

Abundances of rare earth elements in crude oils and their partitions in water

RYOICHI NAKADA,¹ YOSHIO TAKAHASHI,^{1*} GUODONG ZHENG,² YUHEI YAMAMOTO³ and HIROSHI SHIMIZU¹

¹Department of Earth and Planetary Systems Science, Graduate School of Science, Hiroshima University,
Higashi-Hiroshima, Hiroshima 739-8526, Japan

²Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Sciences,
382 West Donggang Road, Lanzhou 730000, China

³Tono Geoscientific Research Unit, Geological Isolation Research and Development Directorate,
Japan Atomic Energy Agency (JAEA), Mizunami, Gifu 509-6132, Japan

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Patterns of the entire range of REE in crude oils and coexisting water, collected from mud volcanoes in Xinjiang Province of China, are reported here for the first time. Crude oils show light REE enriched patterns with flat or depleted patterns in heavy REE, when normalized to chondrite. The REE concentrations in crude oils are larger than those in coexisting water by a factor of more than one hundred. Considering the hydrophobicity of oil and the high ionic characteristics of REE, it is strongly suggested that REE form complexes with ligands present in the crude oils. Based on the ¹³C NMR spectroscopy, it is found that small amounts of phenol and carboxyl groups are contained in the crude oil samples, which could possibly provide complexing sites for REE. REE patterns of crude oils are similar to those of coexisting mud samples collected from the same mud volcanoes, which suggests that the REE in crude oils are derived from rocks and sediments where crude oils were generated.

Keywords: rare earth elements, crude oil, partition coefficient, NMR, Junggar Basin

INTRODUCTION

Rare earth elements (REE) show similar chemical properties with each other, because the outermost electron orbits are same. Their chemical similarities induce systematic partition in various natural systems. Consequently, relative abundances of REE, namely REE pattern, reflect chemical processes occurring in various systems on the earth. These properties enables REE pattern to be a useful effective geochemical tracer (Henderson, 1984). Recently, Zhang *et al.* (2009) suggested that REE patterns of crude oils could provide genetic information on the oils, while Akinlua *et al.* (2008) noted that REE contents of oils are useful in the classification of oils. However, the existing quantum of REE data of crude oil samples is still insufficient. Complete REE patterns are neither reported by Akinlua *et al.* (2008) nor by Takeda and Arikawa (2005). Here we report REE abundances measured in crude oils from the Xingiang Province, China to provide more data towards the building of a database on REE abundances of crude oils.

A correct interpretation of the chemical state of REE in crude oils is necessary to ascertain genetic processes

and provenances of the oils. Further it controls the shape of REE patterns which depends on the REE partition of species between the aqueous and the solid phases (Byrne and Kim, 1990; Takahashi *et al.*, 2005; Yamamoto *et al.*, 2010). For example, complexation with carbonate ions induces a preferential distribution of heavy-REE (HREE) into the aqueous phase (e.g., Byrne and Sholkovitz, 1996; Johannesson *et al.*, 1996). Thus, it is expected that REE distribution between crude oil and water phase involves the information of REE species incorporated into the crude oil. Consequently, REE abundances were measured in both crude oils and coexisting water.

SAMPLES AND METHODS

Samples

Samples of crude oils along with their coexisting muddy water were collected from the mud volcanoes along the southern margin of the Junggar Basin in Xinjiang Uyghur Autonomous Region of China. The Xinjiang Province can be divided into two sedimentary basins, the Junggar Basin in the north and the Tarim Basin, south of the Tianshan Mountains. The Xinjiang Province is well known for its large oil deposits (e.g., Lee, 1985; Desheng, 1996), and several oil fields occur along the margin of these basins. There are several active mud volcanoes along the south margin of the Junggar Basin

*Corresponding author (e-mail: ytakaha@hiroshima-u.ac.jp)

