

原 著

Lanthanoid abundance in some neutral hot spring waters from Japan

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本邦中性温泉水中のランタノイド元素存在量

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Abstract

Lanthanoids (Ln's) in some neutral hot spring waters as well as in acidic hot spring waters were determined by neutron activation analysis. They were, admittedly roughly, at $\mu\text{g}/\text{dm}^3$ levels in acidic waters and at ng/dm^3 levels in neutral waters. It was found that a higher pH resulted in lower Ln's concentrations; the value of correlation coefficient (r) between the logarithm of the concentration of Sm ([Sm]), chosen as a representative of Ln's, and the pH was -0.89. The sum of [Al] and [Fe] was strongly correlated with [Ln]'s in the pH range from 1.3 to 8.8; the correlation was expressed as

$$\log[\text{Sm}] = 0.893 \log([\text{Al}] + [\text{Fe}]) - 5.45$$

with r value of 0.98. The sum of [Al] and [Fe] was thus an excellent measure of the Ln contents in acidic and neutral hot spring waters. A relatively good correlation was also observed between $\log[\text{Sm}]$ and $\log[\text{SO}_4^{2-}]$. The lanthanoid abundance patterns (Ln patterns) of the acidic hot spring waters were mostly horizontal with some with slight enrichment in the light Ln's and were similar to each other, while those of the neutral waters varied from water to water. The diversity in Ln pattern of neutral waters may be due in part to the existence of Ln carbonate species.

Keywords: lanthanoids, acidic hot spring waters, neutral hot spring waters, lanthanoid patterns, neutron activation analysis.

要約

いくつかの中性温泉水及び酸性温泉水中のランタノイド含有量を中性子放射化分析法により決定した。それらは酸性温泉水ではおよそ $\mu\text{g}/\text{dm}^3$ レベル、中性温泉水ではおよそ ng/dm^3 レベルであった。温泉水のpHが高いほどランタノイド濃度は低くなり、ランタノイド元素の代表として選んだサマリウ

ム(Sm)濃度の対数($\log[\text{Sm}]$)とpHとの相関係数(r 値は-0.89であった。pHが1.3から8.8の範囲において、アルミニウム(Al)濃度と鉄(Fe)濃度の和はランタノイド元素濃度と非常に強く相関していた。その相関性はサマリウムの場合、 $\log[\text{Sm}] = 0.893 \log([\text{Al}]+[\text{Fe}]) - 5.45$ で表され、 r 値は0.98であった。このように酸性及び中性温泉水において、アルミニウム濃度と鉄濃度の和はランタノイド元素含有量のよい指標となることがわかった。更に、硫酸濃度の対数とサマリウム濃度の対数にも比較的良好な相関性が観測された。酸性温泉水のランタノイドパターンがわずかに左肩上がりからほぼ水平で、お互いに似ている一方、中性温泉水のそれらは温泉水によりまちまちであった。この原因のひとつとして、ランタノイドイオンと炭酸イオンの錯形成が考えられる。

キーワード：ランタノイド、酸性温泉水、中性温泉水、ランタノイドパターン、中性子放射化分析

1. INTRODUCTION

The lanthanoids (Ln's; $_{57}\text{La} - _{71}\text{Lu}$) form a very coherent group of chemical elements, although $_{58}\text{Ce}$ and $_{63}\text{Eu}$ sometimes exhibit anomalies due to changes in their oxidation states. The most stable oxidation state of all Ln's is Ln(III). The one-by-one filling of the inner 4f electron shell with increasing atomic number results in gradual changes in chemical properties, which is often utilized as an important tool for geochemical studies.

We have been engaged in geochemical study of hot spring water. It includes the study on water quality changes (Ossaka, *et al.*, 1998), behaviors of halide ions (Yamano, *et al.*, 1995) and dissolved oxygen (Ossaka, *et al.*, 1993), and influence of sea water on hot spring waters (Oi, *et al.*, 1993; Oi, *et al.*, 1996). Using Ln's as a geochemical tracer, we also reported the study on the formation mechanism of acidic hot spring waters of volcanic origin in which Ln's were at $\mu\text{g}/\text{dm}^3$ levels (Kikawada, *et al.*, 1993; Kikawada, *et al.*, 1995).

