare earth element (REE) abundance, as a coherent group, is a useful tracer for investigating geochemical processes involved in the formation of various samples [6]. Unfortunately, with the exception of a few reports [4,5], not much work has been published on the application of LA-ICP-MS for the analysis of REE abundance in carbonate samples. This is in contrast to bulk sample analysis using wet chemistry methods, on which many reports have been published [7-9].

In LA-ICP-MS analysis of trace elements, the use of calibration standards, whose major element compositions are the same as the samples that are to be analyzed, is ideal for limiting the influence of the matrix. LA-ICP-MS using matrix-matched standards can provide quantitative analysis, even if elemental fractionation occurs in both the standards and the samples during the laser ablation, transportation and ionization processes. In many studies on carbonate, NIST glass reference materials which are calcium-sodium aluminosilicate glasses have been used as calibration materials for LA-ICP-MS analysis [1-5], in spite of the large compositional differences that exist between the NIST glasses and carbonate samples. The accuracy of LA-ICP-MS analysis using non-matrix-matched standards depends on the difference in the degree of elemental fractionation between the sample and the standards. In order to obtain accurate data using LA-ICP-MS, the influence of matrix composition on the analytical results should be determined.

The influence of the matrix on LA-ICP-MS analysis can be evaluated by comparing quantitative results that have been calibrated using matrix-matched and non-matrix-matched standards. Craig et al. [10] and Hathorne et al. [11] demonstrated the existence of the influence of the matrix, using NIST glasses and in-house $CaCO_3$ standards doped with trace elements. However, their standards were synthesized by just adding a spike solution to $CaCO_3$ powder, so that the trace elements were not incorporated into the bulk of the $CaCO_3$ crystals, but rather adhered to the crystal surfaces. Such standards may not be suitable for analysis of natural carbonate samples because trace elements are possibly incorporated in $CaCO_3$ crystals. Therefore, we synthesized $CaCO_3$ standards doped with REEs using a coprecipitation method. In this study, our interest is mainly on the degree of the influence of the matrix on REE analysis of carbonate samples using LA-ICP-MS.

2. Method

2. 1. Instrumentation and measurement condition

In this study, a UV 213 nm Nd:YAG laser system (UP-213, New Wave Research) was used with an ICP-MS (VG PQ-3). A diagram of the LA-ICP-MS system is illustrated in Fig. 1. For most of the measurements, He gas was flushed into the ablation cell to reduce the deposition of ablated aerosols and to improve signal intensities [12-14]. Measurements in an Ar atmosphere were also carried out to evaluate the effect of gas in ablating samples. Hirata and Nesbitt [15] and Iizuka and Hirata [16] reported enhancement of elemental sensitivities by adding small amounts of N_2 gas into the carrier gas. Therefore, N_2 gas was mixed with Ar carrier gas at a flow rate of 5 ml/min. The N_2 gas flow rate was tuned to maximize signal intensity of ^{140}Ce. The operating conditions for LA-ICP-MS analysis are summarized in Table 1. Signal intensities of about 10^5 and 10^6 cps were obtained for ^{137}Ba and ^{140}Ce, respectively, when NIST SRM 610 was ablated with a 100 μm laser spot at a repetition rate of 5 Hz and laser fluence of 10 J/cm^2 in a He atmosphere. In contrast, the signal intensities of ^{137}Ba and ^{140}Ce in an Ar atmosphere were about 30% lower. In all measurements, ^{43}Ca was used as an internal standard for correcting instrumental drift and rate of ablation. The typical ^{43}Ca count rate for Ca carbonate samples was about 4.0×10^5 cps. The background count for ^{43}Ca was between 1,000 and 2,000 cps and those for the monitored REE isotopes were approximately 0 cps. The background count for ^{43}Ca was not corrected because it was negligibly small relative to the sample counts.

2. 2. Sample preparation

Carbonatite (Ontario, Canada) was used as a carbonate sample for LA-ICP-MS analysis; it was composed of almost pure calcite. The mineralogy of the carbonatite was determined using XRD (M18XHF, MAC Science Ltd.). First, a 2 cm piece of the carbonatite was crushed into 4-5 mm grains. Two grains of these grains, which were labeled CA-1 and CA-2, respectively, were hand-picked. Both of the two 4-5 mm grains were crushed further into three 2-3 mm grains (making up six grains: CA-1-1, CA-1-2, CA-1-3, CA-2-1, CA-2-2 and CA-2-3). Two of the three 2-3 mm grains from each of the 4-5 mm grains (CA-1-1, CA-1-2, CA-2-1 and CA-2-2) were mounted in epoxy resin for LA-ICP-MS analysis. After polishing the surface, the Ca concentrations of these grains were measured using an electron probe micro analyzer

(EPMA: JEOL MXA8200) prior to performing LA-ICP-MS analysis. The Ca concentrations were calibrated using synthetic wollastonite ($CaSiO_3$) standard. Each grain was measured at 15 arbitrarily selected points using a 10 μm diameter beam. The average Ca concentration of 15 spots for each grain was almost constant at 38.8 ± 0.4% (2σ). In addition, variations in Ca concentrations within each grain estimated from measuring 15 spots were 1% or less. Therefore, using Ca as an internal standard element produced insignificant uncertainties in LA-ICP-MS analysis. The remaining CA-1-3 and CA-2-3 were pulverized with an agate mortar, and then dissolved in HCl for REE determination by ICP-MS (solution ICP-MS). REE concentrations in the other eight grains (CA-3 – CA-10) were also determined by solution ICP-MS to examine the spatial heterogeneity of REE distribution in the carbonatite. Before ICP-MS measurement, REEs were separated from major elements by a cation exchange method employing a column with Bio-rad AG50W-X8 resin. Recovery of REEs during the cation exchange procedure was more than 99%. The final solutions used for the ICP-MS measurement were adjusted to 2% HNO_3 solutions which included internal standards of In and Bi. REE standard solutions for solution ICP-MS were made by mixing and diluting 1,000 mg/kg REE solutions (Kanto Chemical Co.). The analytical precision for each measured REE concentration was estimated to be better than 5% from replicate analyses including dissolution and separation processes. Detailed measurement conditions which were employed for solution ICP-MS are described in Takahashi et al. [17].

2. 3. Calibration standards for LA-ICP-MS

We used two sets of standard materials as calibration standards for LA-ICP-MS.

One was glass standards of NIST SRM 610 and 612, and the other was in-house calcium carbonates doped with REEs. Three $CaCO_3$ standards with different REE contents were synthesized by adding NaOH and $NaHCO_3$ solutions to a $CaCl_2$ solution doped with REEs. During the coprecipitation process, solutions were undersaturated with respect to $REE_2(CO_3)_3{\cdot}nH_2O$. After separation with a 0.45 μm filter and drying, the powder of the synthesized standards was mounted on epoxy resin, and then polished. The synthetic standards were identified as calcite using XRD. XRD patterns of the synthetic standards did not show any peaks other than those for calcite, and no differences between pure calcite and the REE-doped standards were observed. This reflects the dilute nature of the REE-calcite solid solutions.

