



# Impact of the decarboxylation reaction on rare earth elements binding to organic matter: From humic substances to crude oil



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## ABSTRACT

The rare earth elements (REEs) are widely used as tracers in studies of various geochemical systems. Their behavior in natural systems such as groundwater and river water is strongly influenced by organic complexation. The behavior of REE during the maturation of organic compounds (e.g., during decarboxylation reaction) is not well understood, and thus forms the topic of this study. In this study, the behavior of REEs during the maturation of organic matters was examined by heating experiments and analysis of crude oil. Heating increased the release of REEs from humic acid, and was associated with a decreased concentration of carboxyl groups in the humic acid. Ternary heating experiments (humic acid + REE + slate) led to the re-adsorption of released REEs to the slate. Carbon-13 nuclear magnetic resonance spectroscopy (<sup>13</sup>C NMR) did not show peaks corresponding to carboxyl groups in the natural crude oils examined here, meaning that the oils are more highly mature than other oils containing carboxyl groups. The abundances of REEs in the oils without carboxyl groups (this study) were about three orders of magnitude lower than those previously found in oils with carboxyl groups, suggesting that the carboxyl group is important to REE retention in crude oil. These findings suggest that a considerable amount of REEs is released during the early stage of diagenesis, or during decarboxylation, and is likely to be subsequently adsorbed to the petroleum source rock. The variation in the Y/Ho ratio among oils suggests the occurrence of a secondary distribution to the oil-hosting rock. Other metallic elements that behave similarly to REEs, such as Ca, Al, and Fe, can also be released from the organic phase, whereas those that behave differently from the REEs may be retained.

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## 1. Introduction

Rare earth elements (REEs) have several characteristics that make them suitable as geochemical tracers (e.g., Henderson, 1984; Taylor and McLennan, 1988). In particular, the unique characteristics shown in REE patterns, namely Ce and Eu anomalies, the Y/Ho ratio, and M- and W-type tetrad effects, provide information on REE behavior in two systems contacting one another, such as sedimentary process (e.g., Schmidt et al., 1963; Wildman and Haskin, 1965; Elderfield and Pagett, 1986; McLennan, 1989), and low- and high-temperature water–rock interactions (e.g., Klinkhammer et al., 1983; Michard et al., 1983; Bau et al., 1998; Takahashi et al., 2002). REEs are also useful for studying organic chemical processes through their adsorption to organic compounds, because humic substances are adsorptive media in

natural groundwater, river water, and seawater (e.g., Takahashi et al., 1997; Tang and Johannesson, 2003, 2010; Pourret et al., 2007a,b). Despite the great importance of these elements to organic geochemistry, their behavior during maturation and in matured organic materials, or crude oil, has not been well studied.

Oils may be classified by their REE contents, the patterns of which can provide a genetic information about the oils (Akinlua et al., 2008; Zhang et al., 2009). However, Akinlua et al. (2008) did not report the abundances of odd-numbered heavy-REEs (HREEs); Tb, Ho, Tm, and Lu. Zhang et al. (2009) reported the abundances of the whole lanthanide series in crude oils, although the anomalous zig-zag patterns that emerged when normalized to mudstone suggest that their REE abundances contain errors. In addition, these reports did not give the abundance of Y, which is useful in discussing water–rock interactions (Bau et al., 1997). The first work on the entire range of REE concentrations with a smooth chondrite-normalized pattern reported that REE concentrations in crude oils are larger than those in coexisting water by more than two orders of magnitude (Nakada et al., 2010). This result, showing a high affinity between REEs and crude oils, appears to be unusual,