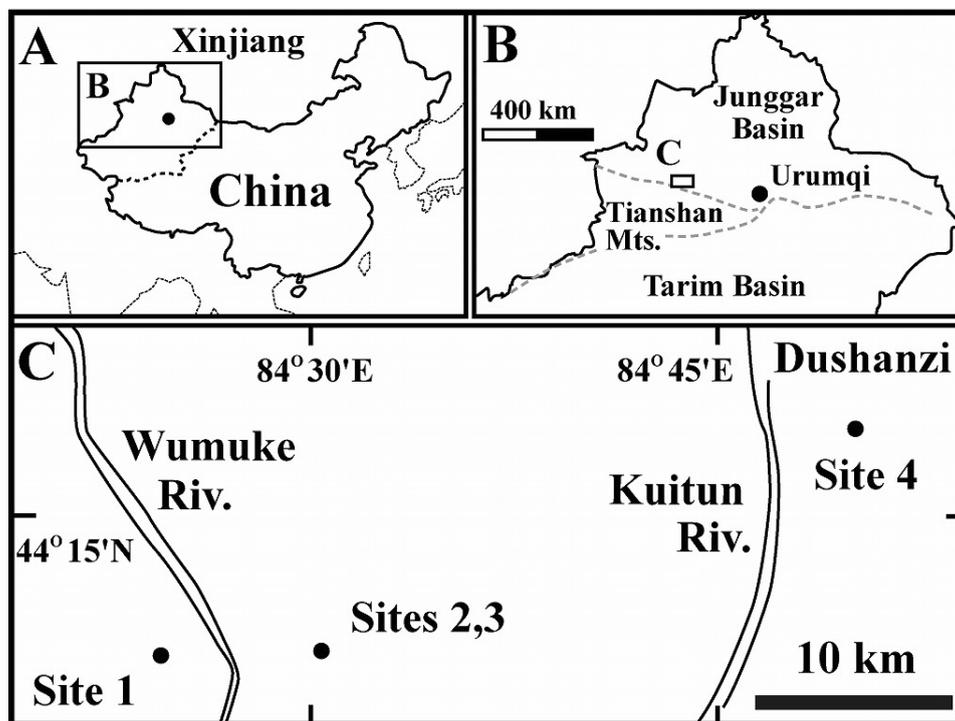


Fig. 1. Schematic map of sampling locations. Map A depicts entire China and the dashed line represents the border of Xinjiang Uyghur Autonomous Region. Map B depicts three quarters of Xinjiang and the dashed lines represent Tianshan Mountains. Location of a square marked on map B is enlarged to map C. Site 4 is situated near Dushanzi District.

(Fu *et al.*, 2007), erupting gas, oil, water and mud. Samples were collected from four sites along the southern margin of the Junggar Basin (Fig. 1). Site 1 is located in an area where many mud pies, flat mud extrusive feature, discharge mud and gas. Sites 2 and 3 are “twin” mud volcanoes which are located in a mountainous region, while site 4 is situated near the Dushanzi refineries. Oil slick and crude oil were seen in all sites studied here. Samples of muddy water were collected directly from the crater of mud volcanoes, and were filtrated on site by 0.45 μm membrane filters. After filtration, samples were acidified to 2 wt.% nitric acid solution to prevent the precipitation of Fe and REE. Samples of crude oils were centrifuged for 20 minutes at 2,000 rpm to separate oil from water and mud. Previous studies (e.g., Clayton *et al.*, 1997) indicate that crude oil samples that we collected in the Dushanzi area have relatively lower maturity with predominance of saturated hydrocarbons relative to aromatics and non-hydrocarbons.

Analytical methods

To determine the molecular structure of sampled crude oils, nuclear magnetic resonance (NMR) spectroscopy was conducted on carbon atom (^{13}C NMR) for samples from sites 2 and 4 using a JEOL ECA600 at the Natural Science Center for Basic Research and Development (N-

BARD), Hiroshima University. The NMR spectra for other crude oils could not be obtained due to the low amount of collected samples. CHNS analysis was not possible because the weight of the oil could not be correctly measured due to the volatilization of volatile components.