In order to confirm homogeneity of the synthetic standards, four fractions for each calcite standard were weighed for REE determination by solution ICP-MS followed by HCl dissolution. The same cation exchange method as that in carbonatite analysis was employed for REE purification before ICP-MS measurement. Internal standards of In and Bi were added to 2% HNO_3 sample solutions for ICP-MS measurement. The average REE concentrations of the four fractions for each synthetic $CaCO_3$ standard were listed in Table 2 together with the standard deviations. Uncertainties of REE concentrations in std-5 were larger than those in std-1 and std-3, which may reflect heterogeneity of std-5 in addition to analytical uncertainties. However, the uncertainties of REE concentrations in std-5 did not exceed 10%.

We also analyzed REE concentrations in NIST SRM 610 and 612 by solution ICP-MS to exclude possible differences in our lot of SRM standards from the reported data [18]. About 100 mg of each glass standard, which had previously been pulverized with an agate mortar, was decomposed with HF-$HClO_4$. REEs in the decomposed samples were separated from major elements using a cation exchange method. Internal standards of In and Bi were added to the sample solutions before measurement. The results of three times repeated analyses of the same piece are listed in Table 3 together with the data compiled by Pearce et al. [18]. Our analytical results are lower than the compiled values by up to 10%, but this is acceptable given the analytical uncertainties. Since each of the compiled data by Pearce et al. [18] was determined using different lots of the NIST glass standards, the uncertainties of the compiled data may reflect possible heterogeneity in the NIST glasses (Table 3). Similarly, such heterogeneity may result in differences between our data and the compiled data. Therefore, we employed our data for calibrating the LA-ICP-MS measurement.

3. Results and Discussion

3. 1. Comparison between LA- and solution ICP-MS

The analytical results for the REE concentrations of the carbonatite samples determined by solution ICP-MS are shown in Table 4. The carbonatite samples show light REE (LREE) enrichment and a negative Eu anomaly in the chondrite-normalized REE abundance patterns (Fig. 2). The REE patterns for CA-1-3, CA-2-3 and CA-3 are very similar, whereas CA-4 exhibits greater LREE enriched patterns compared with the other three grains. On the other hand, the REE concentration levels of CA-5 – CA-10 are lower than those of CA-1 – CA-4 (Fig. 2). In addition, the relative abundances of LREE (i.e. the degree of LREE enrichment or depletion) are different in each grain. The results of solution ICP-MS suggest that the REE distributions within the carbonatite grains seem to be heterogeneous on a millimeter-scale level, in terms of concentration levels and relative abundances across the REE series.

REE concentrations measured by LA-ICP-MS in a He atmosphere are shown in Table 5, Figs. 3a and 3b together with the results of solution ICP-MS. The REE concentrations were calibrated using the synthetic $CaCO_3$ standards. Each grain was measured at eight to ten arbitrarily selected points. In the CA-1 series, CA-1-1 and CA-1-3 gave very close results, while CA-1-2 showed higher REE concentration levels than CA-1-3 (Fig. 3a). Several points on CA-1-2 exhibited pronounced LREE depletion. This trend was also observed in CA-2 (Fig. 3b). In order to clarify the differences between solution ICP-MS and LA-ICP-MS, the results of LA-ICP-MS were normalized using those obtained from solution ICP-MS (Figs. 4a and 4b). Both relative LREE depletion and LREE enrichment can be identified at different points in CA-2 (Fig. 4b). In contrast, every grain showed parallel HREE abundances, although the concentration levels were 0 – 50% higher in CA-2.

In spite of the similarity of bulk sample abundances between the CA-1 and CA-2 series (CA-1-3 and CA-2-3) (Fig. 2), the corresponding results of LA-ICP-MS analysis showed various extent of deviation from the results of solution ICP-MS (Figs. 4a and 4b). Tiny inclusions (1 – 2 μm) were observed in back scattered image for each carbonatite sample. Quantitative analysis could not be carried out because of their smallness, but qualitative analysis of the inclusions by EPMA indicated X-ray fluorescence peaks of light REEs (La, Ce and Nd). The contribution of the REE concentrated inclusions to analytical results is possibly one of the reasons for discrepancy between solution and LA-ICP-MS, and for variations in concentration levels within the same grains. In particular, CA-1-1 exhibited smaller deviation (10 – 20%) from the solution ICP-MS results relative to other grains (Fig. 4a). Probably, this is attributable to the less contribution of the inclusions. Therefore, the accuracy and precision of our LA-ICP-MS analysis were estimated to be better than 20% from the results of CA-1-1. As discussed in the following section, the most important aspect of this study is the comparison of results from samples that had been calibrated by the synthetic $CaCO_3$ and NIST glass standards.

3. 2. The influence of the matrix on LA-ICP-MS

The results of the calibration using synthetic $CaCO_3$ are compared with those of the calibration using NIST glass in Fig. 5. The differences in the results measured in a He atmosphere are less than 10% except for La, which has a difference of 25%. In contrast, the analytical results measured in an Ar atmosphere showed differences within the range of 25–40%.

There are a large number of parameters that influence the analysis of LA-ICP-MS. In particular, the influence of laser wavelength and the absorption behavior of samples on elemental fractionation has been investigated [20,21]. Guillong and Günther [21] reported that a 266 nm Nd:YAG laser produces significantly larger particle sizes than a laser having a wavelength of 193 nm. They proposed an important model in which the ablated particle size distribution is dependent on the laser wavelength and the absorption behavior of samples. Moreover, they pointed out that the large particle fractions of ablated particles are not completely vaporized and ionized in the ICP, which results in elemental fractionation. This means that the influence of the matrix on LA-ICP-MS may be caused by the differences in the particle size distributions between the non-matrix-matched standards and the samples caused by the laser wavelength and its absorbance by the samples. Compared with ablation in an Ar atmosphere, ablation in a He atmosphere using a 193 nm ArF excimer laser reduces the deposition of aerosols around ablation pits and improves transport efficiency [12,14]. This is explained by the fact that ablation in a He atmosphere results in a smaller size distribution of aerosols than that in an Ar atmosphere, especially when a 193 nm laser is used [14]. From the results of the previous studies, it can be concluded that the use of a shorter wavelength laser and sample ablation in a He atmosphere minimizes the influence of the matrix.