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because REEs show ionic characteristics (i.e., high stability in water), while crude oil is hydrophobic. The same work found phenol and carboxyl groups using carbon-13 nuclear magnetic resonance ( $^{13}\text{C}$  NMR), and the partition coefficients of REEs between oil and free ions in water showed that REEs formed complexes with carboxyl groups. Carboxyl and phenol groups show a high affinity for REEs (Sonke and Salters, 2006; Pourret et al., 2007b; Stern et al., 2007; Marsac et al., 2010, 2011; and references therein), which results in the higher REE abundance in crude oils relative to the coexisting water phase. Considering the genetic process of oils, or maturation process of organic matters, carboxylate complexes are not expected to be found in oil because decarboxylation reaction is thought to occur during maturation (diagenesis and catagenesis) at elevated temperature. The lack of carboxyl groups can affect the presence of REEs, because they lose a major complex-forming site. In other words, it is expected that REE abundances in oils decrease as decarboxylation reactions progress. Although some studies have reported the thermal decomposition of humic acid, they did not focus on the release of metal ions (e.g., Lu et al., 1997; Martyniuk et al., 2001). Therefore, in this study we examine the behavior of REEs during maturation (specifically decarboxylation) by performing heating experiments of humic acid, which forms carboxylate complex with REEs, and measuring the REE concentrations in various oil samples.

## 2. Material and methods

### 2.1. Heating experiment of REE-doped humic acid solution

Approximately 0.1 g humic acid (Aldrich) was dissolved into 100 g ultrapure water (hereafter, called as humic solution). The humic solution was passed through a mixed cellulose filter (0.45  $\mu\text{m}$ ; ADVANTEC) to remove suspended organic matter, although none was identified. The ionic strength of the solution was fixed to 0.1 M using NaCl. Humic solution (7 g) was added to a Teflon vessel with 1 g of dilute REE solution (Spex Certiprep., USA) containing all REEs except Pm. The concentration of Y in the REE-doped humic solution was approximately 30 nM, and those of lanthanides were 15–20 nM (La–Lu). Assuming that all the dissociated ligands in the humic substance were carboxyl groups, the REE loading level is calculated to be 50 nmol/eq. The REE-doped humic solution was adjusted to pH 6.0 using dilute NaOH or HCl to prevent precipitation of humic acid, and then shaken for 24 h. The complex formation constants of REEs on humic acid (e.g., Takahashi et al., 1997; Tang and Johannesson, 2003, 2010; Pourret et al., 2007a,b; Yamamoto et al., 2010) suggest that almost all the REEs added to the humic solution should be complexed with carboxyl groups. After shaking, the solution was heated at 40, 60, 80, 100, 120, 140, and 160  $^{\circ}\text{C}$  for 72 h to evaluate the decarboxylation reaction (binary system; Fig. 1). For comparison, 0.1 g of powdered slate (Geological Survey of Japan reference sample: JSI-1; Imai et al., 1996) was placed in a Teflon bottle with REE-doped humic solution to examine the possible redistribution of REE following decarboxylation (ternary system; Fig. 1). Because slate, originally derived from fine-grained mudstone or shale, contains clays after low-grade regional metamorphism, it is suitable to use in simulating reactions occurring in an oil reservoir. One fraction of the ternary system was shaken at 25  $^{\circ}\text{C}$  for 72 h, and the other fraction was heated at 40, 60, 80, 100, 120, 140, and 160  $^{\circ}\text{C}$  for 72 h. The pH was measured both before and after the experimental period, as water–rock interactions can increase the pH through the dissolution of alkaline minerals. However, no significant increase in pH was observed during our experimental period.

At the end of the experimental period, REEs in the humic solution were solvent extracted using di(2-ethylhexyl)phosphoric acid (DEHP) for the binary system (Yamamoto et al., 2010). The humic solution was placed in toluene containing DEHP, and pH was adjusted to 4.7 using acetic acid. After shaking for 72 h, which was long enough to reach equilibrium, the two phases were separated. The slate was