Unlike Ln's contents of acidic hot spring waters, those of neutral spring waters are very low, usually at ng/dm^3 levels. Maybe due in part to the difficulty of measuring such low Ln contents accurately, publications dealing with Ln's in natural neutral waters are limited except for those on sea water (Masuda and Ikeuchi, 1979; De Baar, *et al.*, 1985; Elderfield, 1988; Tanaka, *et al.*, 1990; Piepgras and Jacobsen, 1992). If we confine our attention to Ln's in neutral hot spring waters, only preliminary studies are reported (Oda, 1969; Henderson, *et al.*, 1987; Oi, *et al.*, 1990). In this paper, we reported Ln contents of some neutral hot spring waters in Japan, as well as those of acidic spring waters, and discuss, in terms of Ln contents and Ln abundance patterns, some characteristics observed in neutral hot spring waters.

2. EXPERIMENTAL

2.1 Hot spring water samples

Eight hot spring waters were collected on the Japanese Islands for the present study. Four (Kawayu, KAW; Noboribetsu, NOB; Goshogake, GOS; and Yukawa, YUK) were acidic (pH:1.4-3.03) and the remaining four (Nakabusa, NAK; Matsushiro, MAT; Yunotaira, YUN; and Shima, SHI) were weakly acidic-neutral (pH:5.82-8.8). We designate hot spring waters of the latter category as neutral hot spring waters in this paper. The locations of hot springs are shown in Fig.1.

Water samples for the analysis of major dissolved components were collected in 0.5- or 1- dm^3 polyethylene

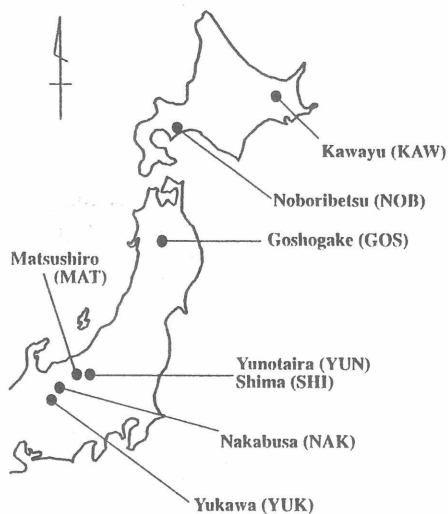


Fig. 1: Locations of the hot springs investigated.

bottles. Those for the determination of Ln's were collected in 1-dm³ or larger polyethylene bottles and conc. HNO₃ was added to all the sampled waters (2 cm³ HNO₃ per 1 dm³ of water except for the MAT water for which 4 cm³ HNO₃ was added per 1 dm³ of water).

The formation mechanism of the hot spring waters examined can be described in a very simple manner as follows. A groundwater formed by infiltration of meteoric water into the ground acquires thermal energy, and sometimes acidity too, from deep-seated volcanic activity. The water acquires cationic components including Ln's from rocks surrounding water channels. Kinds and amounts of cationic species the water takes in must depend on various factors. The most influential factors are probably acidity of the water and the nature of rocks the water contacts underground. Amounts of cationic species are influenced substantially by acidity of the water. Higher acidity generally leads to higher contents of Ln's. Rocks the hot spring waters in this study contact underground are considered to be igneous rocks in most cases, since the waters are of volcanic origin in the sense that they obtain thermal energy (and acidic components) from some kind of volcanic activity.

2.2 Determinations of major dissolved components

Alkali metal ions were determined by flame photometry and those of other metal ions were by ICP-AES. Anionic components were measured by ion chromatography. Total carbon dioxide ($\Sigma \text{CO}_2 = \text{sum of } [\text{CO}_2] + [\text{HCO}_3] + [\text{CO}_3^{2-}]$) dissolved in the MAT water was determined by microdiffusion analysis. The ΣCO_2 was estimated for the other neutral hot spring waters from the difference in chemical equivalent between cationic and anionic species.

Contents of major dissolved components and relevant information on the waters are summarized in Table 1.