The difficulty in measuring the concentrations of REE in crude oils lies in the separation of REE from crude oils (Akinlua *et al.*, 2008; Takeda and Arikawa, 2005). If organic matter is not perfectly decomposed, the residual organic matter can have harmful effects on the measurement of REE by inductively coupled plasma mass spectrometry (ICP-MS); (i) introduction of organic matter into the ICP-MS leads to the formation of carbon-containing ions such as C^{2+} , CO^{2+} and ArC^{+} (Lord, 1991); (ii) some carbon-bearing materials can be deposited at the interface into the mass spectrometer of the ICP-MS; (iii) high viscosity and boiling point of crude oils lower their atomization efficiency. Thus, a complete decomposition of organic matter is necessary to determine the concentration of REE in crude oils. In this study, about 0.1 g of weighed crude oil was decomposed by heating (at *ca.* 180°C) for a week in 68 wt.% HNO_3 solution in a Teflon vessel with a screw cap. After evaporation, the organic matter was thoroughly digested using H_2SO_4 (at *ca.* 230°C). The samples were evaporated again at 230°C and

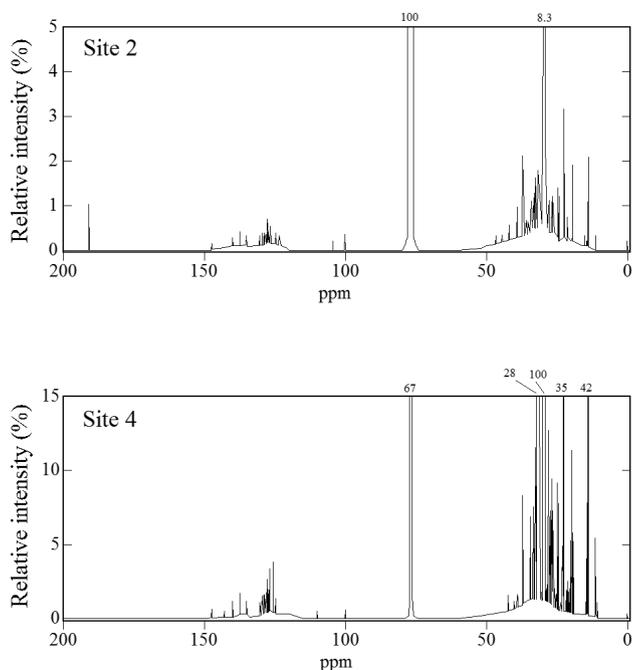


Fig. 2. ^{13}C NMR spectra of crude oil samples at sites 2 and 4. The numbers at the top of the figures indicate the relative intensities of the peaks presently out of range of the figures.

finally dissolved in 2 wt.% HNO_3 and analyzed using an Agilent 7500 ICP-MS. In this study, Y was also determined as well as the lanthanoids. The loss of REE during decomposition, evaporation and redissolution processes is negligible as suggested by results from rock samples treated in the same way (Takahashi *et al.*, 2002).

The REE concentrations in water samples were also determined by ICP-MS. Since concentrations of some REE in groundwater are generally lower than ppt level, REE were pre-concentrated using a column (diameter 1.0 cm, length: 10 cm) loaded with a cation exchange resin AG50W-X8 (Takahashi *et al.*, 2002). About 250 mL of weighed sample was introduced into the column. Major cations were eluted by 2 M HCl solutions and REE were eluted by 40 mL of 6 M HCl solution. The eluted solution containing REE was evaporated and redissolved by 2 wt.% HNO_3 solution, which was used for the REE determination by ICP-MS. In addition, total organic carbon (TOC) in water samples was determined using a TOC analyzer (TOC- V_{CSH} ; Shimadzu). Abundance of iron (Fe) in water samples was determined using an ICP-atomic emission spectrometry (ICP-AES; SII Nano Technology).

RESULTS

The ^{13}C NMR spectra of two samples (sites 2 and 4) show several peaks from 10 to 60 ppm, around 77 ppm

Table 1. REE concentrations ($\mu\text{g/g}$) in crude oil samples

Element	Site 1	Site 2	Site 3	Site 4
Y	22.8	337	1350	242
La	33.6	288	861	386
Ce	66.6	662	2150	843
Pr	7.91	59	278	102
Nd	30.1	233	1140	397
Sm	6.52	47.2	182	84.4
Eu	1.55	11.2	38.2	16.7
Gd	5.70	44.4	166	74.6
Tb	1.01	8.1	32.4	12.0
Dy	5.31	48.0	187	62.2
Ho	1.08	10.1	39.2	11.0
Er	3.23	32.8	125	29.3
Tm	0.446	4.74	17.9	3.45
Yb	2.98	32.4	124	21.0
Lu	0.437	4.93	18.4	2.77
ΣREE	189	1820	6710	2290

and from 120 to 150 ppm. These peaks, often observed in crude oils (Hasan *et al.*, 1983; Sharma *et al.*, 2008) can be ascribed to the presence of functional groups of aliphatic carbons (0–70 ppm), formyl groups (77 ppm) and aromatic carbons (110–160 ppm), respectively (Fig. 2). In addition, we observed peaks at 145 ppm for crude oil samples collected at sites 2 and 4, which suggest the presence of phenol groups (Thorn *et al.*, 1989). A peak at 191 ppm observed in a crude oil sample from site 2 is due to the presence of a carboxyl group.