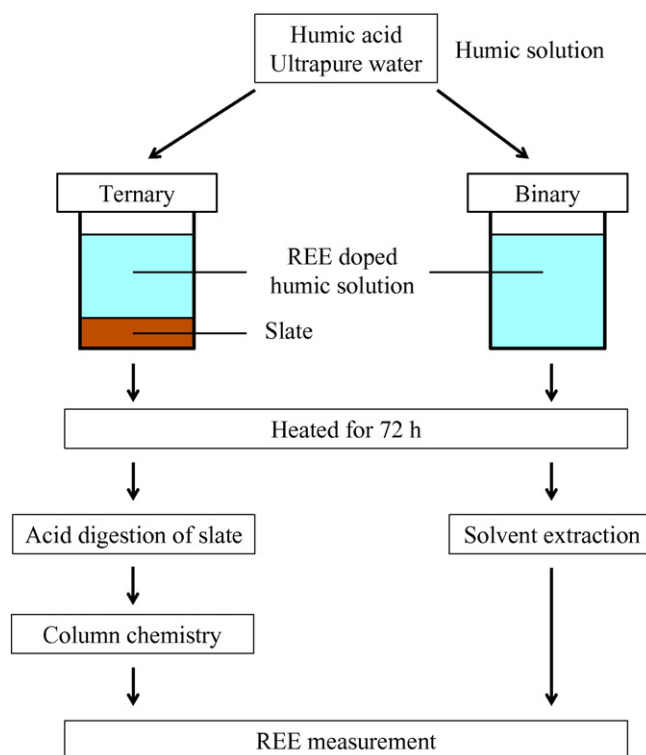


Fig. 1. Schematic illustration of the experimental procedure.

separated from the ternary system using a mixed cellulose filter (0.45  $\mu\text{m}$ ; ADVANTEC) after cooling to room temperature. The filtrated slate was finally dissolved in 0.5 M HCl solution following digestion in a mixture of HF, HClO<sub>4</sub>, and HNO<sub>3</sub> solutions. Purification of the REEs from the decomposed solution was performed by cation column chemistry using an AG 50W-X8 (Bio-Rad). Major cations such as Fe were eluted by 2.0 M HCl solution, while 2.0 M HNO<sub>3</sub> solution was used to elute Mn and Ba. Almost 100% of the REEs was recovered by passing the 6.0 M HCl solution through the column (Takahashi et al., 2002; Yamamoto et al., 2010; Nakada et al., 2011). The eluted REE solution was dried, and finally dissolved in 2 wt.% HNO<sub>3</sub> solution to determine the concentrations of REEs by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700). Internal standards (In and Bi) were added at a concentration of 1  $\mu\text{g/L}$ . The accuracy and precision of the measurements were better than 1% for all the REEs, as estimated from the reported values (Imai et al., 1996) and repeated measurements. The amounts of REEs distributed from the REE-doped humic solution to the slate were then calculated. The experiment was repeated three times. In addition, a blank experiment, namely REE adsorption on slate (without humic solution), was performed. The distribution coefficient ( $K_d$ ) of a REE between the liquid and solid phases is defined as.

$$K_d \text{ (L/g)} = ([\text{REE}]_{\text{ini}} - [\text{REE}]_{\text{fil}}) / (c \times [\text{REE}]_{\text{fil}}), \quad (1)$$

where  $[\text{REE}]_{\text{fil}}$  is the REE concentration in the filtrate, and  $[\text{REE}]_{\text{ini}}$  is the initial concentration of dissolved REE, and  $c$  (g/L) denotes the ratio of slate to humic solution.

The amount of carboxyl groups in the humic acid was determined by titration (Schnitzer, 1972; Tsutsuki and Kuwatsuka, 1978). The humic solutions before and after heating were respectively placed in a conical flask with 50 mL ultrapure water and 10 mL of 1 M calcium acetate solution, and shaken for 16 h at 25  $^{\circ}\text{C}$ . After the experimental period, the reaction solution was filtered through paper (ADVANTEC No. 6), and precipitates on the filter were washed with ultrapure water. The filtrate was titrated using a 0.1 M NaOH solution until the phenolphthalein indicator became slightly red-colored. A blank experiment without humic

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