The effect of laser wavelength could not be examined in this study, but the effect of ablation gas was clearly observed (Fig. 5). Craig et al. [10] reported that the matrix influences trace element analyses between NIST glass standards and carbonate using a 266 nm Nd:YAG laser in an Ar atmosphere. Similarly, Hathorne et al. [11] compared analytical results calibrated by NIST SRM 612 and a synthetic $CaCO_3$ standard using a 213 nm Nd:YAG laser in a He atmosphere. The differences in Mg, Sr and Ba were about 20% [11], which was much smaller than those measured by Craig et al. [10]. Calcite absorbance of 213 nm radiation is much larger than that of 266 nm radiation [22]. The influence of the matrix reported by Craig et al. [10] may be due to the poor absorbance of 266 nm radiation and difference in ablation gas. The combination of using a 213 nm laser and carrying out ablation in a He atmosphere effectively reduces the production of large particles and elemental fractionation [12,14,21]. Using this kind of LA-ICP-MS system, the present results strongly support the proposition that REE abundances in carbonate can be determined based on calibration using the NIST glass standards, in spite of the large compositional differences between $CaCO_3$ and SiO_2 glass. This fact suggests that application of NIST glass standards can be extended to various geochemical samples, whose matrix composition is not necessarily equivalent to that of the standards, by means of careful setup of the LA-ICP-MS system.

4. Conclusions

We have measured REE concentrations in carbonatite using a UV 213 nm Nd:YAG laser system coupled to an ICP-MS. The effect on LA-ICP-MS caused by matrix was investigated using NIST glasses and synthetic $CaCO_3$ doped with REEs as calibration standards. The influence of the matrix on LA-ICP-MS analysis was relatively small, and differences in the results obtained by calibration using the NIST glass and synthetic standards, were less than 10%, except for La which had a difference of 25%, when laser ablation was carried out in a He atmosphere. Laser ablation in an Ar atmosphere, however, produced larger differences in the results between the NIST glass and synthetic standards. Our LA-ICP-MS setup, which involves laser ablation in a He atmosphere and the addition of N_2 to the carrier gas, effectively reduces the effect caused by the matrix between carbonate and silicate glasses. The LA-ICP-MS system can provide quantitative analysis of REE concentrations in carbonate samples using NIST glass standards.

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References

[1] H. A. III Stecher, D. E. Krantz, C. J. III Lord, G. W. III Luther, K. W. Bock, Geochim. Cosmochim. Acta 60 (1996) 3445.

[2] D. J. Sinclair, L. P. J. Kinsley, M. T. McCulloch, Geochim. Cosmochim. Acta 62 (1998) 1889.

[3] E. V. Putten, F. Dehairs, E. Keppens, W. Baeyens, Geochim. Cosmochim. Acta 64 (2000) 997.

[4] T. Wyndham, M. McCulloch, S. Fallon, C. Alibert, Geochim. Cosmochim. Acta 68 (2004) 2067.

[5] F. Stoppa, G. Rosatelli, F. Wall, T. Jeffries, Lithos 85 (2005) 26.

[6] P. Henderson, Rare Earth Element Geochemistry, Elsevier, New York, 1984.

[7] B. S. Kamber, G. E. Webb, Geochim. Cosmochim. Acta 65 (2001) 2509.

[8] K. Tanaka, N. Miura, Y. Asahara, I. Kawabe, Geochem. J. 37 (2003) 163.

[9] L. D. Nothdurft, G. E. Webb, B. S. Kamber, Geochim. Cosmochim. Acta 68 (2004) 263.

[10] C.-A. Craig, K. E. Jarvis, L. J. Clarke, J. Anal. At. Spectrom. 15 (2000) 1001.

[11] E. C. Hathorne, O. Alard, R. H. James, N. W. Rogers, Geochem. Geophys. Geosyst. 4(12) (2003) 8408, doi:10.1029/2003GC000539.

[12] S. M. Eggins, L. P. J. Kinsley, J. M. G. Shelley, Appl. Surf. Sci. 127-129 (1998) 278.

[13] D. Günther, C. A. Heinrich, J. Anal. At. Spectrom. 14 (1999) 1369.

[14] I. Horn, D. Günther, Appl. Surf. Sci. 207 (2003) 144.

[15] T. Hirata, R. W. Nesbitt, Geochim. Cosmochim Acta 59 (1995) 2491.

[16] T. Iizuka, T. Hirata, Chem. Geol. 220 (2005) 121.

[17] Y. Takahashi, H. Yoshida, N. Sato, K. Hama, Y. Yusa, H. Shimizu, Chem. Geol. 184 (2002) 311.

[18] N. J. G. Pearce, W. T. Perkins, J. A. Westgate, M. P. Gorton, S. E. Jackson, C. R. Neal, S. P. Chenery, Geostandards Newsl. 21 (1997) 115.

[19] E. Anders, N. Grevesse, Geochim. Cosmochim. Acta 53 (1989) 197.

[20] R. E. Russo, X. L. Mao, O. V. Borisov, H. Liu, J. Anal. At. Spectrom. 15 (2000) 1115.

[21] M. Guillong, D. Günther, J. Anal. At. Spectrom. 17 (2002) 831.

[22] T. E. Jeffries, S. E. Jackson, H. P. Longerich, J. Anal. At. Spectrom. 13 (1998) 935.

Figure legends

Fig. 1. Schematic diagram of LA-ICP-MS system.

Fig. 2. Chondrite-normalized REE abundance patterns for carbonatite samples determined by solution ICP-MS. The chondrite values reported by Anders and Grevesse [19] were used for normalization.

Fig. 3. Comparison of chondrite-normalized REE patterns between solution and LA-ICP-MS. The LA-ICP-MS data measured in a He atmosphere were calibrated by the synthetic $CaCO_3$ standards. (a) CA-1 series. (b) CA-2 series.

Fig. 4. Ratios of REE concentrations measured by LA-ICP-MS to those measured by solution ICP-MS. (a) CA-1 series. (b) CA-2 series.

Fig. 5. Comparison of REE concentrations calibrated by the synthetic $CaCO_3$ standards and NIST glasses. Error bars are within symbols.

Table 1. Laser ablation system and operation conditions for LA-ICP-MS analysis.

ICP-MS in laser ablation mode	
Instrument	VG PQ-3
Gas flow rate	Cool Ar: 16.0 L/min Aux Ar: 1.4 L/min Carrier Ar: 1.0 L/min Mixing N_2: 5 mL/min
Forward power	1336 W
Reflection power	<1 W
Detector mode	Pulse counting
Detector dead time	35 nsec
Isotopes monitored	^{43}Ca, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu
Integration time	14 sec
Laser ablation system	
Instrument	UP-213 (New Wave Research)
Beam	UV 213 nm (Nd : YAG)
Repetition rate	5 Hz
Crater diameter	100 µm
Fluence	10 J/cm^2
He gas flow rate	0.24 L/min

Table 2. REE concentrations (mg kg^{-1}) in synthetic $CaCO_3$ standards.

	std-1	1σ(n=4)	std-3	1σ(n=4)	std-5	1σ(n=4)
La	151.0	0.5	3.07	0.05	20.5	1.1
Ce	158.5	2.2	3.01	0.05	20.1	1.1
Pr	161.7	1.5	3.07	0.03	20.2	1.1
Nd	163.5	1.6	3.12	0.02	20.1	1.0
Sm	165.3	3.0	3.11	0.01	20.0	1.1
Eu	164.5	2.3	3.14	0.05	20.0	1.1
Gd	164.3	1.8	3.13	0.01	20.2	1.1
Tb	165.2	2.8	3.12	0.03	20.2	1.1
Dy	165.7	2.3	3.12	0.02	19.9	1.0
Ho	165.5	2.3	3.11	0.02	20.1	1.1
Er	165.7	2.2	3.13	0.01	20.3	1.1
Tm	163.2	2.7	3.04	0.01	20.2	1.1
Yb	164.1	1.5	3.11	0.01	20.3	1.1
Lu	162.1	2.2	3.03	0.04	20.2	1.1

Table 3. Comparison of REE concentrations (mg kg^{-1}) in NIST glass standards between this study and compilation data by Pearce et al. [18].