The REE concentrations in crude oil samples have been normalized to a CI chondrite (Anders and Grevesse, 1989; Table 1, Fig. 3a). Light-REE (LREE) enrichment is observed in all the REE patterns of crude oils. Flat heavy-REE (HREE) patterns are observed for oil samples collected from sites 1, 2 and 3, while HREE-depleted pattern is observed for that collected from site 4. The former three samples from sites 1 to 3 have convex patterns in the Gd–Tb–Dy–Ho span, i.e., M-type effect shown in the third tetrad (Masuda *et al.*, 1987). The concentrations of REE collected from site 3 are the highest among all collected crude oils, while site 1 has the lowest REE concentrations. Although the concentrations of REE have wide variations among each site, such a variation can be caused by different abundances of functional groups in crude oils (Zhang *et al.*, 2009). All the crude oil samples showed negative Eu anomalies, whereas no distinct Ce anomalies were found.

The concentrations of REE in coexisting water were also determined and have been normalized to the CI chondrite (Anders and Grevesse, 1989; Table 2, Fig. 3b). The chondrite-normalized REE pattern for water sample of site 1 is enriched in LREE, while that for water collected at site 2 shows a V-shaped pattern (Fig. 3b). Both

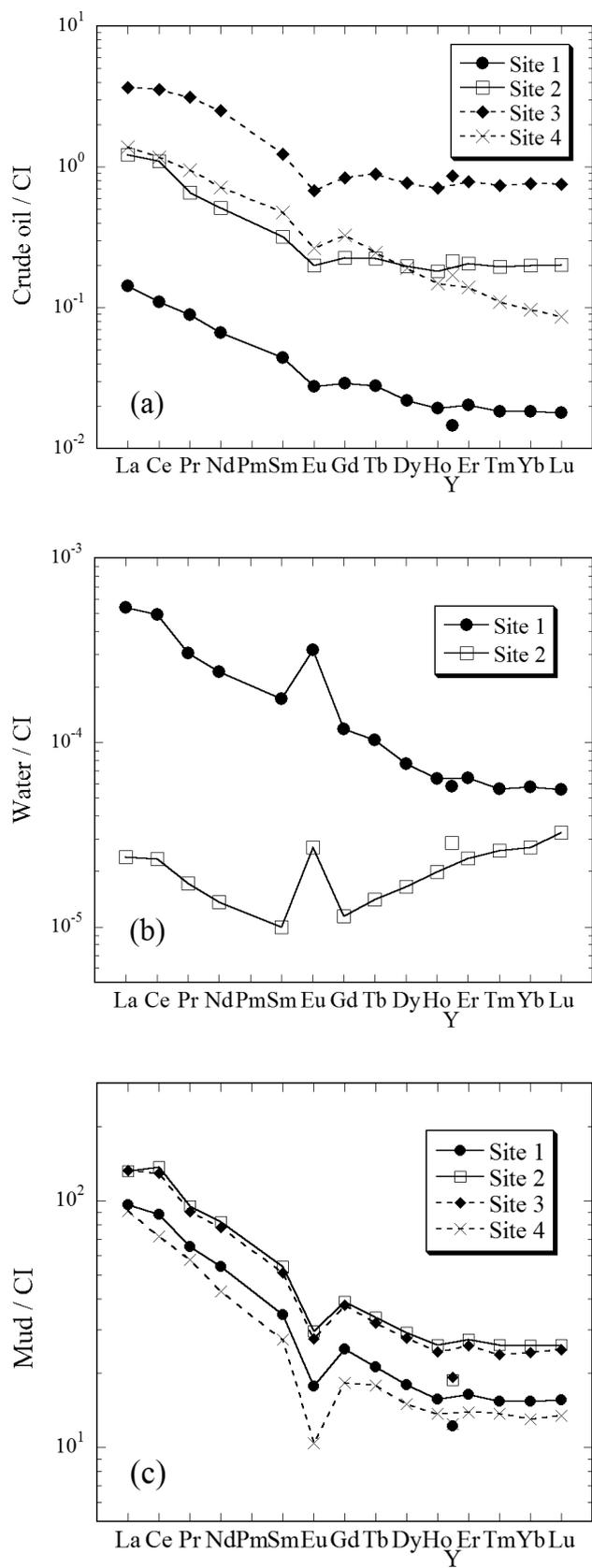


Fig. 3.

REE patterns have distinct positive Eu and small positive Ce anomalies, respectively. The results of XRD analysis of mud samples showed that the mud contained feldspars. Thus, the positive Eu anomalies shown in the REE patterns can be induced by the dissolution of anorthite (Byrne and Sholkovitz, 1996), while the positive Ce anomalies can be related to the formation of Ce(IV)-carbonate species in alkaline water with a high carbonate content (Möller and Bau, 1993). Actually, according to the classification of the “true Ce anomaly” suggested by Bau and Dulski (1996), water sample collected at site 1 exhibits positive Ce anomaly. On the other hand, water sample collected at site 2 shows negative La anomaly, suggesting the presence of M-type tetrad effect as seen in the upward concave curve in the La–Ce–Pr–Nd span in the REE patterns (e.g., Bau, 1996; Takahashi *et al.*, 2002). The REE concentrations in mud and surface soil samples have been normalized to the CI chondrite (Anders and Grevesse, 1989; Table 3, Fig. 3c). All samples are rich in LREE, typical for sedimentary rocks, with negative Eu anomalies with Eu/Eu* varying from 0.47 to 0.68.