Table 1 Relevant information on the hot spring waters and the contents of major dissolved components in mg/dm³

Sample	Nakabusa (NAK)	Yunotaira (YUN)	Shima (SHI)	Matshiro (MAT)	Kawayu (KAW)	Noboribetsu (NOB)	Goshogake (GOS)	Yukawa (YUK)
Sampling date	'88.8.2	'92.5.17	'92.7.26	'94.5.3	'88.6.14	'88.6.12	'88.6.11	'89.9.19
Atm. Temp. /°C	-	16.7	30.1	27.5	13.1	13.3	16.1	-
Water Temp. /°C	81.0	73.9	51.4	46.4	55.2	81.2	87.0	40
pH	8.8	5.82	7.3	6.35	1.4	1.7	3.03	3
Eh / mV	-	51	312	58	-	-	-	-
Content (mg/dm ³)								
Na ⁺	132	218	281	3340	328	60.5	4.0	56.7
K ⁺	18.2	5.52	19.9	459	52	18.7	1.1	16.8
Mg ²⁺	tr.	1.92	0.13	297	72	11.7	4.6	19.9
Ca ²⁺	2.66	117	156	1240	181	38.2	8.1	50.1
Al ³⁺	0.154	0.2	0.117	0.2	129	64.1	7.2	4.9
Mn ²⁺	none	0.10	0.12	2.4	10	1.2	0.30	3.0
Fe ²⁺ , Fe ³⁺	0.024	0.3	0.03	23.2	84	9.6	5.7	0.6
Cl ⁻	84.3	246	444	7400	890	66.6	2.6	53.8
SO ₄ ²⁻	61.9	418	268	281	2735	1680	146	510
H ₂ SiO ₃	294	217	194	182	143	433	70.6	67.5
ΣCO_2 (meas.)*1	-	-	-	1890	-	-	-	-
ΣCO_2 (calc.)*2	118	0.7	107	-	-	-	-	-

*1: measured.

*2: calculated.

2.3 Determination of lanthanoids

Ln's were determined by neutron activation analysis. The sample pretreatment for neutron irradiation was described in previous papers (Oi, *et al.*, 1990; Honda, *et al.*, 1989a,b). The neutron source was the nuclear reactors for research use at Musashi Institute of Technology (MIT) and at Rikkyo University. The γ -ray measurements were carried out at MIT using an ultra-pure Ge detector and a 4096 channel pulse-height analyzer.

Table 2 The contents of the lanthanoids of the hot spring waters

Sample	Nakabusa (NAK)	Yunotaira (YUN)	Shima (SHI)	Matsushiro (MAT)
Content (ng/dm ³)				
⁵⁷ La	(1.80±0.03) ×10 ²	(9.1±0.3) ×10 ¹	(4±1) ×10 ¹	(7.0±0.4) ×10 ²
⁵⁸ Ce	(3.36±0.03) ×10 ²	(3.4±0.6) ×10 ²	(1.1±0.4) ×10 ²	(1.32±0.05) ×10 ³
⁵⁹ Pr	ND	ND	ND	ND
⁶⁰ Nd	(7.7±0.6) ×10 ¹	ND	ND	(1.0±0.1) ×10 ³
⁶¹ Pm	-	-	-	-
⁶² Sm	(4.5±0.5) ×10 ⁰	(3.5±0.2) ×10 ¹	(1.9±0.2) ×10 ¹	(3.63±0.04) ×10 ²
⁶³ Eu	(6.4±0.4) ×10 ⁻¹	(7.7±0.8) ×10 ⁰	(5±1) ×10 ⁰	(2.17±0.03) ×10 ²
⁶⁴ Gd	ND	ND	ND	(8±1) ×10 ²
⁶⁵ Tb	(2±1) ×10 ⁻¹	ND	ND	(1.68±0.06) ×10 ²
⁶⁶ Dy	ND	(4.2±0.9) ×10 ¹	ND	(1.42±0.05) ×10 ³
⁶⁷ Ho	ND	ND	(1.6±0.6) ×10 ⁰	(3.3±0.5) ×10 ²
⁶⁸ Er	ND	ND	ND	ND
⁶⁹ Tm	ND	ND	ND	(1.60±0.06) ×10 ²
⁷⁰ Yb	(2.0±0.2) ×10 ⁰	(2.7±0.6) ×10 ¹	(1.0±0.2) ×10 ¹	(8.9±0.3) ×10 ²
⁷¹ Lu	(4.8±0.3) ×10 ⁻¹	(6±1) ×10 ⁰	(2.2±0.3) ×10 ⁰	(1.41±0.03) ×10 ²