	This study NIST 610	1σ (n=3)	NIST 612	1σ (n=3)	Compilation data NIST 610	1σ (n=5-10)	NIST 612	1σ (n=7-16)	This study /Compilation NIST 610	NIST 612
La	405.8	2.9	33.54	0.20	457.4	72.4	35.77	2.15	0.89	0.94
Ce	422.0	3.7	36.16	0.20	447.8	16.8	38.35	1.64	0.94	0.94
Pr	421.6	6.1	36.06	0.16	429.8	30.0	37.16	0.93	0.98	0.97
Nd	400.6	3.4	33.39	0.35	430.8	37.5	35.24	2.44	0.93	0.95
Sm	423.1	1.3	35.63	0.42	450.5	20.6	36.72	2.63	0.94	0.97
Eu	420.2	4.7	33.59	0.44	461.1	52.1	34.44	1.59	0.91	0.98
Gd	423.4	1.9	35.95	0.30	419.9	25.2	36.95	1.06	1.01	0.97
Tb	418.4	3.7	36.22	0.41	442.8	22.4	35.92	2.68	0.94	1.01
Dy	403.1	4.0	33.68	0.25	426.5	18.0	35.97	0.82	0.95	0.94
Ho	422.0	0.6	36.48	0.12	449.4	24.6	37.87	1.09	0.94	0.96
Er	426.1	2.6	36.57	0.40	426.0	23.9	37.43	1.50	1.00	0.98
Tm	416.4	3.8	35.75	0.24	420.1	19.2	37.55	1.25	0.99	0.95
Yb	424.6	2.5	36.82	0.35	461.5	30.6	39.95	2.86	0.92	0.92
Lu	413.0	2.4	35.08	0.21	434.7	31.0	37.71	1.95	0.95	0.93

Table 4. REE concentrations (mg kg^{-1}) in carbonatite determined by solution ICP-MS.

	CA-1-3	CA-2-3	CA-3	CA-4	CA-5	CA-6	CA-7	CA-8	CA-9	CA-10
La	113	115	116	167	60.8	98.9	84.8	142	105	116
Ce	322	338	300	439	188	280	242		303	
Pr	44.1	45.7	39.8	56.4	24.5	32.8	28.3	37.8	36.3	36.4
Nd	184	190	167	221	105	130	112	146	147	144
Sm	37.0	37.5	33.9	40.0	21.3	23.3	20.3	25.0	26.7	25.5
Eu	8.72	8.74	8.30	9.67	5.27	5.50	4.84	5.98	6.34	6.02
Gd	29.6	29.7	28.3	36.2	17.1	16.5	14.6	21.0	19.2	21.2
Tb	4.69	4.67	4.54	5.27	2.90	2.89	2.55	3.14	3.31	3.17
Dy	26.9	26.7	26.7	27.8	16.3	15.9	14.0	17.1	18.2	17.1
Ho	5.77	5.74	5.81	5.97	3.57	3.48	3.10	3.77	3.96	3.76
Er	18.6	18.6	18.8	19.7	11.4	11.2	9.85	12.1	12.8	12.1
Tm	2.82	2.82	2.80	2.90	1.77	1.72	1.54	1.87	1.97	1.87
Yb	19.0	18.9	19.1	19.4	11.7	11.4	10.2	12.2	13.0	12.3
Lu	2.72	2.68	2.75	2.71	1.70	1.66	1.48	1.78	1.88	1.79

Table 5. REE concentrations (mg kg^{-1}) in carbonatite determined by LA-ICP-MS in a He atmosphere.*

	CA-1-1	CA-1-1	CA-1-1	CA-1-1	CA-1-1	CA-1-1	CA-1-1	CA-1-1	CA-1-1	CA-1-1	CA-1-2	CA-1-2	CA-1-2	CA-1-2	CA-1-2	CA-1-2	CA-1-2	CA-1-2
La	98.4	106	104	110	112	121	114	124	132	127	102	72.7	49.2	66.5	60.5	111	91.5	60.2
Ce	285	312	304	322	324	336	329	361	375	367	346	269	185	241	247	382	327	246
Pr	39.2	43.3	42.5	45.1	44.3	47.4	45.7	48.7	50.5	49.8	50.6	42.3	32.8	40.7	40.4	55.4	49.2	40.2
Nd	171	184	183	193	192	202	200	206	219	212	225	195	160	196	191	240	222	192
Sm	33.4	36.5	36.6	39.2	37.4	41.0	40.2	40.5	43.2	42.2	46.3	42.2	39.7	43.4	42.0	48.0	45.7	43.9
Eu	8.87	9.71	9.68	10.3	10.1	10.6	10.8	10.5	11.4	11.1	12.1	11.5	11.1	11.7	11.4	12.5	12.3	11.9
Gd	28.3	30.1	31.6	32.6	32.4	35.1	34.8	33.6	36.7	35.2	38.0	35.8	35.7	37.6	35.9	39.9	39.2	37.9
Tb	4.27	4.52	4.77	4.97	4.89	5.24	5.20	4.90	5.39	5.19	5.85	5.52	5.51	5.80	5.58	6.06	5.90	5.82
Dy	26.3	28.2	29.1	30.4	29.8	33.1	32.6	30.8	34.8	32.7	35.4	34.1	34.3	36.3	35.0	36.9	37.2	35.7
Ho	5.64	5.96	6.28	6.62	6.27	6.98	6.98	6.56	7.45	7.20	7.66	7.22	7.47	7.80	7.39	8.01	7.83	7.68
Er	16.9	18.3	19.8	20.0	19.6	21.6	21.6	20.5	22.4	21.8	23.3	22.1	23.0	23.7	22.9	24.3	23.9	23.0
Tm	2.57	2.75	2.90	3.02	2.93	3.29	3.22	3.10	3.43	3.36	3.55	3.29	3.51	3.57	3.39	3.60	3.65	3.43
Yb	16.9	18.2	19.9	21.0	19.6	21.9	21.6	20.3	23.0	22.9	24.5	22.2	23.5	24.7	22.6	24.6	23.8	23.0
Lu	2.37	2.59	2.75	2.84	2.68	2.99	2.95	2.80	3.10	3.11	3.34	3.06	3.26	3.38	3.08	3.29	3.31	3.18