DISCUSSION

Comparison of REE abundances in crude oils with previous reports

Previous reports on REE abundances in crude oils (Akinlua *et al.*, 2008; Takeda and Arikawa, 2005) mostly provided patterns of LREE, but not the complete REE patterns. Total REE abundances reported by Akinlua *et al.* (2008) and Takeda and Arikawa (2005) are less than 3 ng/g. Recently, Zhang *et al.* (2009) reported REE patterns for crude oils, which show a zigzag structure with enrichments of Nd, Eu, Tb, Ho, Tm and Lu in all their crude oil samples except one. They suggested that the enrichment of MREE with an even number of f electrons and the enrichment of HREE in crude oils result from higher stability constants of organic complexes with these elements. However, such zigzag REE patterns can be an analytical artifact, because the odd numbered REE generally occur in lower concentrations, often well below the detection limit of available instruments. Our report of complete REE patterns of crude oils is thus important, since resolution of the fine structure of REE patterns allows us to estimate the REE species in the samples. Total REE abundances of the crude oil samples showing zigzag patterns in Zhang *et al.* (2009) are less than 30 $\mu\text{g/g}$, while

Fig. 3. Chondrite-normalized REE patterns of (a) crude oil, (b) water and (c) mud samples collected at mud volcanoes in Xinjiang Province, China. REE concentrations of CI chondrite are taken from Anders and Grevesse (1989).

Table 2. REE concentrations (ng/L), pH, alkalinity (mM), calculated CO_3^{2-} concentrations (mM), TOC (mg/L) and concentration of iron ($\mu\text{g/L}$) in water samples

Element	Site 1	Site 2
Y	90.7	44.5
La	126	5.61
Ce	299	14.1
Pr	27.2	1.53
Nd	110	6.17
Sm	25.3	1.47
Eu	17.9	1.52
Gd	23.2	2.26
Tb	3.73	0.511
Dy	18.6	4.03
Ho	3.54	1.10
Er	10.2	3.74
Tm	1.35	0.630
Yb	9.31	4.39
Lu	1.35	0.790
ΣREE	767	92.3
pH	8.40	7.35
Alkalinity	71	53
CO_3^{2-}	70	48
TOC	7.20	6.54
Fe	4.52	3.85

the sample with smooth pattern contains more than 140 $\mu\text{g/g}$ (Zhang *et al.*, 2009). Compared with the Zhang *et al.* (2009) data, our crude oil samples have higher REE abundances (except for Y), *ca.* 160, 1500, 5360, 2050 $\mu\text{g/g}$ for sites 1, 2, 3 and 4, respectively (Table 1).