Sample	Kawayu (KAW)	Noboribetsu (NOB)	Goshogake (GOS)	Yukawa (YUK)
Content (ng/dm ³)				
⁵⁷ La	(1.70±0.02) ×10 ⁴	(4.73±0.06) ×10 ³	(3.53±0.06) ×10 ²	(3.57±0.09) ×10 ²
⁵⁸ Ce	(4.65±0.05) ×10 ⁴	(1.12±0.02) ×10 ⁴	(9.9±0.1) ×10 ²	(9.9±0.2) ×10 ²
⁵⁹ Pr	ND	ND	ND	ND
⁶⁰ Nd	(2.8±0.2) ×10 ⁴	ND	ND	ND
⁶¹ Pm	-	-	-	-
⁶² Sm	(1.03±0.01) ×10 ⁴	(2.03±0.01) ×10 ³	(2.27±0.04) ×10 ²	(2.95±0.04) ×10 ²
⁶³ Eu	(2.24±0.03) ×10 ³	(6.0±0.1) ×10 ²	(6.7±0.1) ×10 ¹	(9.9±0.2) ×10 ¹
⁶⁴ Gd	(1.4±0.1) ×10 ⁴	ND	ND	ND
⁶⁵ Tb	(2.40±0.03) ×10 ³	(4.9±0.2) ×10 ²	(5.42±0.08) ×10 ¹	ND
⁶⁶ Dy	(1.77±0.02) ×10 ⁴	(2.89±0.02) ×10 ³	(3.14±0.03) ×10 ²	(6.6±0.7) ×10 ²
⁶⁷ Ho	(3.2±0.2) ×10 ³	(6.1±0.2) ×10 ²	(5.1±0.3) ×10 ¹	ND
⁶⁸ Er	ND	ND	ND	ND
⁶⁹ Tm	(1.84±0.04) ×10 ³	ND	ND	ND
⁷⁰ Yb	(8.6±0.2) ×10 ³	(1.76±0.03) ×10 ³	(1.58±0.04) ×10 ²	(4.45±0.09) ×10 ²
⁷¹ Lu	(1.41±0.02) ×10 ³	(3.3±0.1) ×10 ²	(2.83±0.09) ×10 ¹	(6.5±0.1) ×10 ¹

± : Errors in Gamma-ray counting.

ND: Not detected.

3. RESULTS AND DISCUSSION

Seven~twelve Ln's were determined. In addition to Pm that has no stable isotope, Pr and Er were not determined in any of the samples. Nuclear characteristics of the nuclides of Pr and Er (^{141}Pr and ^{170}Er) used for the analysis are unfavorable for their determination by the neutron activation analysis(IAEA, 1970; 1974). The

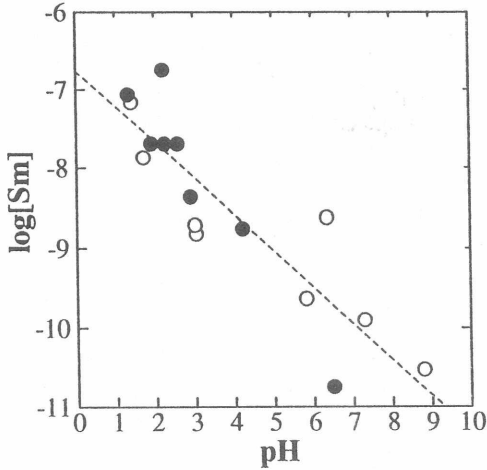


Fig. 2: The plot of the $\log[\text{Sm}]$ against pH. Concentrations are in units of mol/dm^3 .
○, present data; ●, previous data
(Kikawada, et al., 1993; 1995; Oi et al., 1990).

contents of Ln's of the present water samples, expressed in units of ng/dm^3 , are listed in Table 2. They are at $\mu\text{g}/\text{dm}^3$ levels in acidic waters and at ng/dm^3 levels in neutral waters. Contents of Ln's are much lower in the neutral waters than in the acidic waters, but they are higher than those in sea water.

3.1 Correlation of concentrations of lanthanoids with pH

A comparison of the pH values in Table 1 and contents of Ln's in Table 2 suggests the existence of a correlation between them. We chose Sm as a representative of Ln's and plotted the logarithm of the molar concentration of Sm ($[\text{Sm}]$) against the pH in Fig. 2. The data plotted are not only the present ones (○) but also those (●) in the previous papers(Kikawada, et al., 1993; Kikawada, et al. 1995; Oi, et al., 1990). The value of the correlation coefficient (r) is -0.89 with the number of the data points,

$n=16$, showing a strong negative correlation between the pH and $\log[\text{Ln}]$ in the pH range form 1.32 to 8.8. This correlation must be a reflection of the fact that the solubility of a lanthanoid salt/oxide is in general large in acidic solution and decreases with increasing pH of the solution.