	CA-2-1	CA-2-1	CA-2-1	CA-2-1	CA-2-1	CA-2-1	CA-2-1	CA-2-1	CA-2-2	CA-2-2	CA-2-2	CA-2-2	CA-2-2	CA-2-2	CA-2-2	CA-2-2
La	143	175	220	192	172	153	130	133	156	130	72	114	162	196	226	252
Ce	417	491	581	538	499	468	429	433	486	434	259	367	529	609	661	727
Pr	55.4	64.1	73.1	69.7	65.8	63.8	60.5	63.4	69.2	62.2	41.9	54.9	71.8	80.8	84.4	93.3
Nd	223	259	289	278	266	265	257	265	297	267	194	240	300	333	342	367
Sm	41.6	46.3	50.7	49.9	48.4	50.6	49.8	50.4	55.5	52.2	43.7	48.4	55.4	59.9	57.7	60.3
Eu	10.6	12.2	12.8	12.9	12.5	13.0	12.9	13.4	14.1	13.7	12.1	12.2	14.3	14.8	14.4	14.9
Gd	33.3	37.3	39.4	40.0	39.5	40.8	39.8	42.3	44.8	42.9	39.1	41.7	44.5	45.9	44.4	46.6
Tb	4.86	5.51	5.65	6.03	5.82	6.11	6.11	6.22	6.62	6.51	6.20	6.36	6.54	6.72	6.52	6.69
Dy	30.4	34.6	36.1	36.9	37.1	38.0	36.8	38.7	41.8	39.8	37.5	39.7	40.6	41.6	39.8	41.9
Ho	6.42	7.50	7.74	8.02	7.99	8.15	7.82	8.27	8.89	8.44	8.30	8.58	8.57	8.87	8.58	8.76
Er	19.6	22.6	24.0	24.2	24.7	25.1	24.1	24.7	27.1	25.9	25.2	26.4	26.1	26.8	27.0	26.4
Tm	2.92	3.44	3.55	3.65	3.67	3.69	3.59	3.73	4.15	3.92	3.81	4.03	3.92	3.97	3.94	4.02
Yb	20.1	22.9	23.8	24.8	25.4	25.4	24.6	25.2	28.1	26.1	26.0	27.3	27.2	27.5	27.5	27.4
Lu	2.83	3.17	3.27	3.38	3.40	3.50	3.38	3.46	3.93	3.63	3.57	3.68	3.70	3.78	3.76	3.92

* The data were calibrated using synthetic $CaCO_3$ standards.

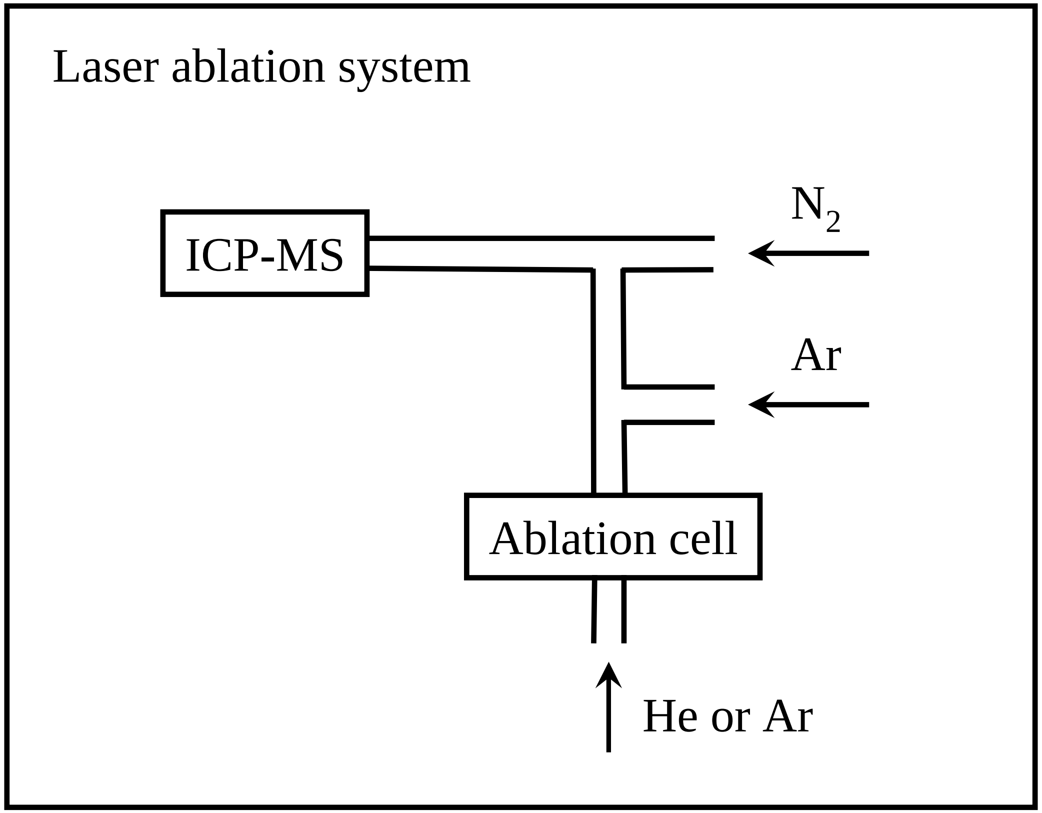

Fig. 1 Tanaka et al.