REE complexes in crude oils

It must be noted that concentrations of REE in crude oils are much larger than those in water. The preferential REE partitioning into the crude oil rather than water suggests that REE form neutral species and complexes with organic matter in the oil phase, because crude oil is hydrophobic and REE have high ionic properties. ^{13}C NMR spectra of crude oils collected from the sites 2 and 4 demonstrate the presence of aliphatic carbons, formyl group, aromatic carbons and phenol groups. Furthermore, the crude oil collected from site 2 shows a peak at 191 ppm, which indicates the presence of carboxyl group (Fig. 2). The phenol and carboxyl groups can act as binding sites for metal cations, similarly to metal complexation in humic substances (Tipping, 2002). Thus, it is suggested that the large partition of REE into crude oil relative to water can be caused by the formation of complexes with these ligands occurring in crude oils.

The evidence that REE form complexes with ligands in the oils is supported by the M-type tetrad in the Gd–

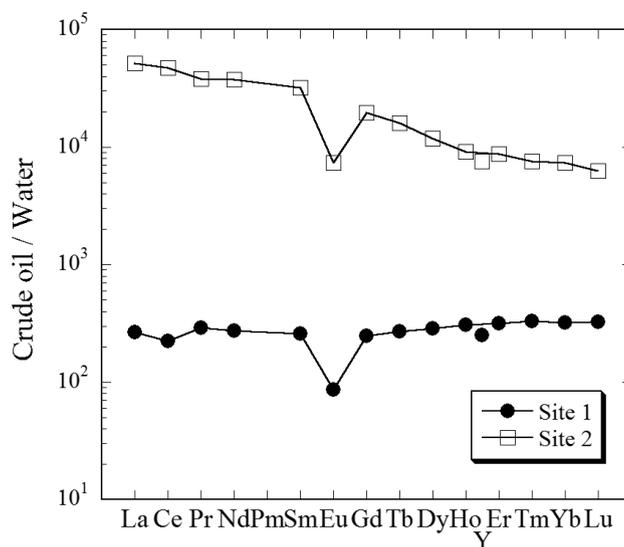


Fig. 4. Partition coefficients between crude oil and water.

Tb–Dy–Ho span observed for some of our oil samples. It has been often reported that M-type tetrad is observed in complex formation of REE with ligands such as found in the complexation with extractant in organic phases in liquid-liquid extraction system (Peppard *et al.*, 1969; Yaita and Tachimori, 1996; Yamamoto *et al.*, 2010). In addition, the differences observed in the REE patterns between crude oils collected from sites 2 and 4 could be due to the presence of different REE complexes they are bound to.

Partition coefficients of REE between crude oil and water

REE partition coefficients between crude oil and water were calculated for samples from sites 1 and 2, where both phases were collected. Partition coefficient patterns show that the coefficients for the samples collected from site 2 are higher than those of the samples collected from site 1 by more than an order of magnitude, with negative Eu anomalies presented in both patterns (Fig. 4). If REE in both phases were in equilibrium, the degree of Eu anomalies would be expected to be similar between oil and water phases, which obviously is not the case. Our results suggest that although the two phases are in contact, the REE partition between oil and water is not at equilibrium. The strong binding of REE in the oil phase perhaps inhibits the redistribution of REE into the water phase. This might also explain the large discrepancy of the partition coefficients calculated in samples collected from sites 1 and 2.