3.2 Correlation of concentrations of lanthanoids with concentrations of major components

We calculated the values of r between $[\text{Ln}]$'s and concentrations of major dissolved components, using the present and previous data(Kikawada, et al., 1993; Kikawada, et al. 1995; Oi, et al., 1990). Selected results are summarized in Table 3. Na, Ca and Sm are chosen as representatives of alkali metals, alkaline earth metals and lanthanoids, respectively. We notice in Table 3 a high correlation between $\log[\text{Sm}]$ and $\log[\text{Al}]$ ($r=0.93$, $n=15$) and between $\log[\text{Sm}]$ and $\log[\text{Fe}]$ ($r=0.90$, $n=15$).

Table 3 Values of the correlation coefficient (r) between the concentration of Sm and those of the selected components

	Na	Ca	Al	Fe	Al+Fe	Cl	SO_4	H_2SiO_3
r value	-0.14	0.40	0.93	0.90	0.98	0.27	0.89	0.27

In the previous paper (Kikawada, et al., 1993), we pointed out there existed a high correlation between $\log[\text{Ln}]$'s and the logarithm of the sum of $[\text{Fe}]$ and $[\text{Al}]$ for acidic hot spring waters in the Kusatsu-Shirane volcano area. We made a similar plot in Fig. 3, using the present (○) and previous (●) data. The linear relation in Fig. 3 is mathematically expressed as $\log[\text{Sm}] = 0.893 \log([\text{Al}] + [\text{Fe}]) - 5.45$. The r value with $n=15$ is 0.98. This

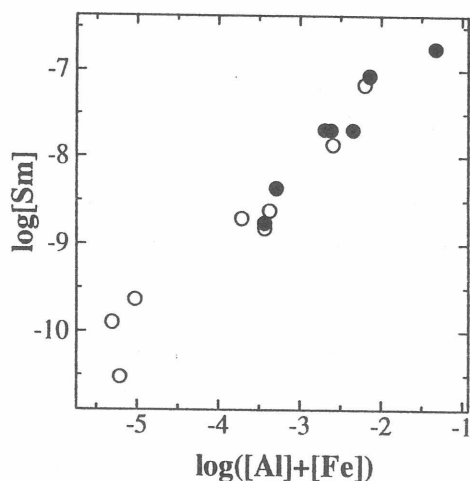


Fig. 3: The plot of $\log[Sr]$ against $\log([Al]+[Fe])$. Concentrations are in units of mol/dm^3 . ○, present data; ●, previous data (Kikawada, *et al.*, 1993, 1995).

result extends the previous conclusion concerning the $[Sr] - ([Al] + [Fe])$ relation in the Kusatsu-Shirane area in two respects. One is that the good $\log[Ln] - \log([Al] + [Fe])$ correlation is not confined to acidic hot spring waters but is extendable to neutral hot spring waters. The other is that the correlation is not confined to one specific area but seems to be generally held, irrespective of area. Thus, the sum of $[Al]$ and $[Fe]$ is an excellent measure of $[Ln]$'s.

To investigate correlation of $[Ln]$'s with $[Al]$ and $[Fe]$ in more detail, $\log[Sr]$ is plotted individually against $\log[Al]$ and $\log[Fe]$ in Figs. 4a and 4b, respectively. A minute but definitive difference can be observed in the two figures. A good correlation between $\log[Sr]$ and $\log[Fe]$ holds over the whole range of the $[Fe]$ examined, although the r value is smaller than that of the $\log[Sr] - \log([Al] + [Fe])$ correlation. Contrary to this, while the