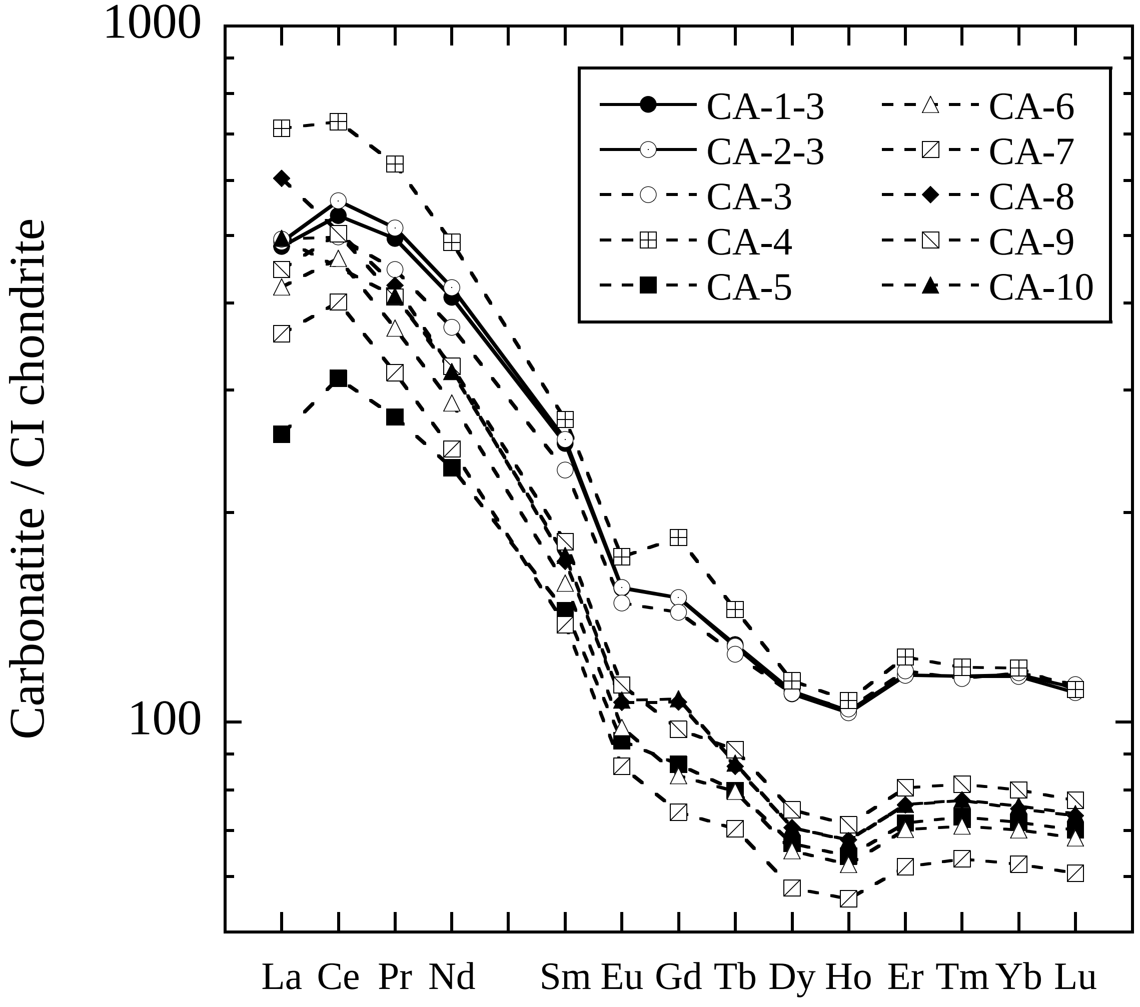

Fig.2 Tanaka et al.

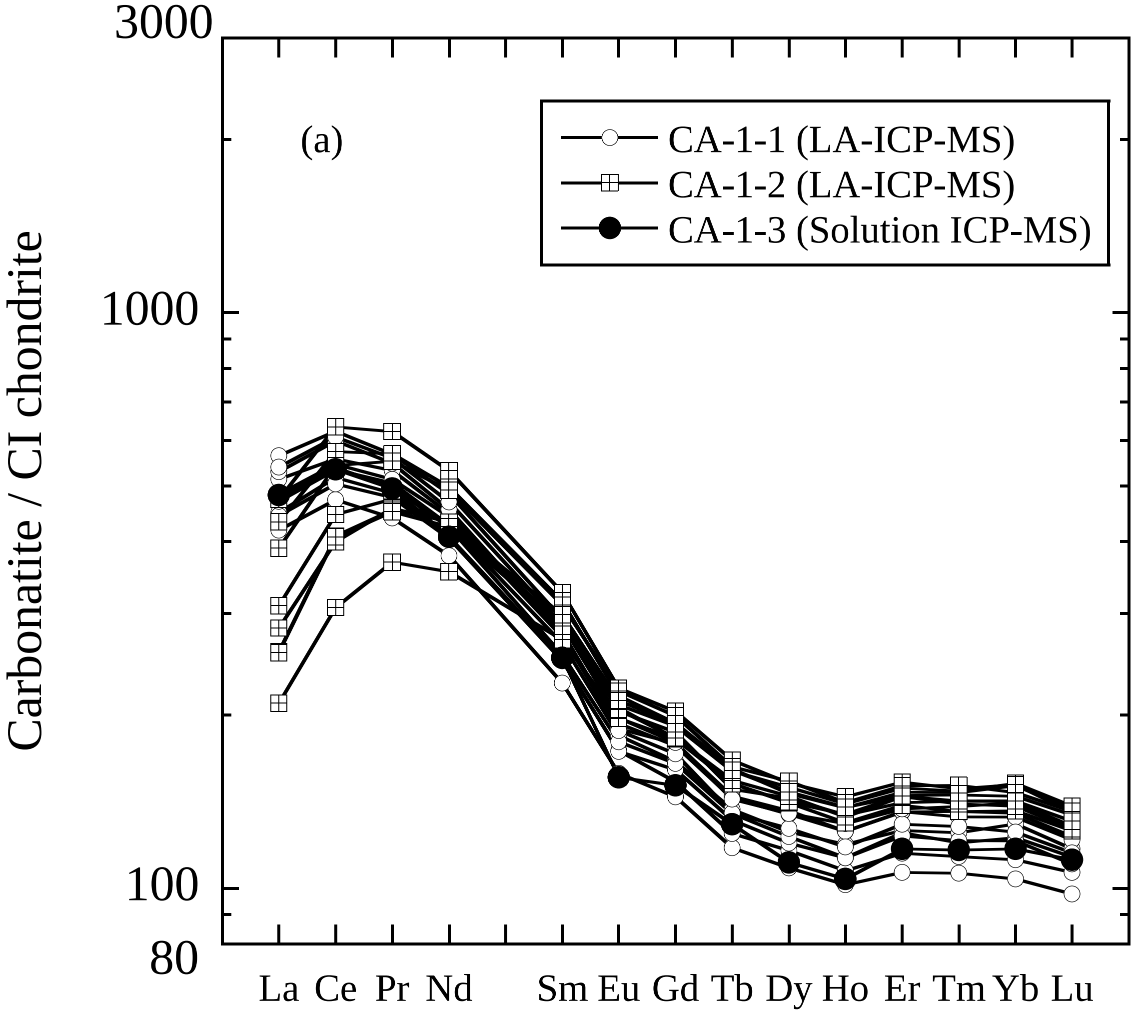

Fig. 3a Tanaka et al.