To evaluate the complexation of REE in the oil phase, it is better to obtain partition of REE in the oil phase relative to free REE ions in water. The partition coefficient

Table 3. REE abundances (mg/kg) of mud and rocks determined using ICP-MS

Element	Rock (i)	Mud Site 1	Rock (ii)	Mud Site 2	Mud Site 3	Rock (iii)	Mud Site 4
Y	23.6	19.0	28.7	29.2	30.1	21.2	19.4
La	30.5	22.6	29.5	31.0	31.3	26.7	21.4
Ce	75.7	53.1	75.4	82.5	78.2	57.8	43.3
Pr	8.00	5.80	7.91	8.50	8.07	6.11	5.15
Nd	34.1	24.4	34.3	37.2	35.2	25.9	19.5
Sm	7.03	5.07	7.41	7.98	7.52	5.48	4.03
Eu	1.36	1.00	1.62	1.66	1.55	1.10	0.583
Gd	6.55	4.91	7.17	7.67	7.40	5.33	3.60
Tb	1.03	0.769	1.15	1.22	1.16	0.847	0.646
Dy	5.93	4.35	6.84	7.10	6.76	4.98	3.63
Ho	1.18	0.869	1.40	1.45	1.36	1.00	0.764
Er	3.50	2.60	4.22	4.35	4.10	3.02	2.21
Tm	0.508	0.373	0.606	0.628	0.576	0.421	0.331
Yb	3.34	2.51	4.09	4.20	3.93	2.87	2.11
Lu	0.503	0.378	0.618	0.634	0.604	0.429	0.326
Ce/Ce*	1.16	1.11	1.18	1.22	1.18	1.09	0.99
Eu/Eu*	0.61	0.61	0.68	0.64	0.63	0.62	0.47
ΣREE	203	148	211	225	218	163	127

$Ce/Ce^* = Ce_{CN} / \sqrt{La_{CN} \times Pr_{CN}}$, $Eu/Eu^* = Eu_{CN} / \sqrt{Sm_{CN} \times Gd_{CN}}$ where CN means chondrite normalized values.

Note that rock (i) is a sedimentary rock sample collected around mud volcanoes locate site 1, rock (ii) is collected around sites 2 and 3, and rock (iii) is collected around site 4.

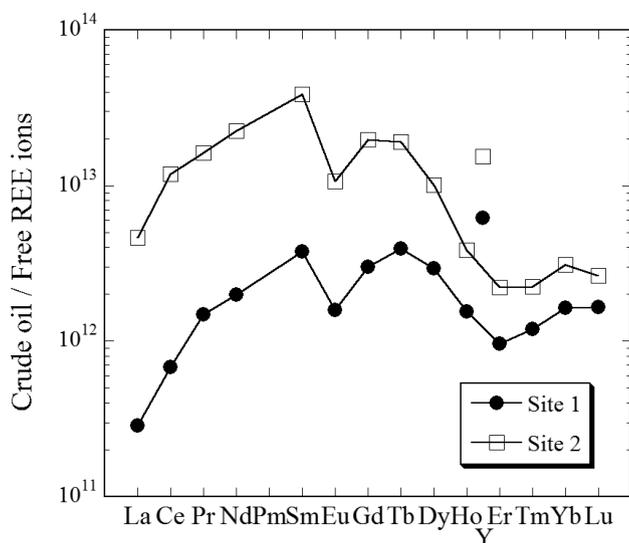


Fig. 5. Partition coefficients between crude oil and free REE ions in water.

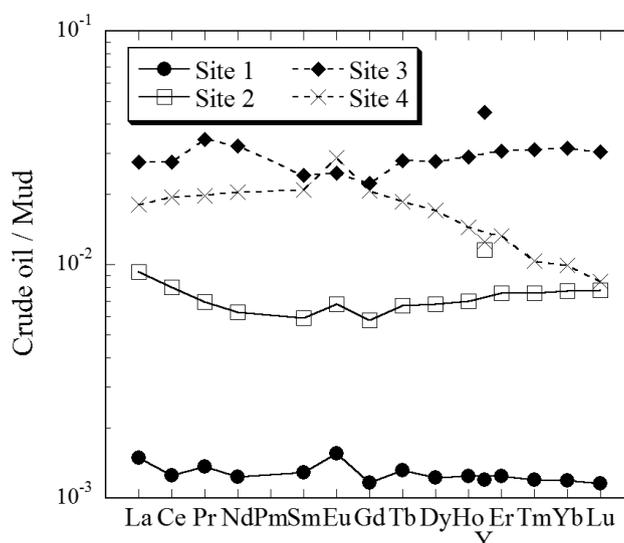


Fig. 6. Coexisting mud-normalized REE patterns of crude oils.