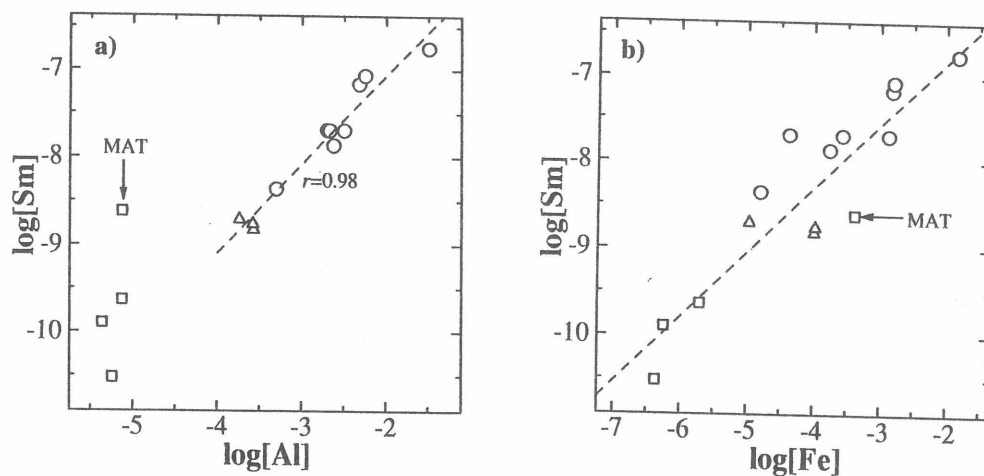


Fig. 4: a) The plot of $\log[Sr]$ against $\log[Al]$ and b) the plot of $\log[Sr]$ against $\log[Fe]$. Concentrations are in units of mol/dm^3 . ○, hot spring waters with $\text{pH} < 3$; △, hot spring waters with $3 \leq \text{pH} < 5$; and □, hot spring waters with $5 \leq \text{pH}$. The broken line in a) is the least-squares-fitted line obtained using the data of $\text{pH} < 5$ and that in b) is the least-squares-fitted line obtained using all the data points.

correlation between $\log[Sr]$ and $\log[Al]$ is quite high in the acidic region ($r = 0.98$ with $n = 11$ in the region of $\text{pH} < 5$; ○ and △ in Fig. 4a), the correlation is ambiguous in the neutral pH region (□ in Fig. 4a).

The seeming non-correlation between $\log[Sr]$ and $\log[Al]$ in the neutral pH region appears attributable to the MAT water. In fact, if we omit the MAT water from Fig. 4a, the linear relation in the acidic pH region can be extended to the neutral pH region quite naturally. $[Al]$ of the MAT water is normal as the concentration of Al in a neutral hot spring water. Thus, the substantial deviation of the MAT point from the correlation line in Fig. 4a is due to its exceptionally high $[Sr]$. $[Fe]$ of the MAT water is also exceptionally high, and hence no anomaly reveals itself in the $\log[Sr] - \log([Al] + [Fe])$ and $\log[Sr] - \log[Fe]$ plots in Figs. 3 and 4b.

$\log[\text{Sm}]$ is plotted against $\log[\text{SO}_4^{2-}]$ and $\log[\text{Cl}^-]$ in Figs.5a and 5b, respectively. As in Figs.4a and 4b, the data for waters with $\text{pH}<3$, $3\leq\text{pH}<5$ and $\text{pH}\geq 5$ are represented respectively by \circ , \triangle and \square . Evidently, $\log[\text{Sm}]$ is more strongly correlated with $\log[\text{SO}_4^{2-}]$ ($r=0.89$) than with $\log[\text{Cl}^-]$ ($r=0.27$). Although the data points are scant, a close examination of Fig. 5a shows that the correlation between $\log[\text{Sm}]$ and $\log[\text{SO}_4^{2-}]$ may be divided into two parts; one for waters with $\text{pH}<5$ (\circ and \triangle) and another for waters with $\text{pH}\geq 5$ (\square). That is, $\log[\text{Sm}]$ seems linearly correlated with $\log[\text{SO}_4^{2-}]$ differently in weakly~strongly acidic region and in neutral region with the exception of the MAT water. This suggests that determining factors of Ln contents are different between acidic and neutral hot spring waters. A similar tendency is also observed for the $\log[\text{Sm}]-\log[\text{Cl}^-]$ correlation in Fig.5b.