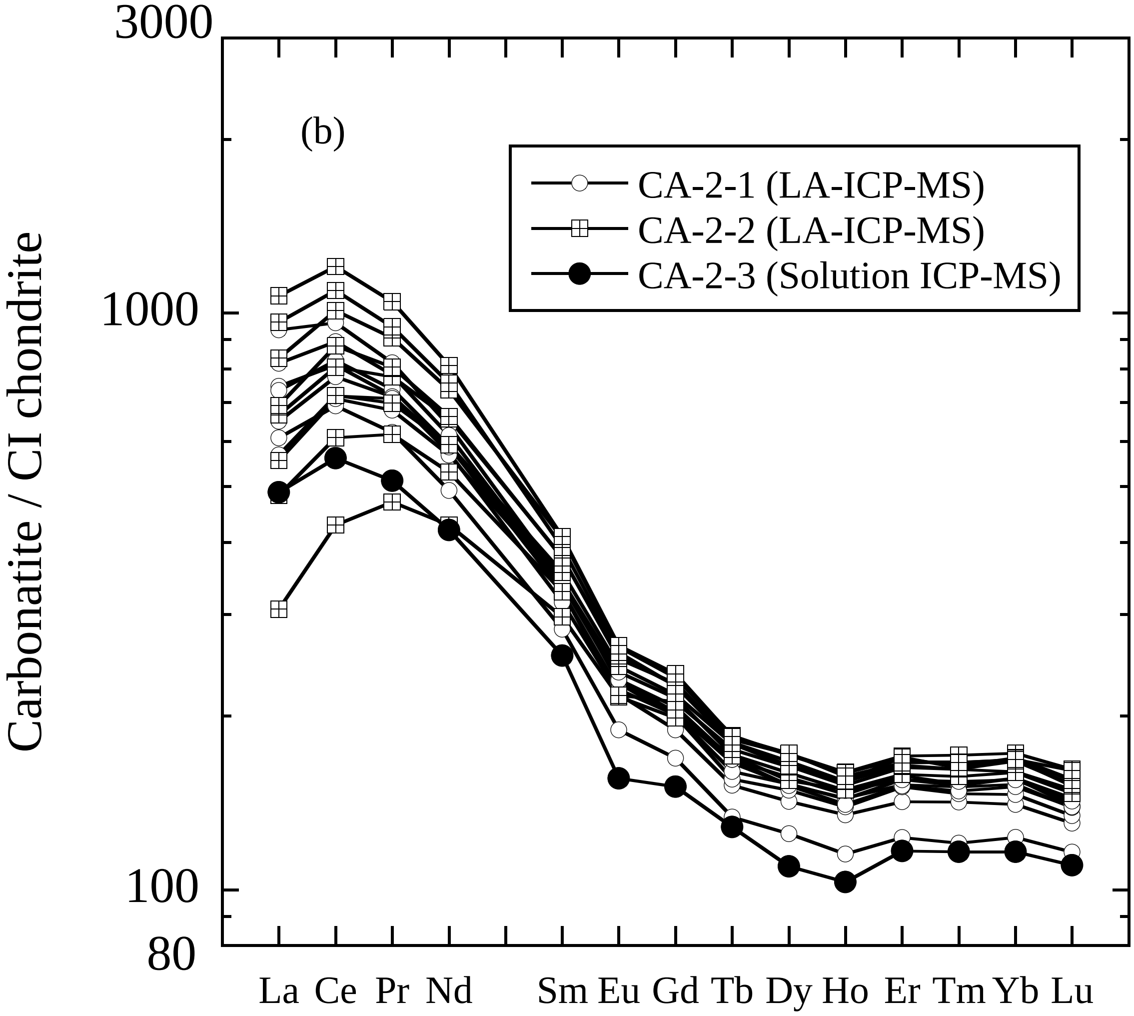

Fig. 3b Tanaka et al.

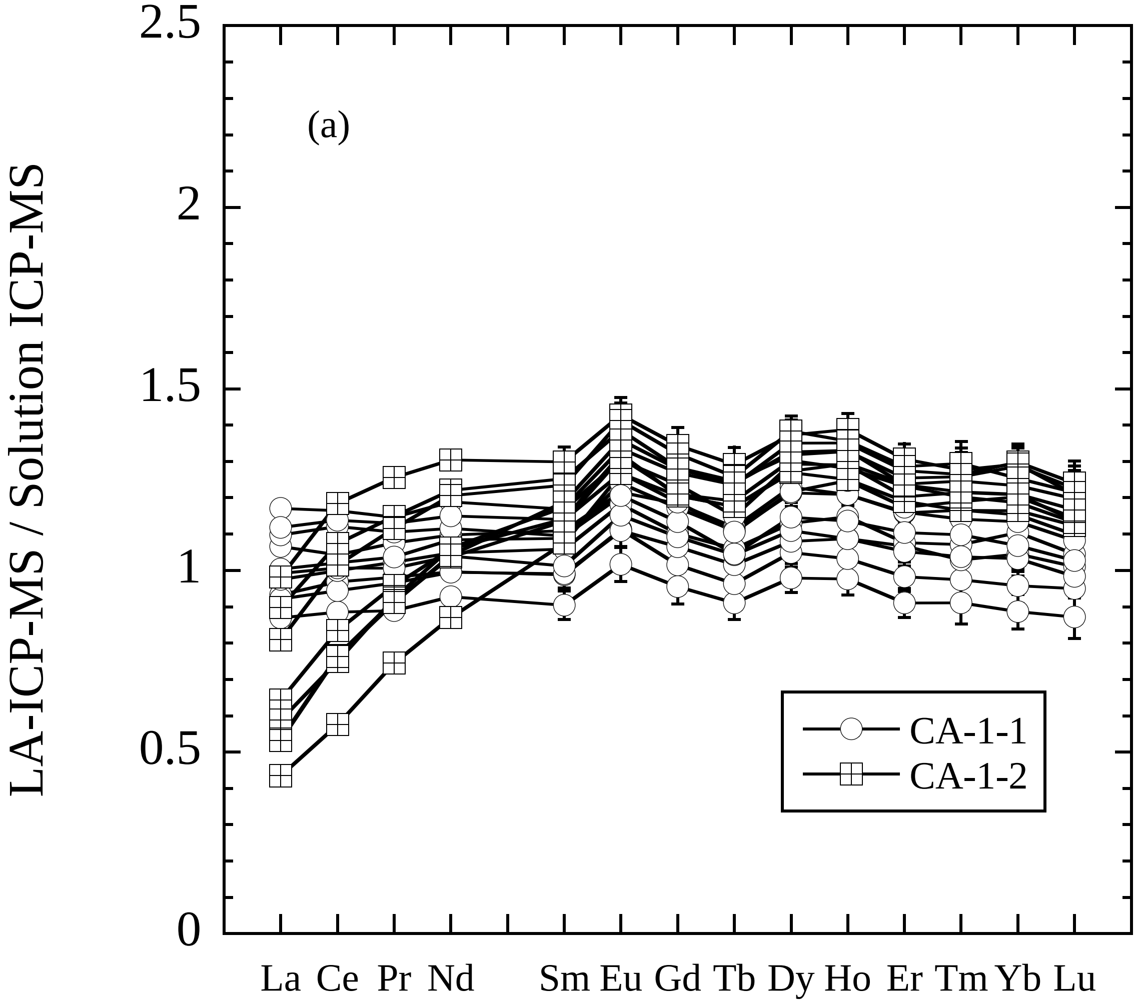

Fig. 4a Tanaka et al.