of REE in the oils phase to free ions in the aqueous phase can be directly compared with the stability constants (β) of REE with known ligands ($=L^{z-}$) formulated for free REE ions ($=Ln^{3+}$) as $\beta_{REE-L} = [Ln-L^{(3-z)+}] / ([Ln^{3+}][L^{z-}]$). A speciation calculation using the Windermere Humic Aqueous Model (WHAM; Tipping, 1994) was conducted to determine the free REE ions in our water samples. In-

trinsic stability constant ($\log K_{MA}$) values of REE and humic complexes were obtained from Yamamoto *et al.* (2010). We assumed that humic acid constitutes 50% of the total organic carbon and that all iron dissolved in the water is bound to humic acid as Fe(III) (Herbert and Bertsch, 1995; Yamamoto *et al.*, 2009). Based on the concentrations of free REE ions, we reevaluated the parti-

tion coefficient of REE into oil phase normalized by free REE ions in the water. A relatively high pH and a large content of carbonate ions in the water samples (Table 2) can lead to lower fractions of free REE ions for the heavier REE. Although a complete equilibrium of REE between oil and water phases may not be attained, the REE partition coefficients to free REE ions in water phase clearly show enrichments for Sm and Lu (Fig. 5). Such a trend is known for the stability constants of REE with carboxylic acids (Smith and Martell, 1987), which were detected in our crude oil samples by ^{13}C NMR spectra. It is most likely that the complexation of REE with these ligands induces larger partitions of REE into crude oils relative to the water phase.

Origin of REE in crude oil

The REE patterns of the crude oils were compared with those of coexisting mud (Table 3; Fig. 6). Samples of crude oils collected from sites 1, 2 and 3 show flat mud-normalized REE patterns, while the crude oil collected from site 4 shows an HREE-depleted pattern. The flat patterns suggest that REE in crude oils principally inherit those in coexisting mud which originates from surrounding sedimentary rocks. The HREE depletion observed at sample collected from site 4 in Fig. 6 can be due to the lower abundances of HREE in crude oil itself shown in Fig. 3a, since REE patterns of mud samples erupted from mud volcanoes were very similar among all sites (Table 3). The absence of carboxyl groups, as discussed above, can cause the depletion of HREE in the oil samples. Thus, we speculate that REE in crude oil sample collected from site 4 is also derived originally from sediments.

Difference of Y/Ho ratio shown in Fig. 6 can be caused by the difference of their source reservoirs, in particular REE abundances in water contacted with oil in each reservoir. Although the Y/Ho ratios of mud samples are almost the same in a range from 20.1 to 25.4 (Fig. 3c), the ratio varies greatly among water samples with the ratio of 25.6 for site 1 while 40.5 for site 2 (Fig. 3b). Water-rock interactions can induce the increase of Y/Ho ratio in water relative to the original rock source to various extents depending on the degree of water-rock interaction (Bau, 1996; Takahashi *et al.*, 2002). Since REE abundances in water primarily affect REE abundances in oils, the Y/Ho ratio in oil can be variable depending on the ratio in water in each system. In addition, water-rock interaction causes positive Eu anomalies in water samples, which in turn induces positive Eu anomaly in the oil normalized to mud as shown in Fig. 6. The degree of Eu anomaly is also dependent on the water-rock interaction in each system. Thus, both Y/Ho ratio and degree of Eu anomaly are variable among different samples (Fig. 6).

The cerium anomaly, which is often observed in plants

(Fu *et al.*, 1998) or in marine organic matters (e.g., Fleet, 1984), is absent in our crude oil samples. If REE in crude oils are originated from the precursors of oils such as the plants and the marine organic matters, it is most likely that REE patterns of the crude oils have Ce anomalies, which is obviously not the case in our samples. This implies that REE in our crude oil samples are originated from those in surrounding rocks during diagenetic processes associated to the maturation of the crude oils.

CONCLUSIONS

The study of REE abundance patterns in crude oils and coexisting water and mud samples from the Xingiang Province, China, brought to the following conclusions:

- (1) REE in crude oils derived from their source rocks and sediments;
- (2) REE in crude oils mainly form carboxylate and phenolate complexes, which induce a larger partition of REE into the crude oil relative to the coexisting water phase.

Due to a lack of reported data of REE in crude oils, the present study can constitute a preliminary database which may contribute to understand the genetic processes of maturation of hydrocarbons.

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