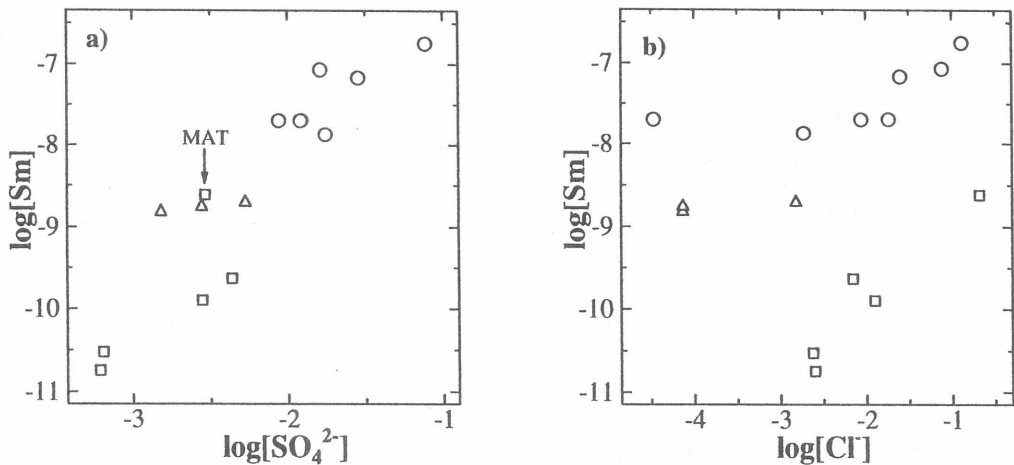


Fig. 5: a) The plot of $\log[\text{Sm}]$ against $\log[\text{SO}_4^{2-}]$ and b) the plot of $\log[\text{Sm}]$ against $\log[\text{Cl}^-]$. Concentrations are in units of mol/dm^3 . \circ , hot spring waters with $\text{pH}<3$; \triangle , hot spring waters with $3\leq\text{pH}<5$; and \square , hot spring waters with $5\leq\text{pH}$.

3.3 Lanthanoid abundance patterns

The variation in the shape of the lanthanoid abundance patterns (Ln patterns) is interesting and informative, although the elucidation of the Ln patterns of the individual hot spring waters is beyond the scope of this study. The Ln pattern is a plot of the ratios of Ln contents in a sample to those in chondrites (Leedeey chondrites) (Masuda, *et al.*, 1973; Masuda, 1975) against the Ln symbols arranged in the order of increasing atomic number. The Ln patterns are depicted for the hot spring waters in this study and additionally for waters (Kusatsu-yubatake, KUS and Tamagawa, TAM) from the previous work (Kikawada, *et al.*, 1995), and for three igneous rocks in Fig.6.

The Ln patterns of the acidic hot spring waters examined are similar to each other, irrespective of the absolute values of $[\text{Ln}]$'s. They are mostly horizontal, with some waters with slight enrichment in the light Ln's. They also resemble the Ln patterns of the igneous rock samples. Since the source of Ln's in a hot spring water is usually rocks the water contacts underground, the resemblance in Ln pattern between the water and rock samples strongly suggests that the Ln pattern of an acidic hot spring water well reflects the pattern of the rocks it contacts underground.

Unlike those of acidic hot spring waters, the Ln patterns of the neutral hot spring waters examined vary from water to water. The Ln patterns of SHI and NAK waters show concave shapes, but the depth of the dent in the pattern is quite different between the two. The YUN water may be regarded as having the Ln pattern similar to those of SHI and NAK waters, but with much shallow dent, or may be regarded as having a Ln pattern similar to