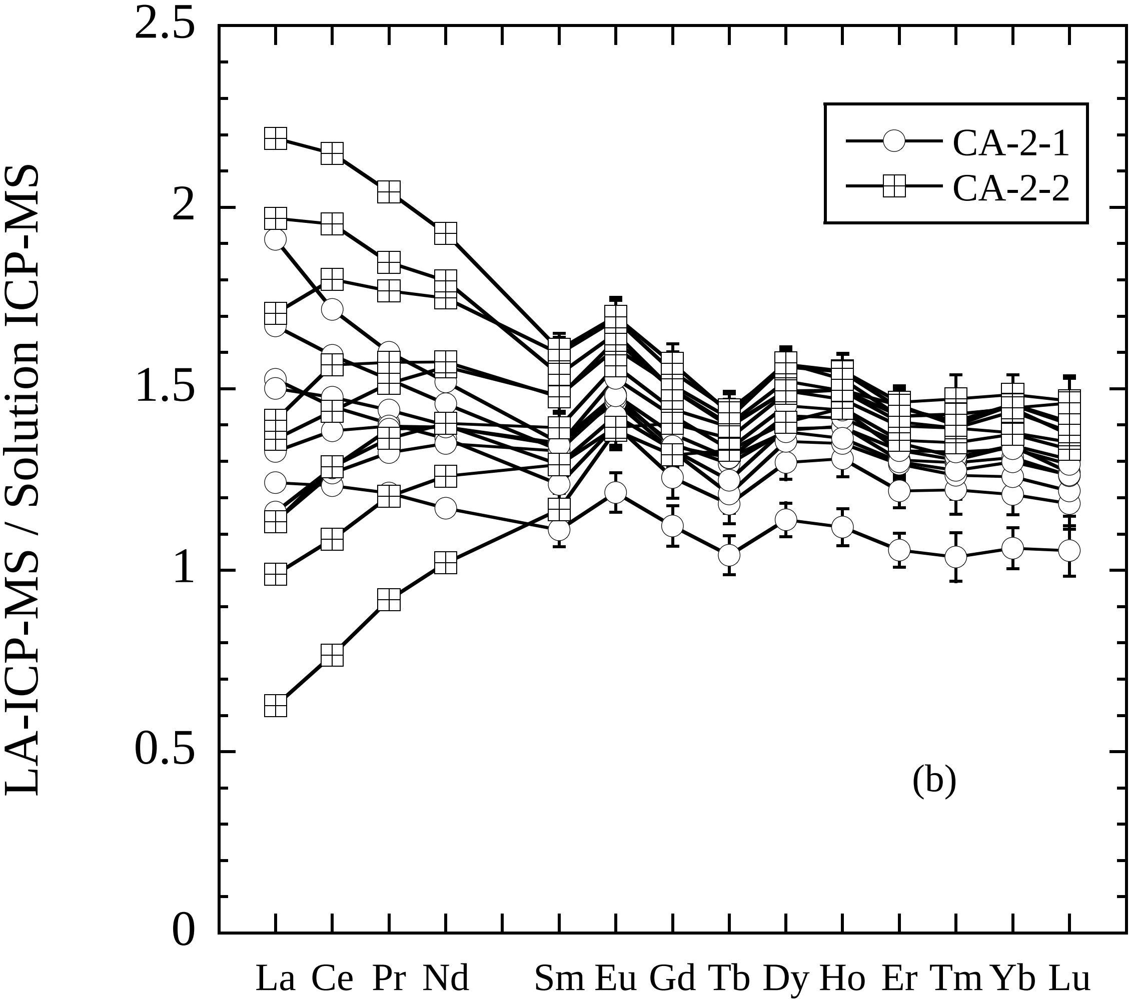

Fig. 4b Tanaka et al.

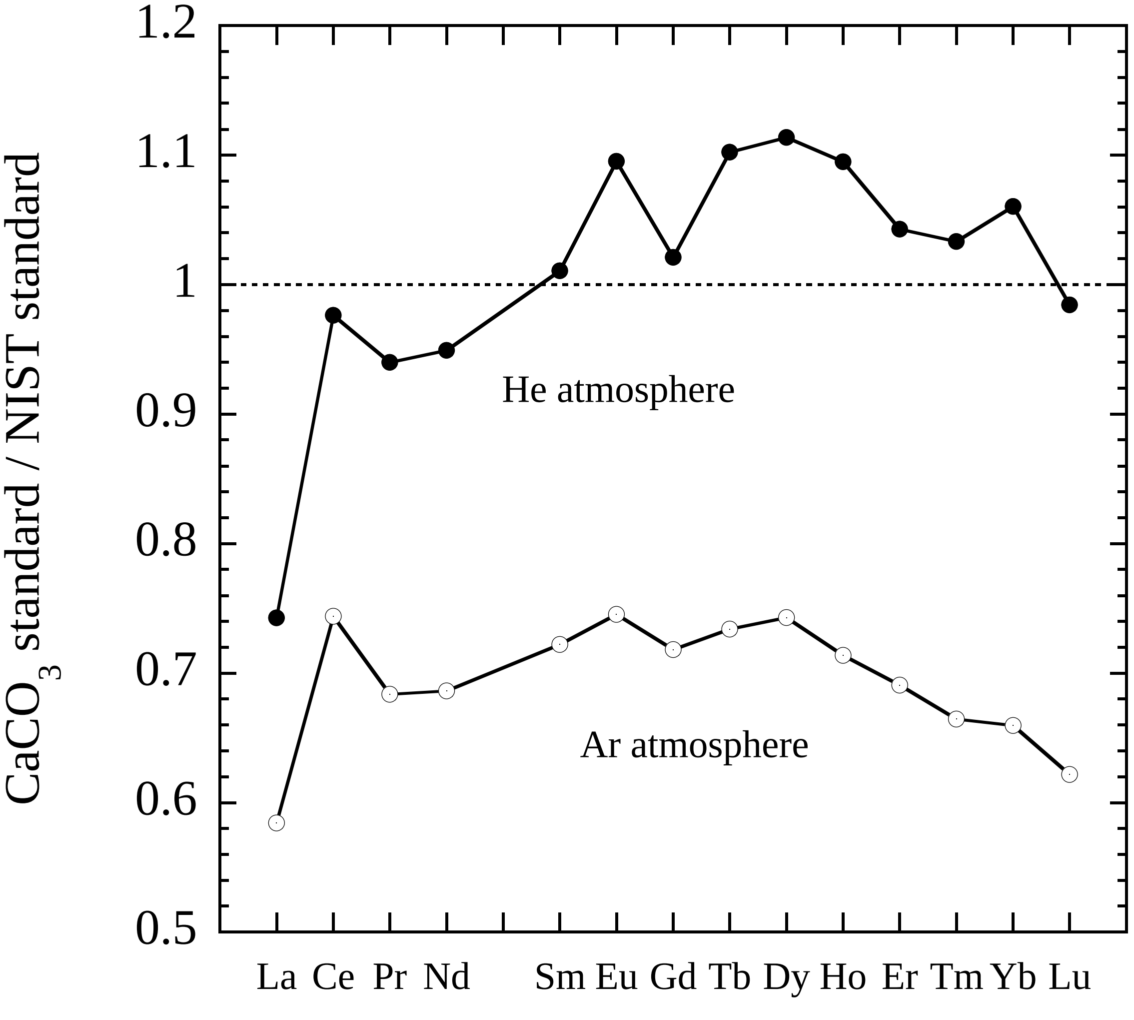

Fig. 5 Tanaka et al.