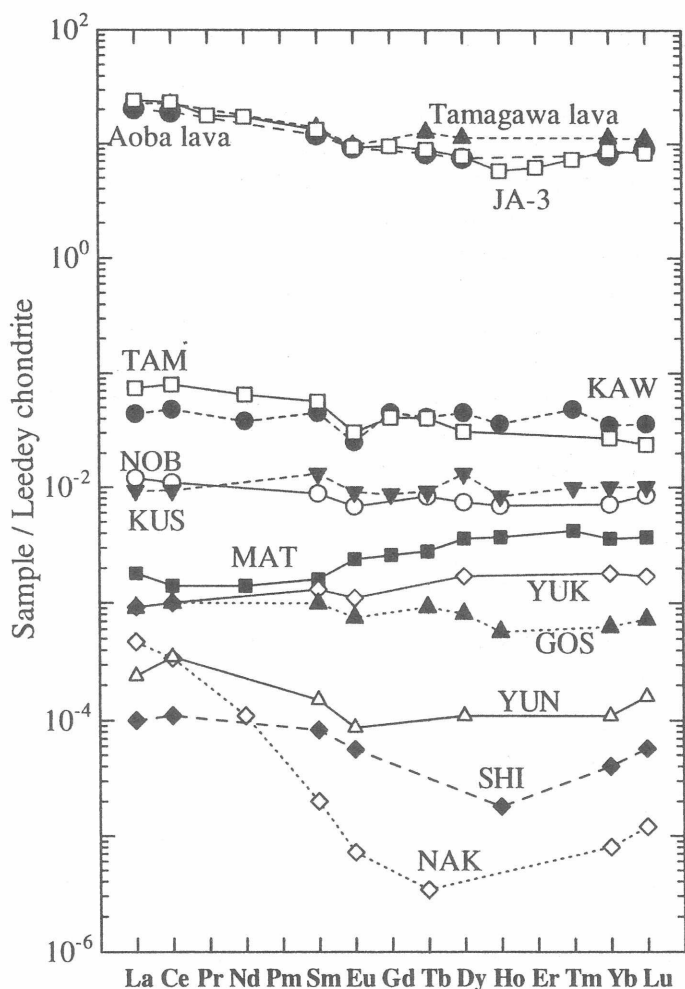


Fig. 6: The lanthanoid abundance patterns of hot spring water and rock samples. The data of TAM and KUS waters and the rocks, all igneous rocks, are taken from the previous paper (Kikawada, *et al.*, 1993). JA-3 is a rock reference sample issued by Geological Survey of Japan (Imai, *et al.*, 1995)

those of the rocks with a slight enrichment in the light Ln's. The MAT water has a Ln pattern with a slight enrichment in the heavy Ln's (It is also unique in that its [Ln]'s are higher than those of the GOS water with pH=3.03).

In neutral hot spring waters in which the solubility of Ln oxides/salts is usually very low, kinds and amounts of coexisting chemical species, especially anionic components, certainly have profound influence on chemical forms of Ln's and hence on their concentrations. This is probably explains the diversity in Ln pattern observed for the neutral hot spring waters.

It has been pointed out by several authors that the complexation of Ln's with carbonate species plays an important role in Ln contents in neutral aqueous environments (Turner, *et al.*, 1981; Michard, *et al.*, 1987; Cantrell, *et al.*, 1987; Millero, 1992; Lee and Byrne, 1993; Johannesson, *et al.*, 1996). For instance, based on speciation calculations modeling fresh water at 25 °C, Turner *et al.* (1981)

estimated that 60-70% of Ln exist as free Ln(III) at pH=6, while Ln hydroxide and carbonate are major Ln species at pH=9. This may be the case with the present hot spring waters. The diversity in the Ln patterns of neutral hot spring waters may be traceable in most part to Ln carbonate complexation, and this complexation may also explain the exceptionally high [Ln]'s of the MAT water. In any case, a detailed speciation is certainly necessitated to elucidate [Ln]'s and Ln patterns of the present neutral hot spring waters in a satisfactory and quantitative manner, which remains unsolved in this paper.

4. CONCLUSION

To summarize, we make the following statements:

- 1) While Ln concentrations in acidic hot spring waters are in general at $\mu\text{g}/\text{dm}^3$ levels, those in neutral hot spring waters are in general at ng/dm^3 levels. It is found that Ln concentrations increase with decreasing pH

of water. This is consistent with the tendency that the solubility of a metal oxide/salts is generally higher at lower pH's.

- 2) There is an excellent correlation between Ln concentrations and the sum of the Al and Fe concentration in the pH range from 1.3 to 8.8. This correlation is not confined to hot spring waters in a restricted area but holds for hot spring waters in various areas in the Japanese Islands. The sum of Al and Fe concentrations was thus a good measure of the Ln contents in acidic and neutral hot spring waters. A good correlation is also found between the Ln concentration and the sulfate ion concentration.
- 3) Ln patterns of acidic hot spring waters, relatively similar to each other, are nearly horizontal, with some with slight enrichment in the light Ln's and seem to reflect quite well Ln patterns of rocks the waters contact underground. Contrary to this, Ln patterns of neutral hot spring waters vary from water to water and seem to be substantially influenced by the kinds and amounts of co-existing chemical species of anions. Most of Ln patterns of the neutral hot spring water examined are of concave shape. The Ln concentrations of the MAT water are exceptionally high and its Ln pattern is quite different from the other neutral hot spring waters examined. This may be due to the exceptionally high ΣCO_2 .

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