Systematics of Stability Constants of Fulvate Complexes with Rare Earth Ions

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Stability constants of all rare earth ions (REE) with fulvic acid were determined using solvent extraction coupled with ICP-MS detection. REE pattern of the stability constant of REE fulvates shows a similar pattern to REE–carboxylate complex, suggesting that carboxylic group is the main binding site of REE in humic substances. The stability constants for all REE are indispensable for the understanding of REE patterns in natural aquifer.

Humic substances (HS) like humic and fulvic acids are typical organic matter interacting with metal ions in natural aquifer.[1,2] The interaction of rare earth elements (REE) with HS have been studied widely relating to radioactive waste management as analogues of actinides(III).[3–5] However, stability constant (β) of HS complexes has been determined for only a few elements among REE. On the other hand, REE pattern, relative abundances of all REE plotted according to the atomic number, can show origin and chemical state of REE in natural aquifer.[6] In addition, it is expected that the REE pattern of β with HS may indicate main binding site in HS by comparing the values with reported β for simple ligands. Therefore, the aim of this study is to determine the apparent stability constants of all REE with fulvic acid using solvent extraction method.[3] In particular, simultaneous determination of β for many REE as possible is essential to observe slight differences among REE over the experimental error.

Fulvic acid used in this study was the standard Suwannee River fulvic acid (SRFA) received from international humic substances society.[7] DEHP (di(2-ethylhexyl)phosphoric acid), selective extractant for trivalent REE, was purified before use.[3] All the other chemicals were reagent grade and were used without further purification.

The solvent extraction method to determine β followed Torres and Choppin (1984),[3] coupled with ICP-MS measurements (internal standards: In and Bi), instead of using radioisotope tracer because of lack of proper tracers for many REE. When using ICP-MS, (i) we need to reduce the total concentration of REE relative to fulvic acid and (ii) the difference among REE in extraction efficiency by DEHP may inhibit simultaneous measurement of partitioning ratio for all REE in one solvent extraction system. Therefore, REE were separated into three groups, Group I (La, Ce, Pr, Nd, Sm, and Eu), Group II (Eu, Gd, Tb, Dy, Ho, and Y), and Group III (Ho, Er, Tm, Yb, and Lu). The aqueous phase ($I = 0.10\,\mathrm{M}$ by $NaClO_4$) containing one of the REE Group (30–350 nM), fulvic acid (0–100 mg/dm^3), and buffer (acetic acid, 1.0 mM) were mixed with toluene phase containing DEHP, and the mixture was shaken for 72 h. After determination of final pH and fulvic acid concentration by photospectrometry, the aqueous phase was evaporated with the addition of HNO_3 to decompose fulvic acid, since fulvic acid affects the sensitivity of REE measurement by ICP-MS. The difference in concentration of fulvic acid before and after the solvent extraction was negligible (<5%). The REE were redissolved by 2% HNO_3 for ICP-MS measurement. REE in the organic phase were back extracted to 30% HCl(aq) by shaking for 24 h. The HCl solution was evaporated and REE in the residue were redissolved by 2% HNO_3 for ICP-MS analysis.

The apparent stability constant, β_{MA}, of fulvate with metal ion (M^{z+}) can be expressed as $\beta_{MA} = [MA]/([M^{z+}][A])$, where A is dissociated ligand of fulvic acid.[3] The relationship between β_{MA} and the partitioning ratio of solvent extraction can be expressed as $D_0\,(1/D_2 - 1/D_1) = \beta_{MA}[A]$, where D_0 is the partitioning ratio without any aqueous ligands. D_1 is the partitioning ratio in the presence of buffer anion at pH where we obtain β_{MA}, while D_2 is the partitioning ratio with fulvic acid. The details of derivation of β_{MA} from the partitioning ratios were described in the Supporting Information. The D_2 depends on [A] in the unit of equivalent concentration (equiv./dm^3), which is determined from the proton exchange capacity of fulvic acid and the degree of ionization at each pH determined by pH titration.[7]

Log β_{MA} decreased with the increase in [MA]/[A] ratio at lower degree of site occupation (= [MA]/[A] < 0.3 mmol/equiv.), but it was almost constant in the higher degree (>0.3 mmol/equiv.). This means that the fulvic acid contains minor but stronger binding site to REE.[8] REE pattern of log β_{MA} at pH 4.7 and $[MA]/[A] = 0.20 \pm 0.02$ mmol/equiv. was illustrated in Figure 1. Differences among the three groups were corrected based on the results of the common elements in the three groups (Eu and Ho). In the case of fulvate complexes, β_{MA} is an apparent value which depends on pH, ionic strength, and the degree of site occupation.[9] Log $\beta_{Eu(III)A}$ values for fulvates were reported in the range from 5.79 to 7.90 at pH from 2.7 to 6.51.[4,5,10] Log $\beta_{Eu(III)A}$ of this study is within this range. The pattern of log β_{MA} in Figure 1 shows a weak peak in the middle REE part and an increase with the atomic number in the heavier REE part.

The binding site of REE in fulvic acid can be estimated from the comparison of REE pattern of log β between fulvate and simple ligands based on the linear free energy relationships.[11–13] In this study, the REE patterns of log β were compared with those for EDTA (ethylenediaminetetraacetate),[14] oxinate,[15] hydroxide,[16] and diacetate (Figure 1).[17] The characteristics of the REE systematics for log β_{MA} of fulvate is similar to that for diacetate, which shows that carboxylic group is responsible for the binding site of REE in fulvic acid. It must be noted that REE pattern of log β_{MA} can be used as a probe of the binding site, since it is normally difficult to estimate the binding site in the heterogeneous polymolecule such as HS. Such an approach has already been adopted by some studies,[12,13] but not for HS, because there was no report on log β_{MA} of HS for all REE. By spectroscopic

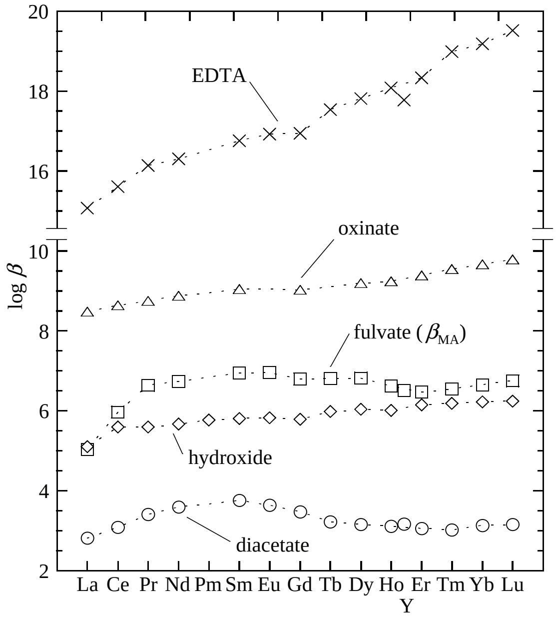

Figure 1. Comparison of REE patterns of stability constants (β) among fulvate and reference complexes. The stability constants of fulvate (β_{MA}) were determined at pH 4.7, ionic strength 0.10 M, and the degree of site occupation 0.20 ± 0.02 mmol/equiv. Uncertainty of β_{MA} is smaller than the size of the symbol.

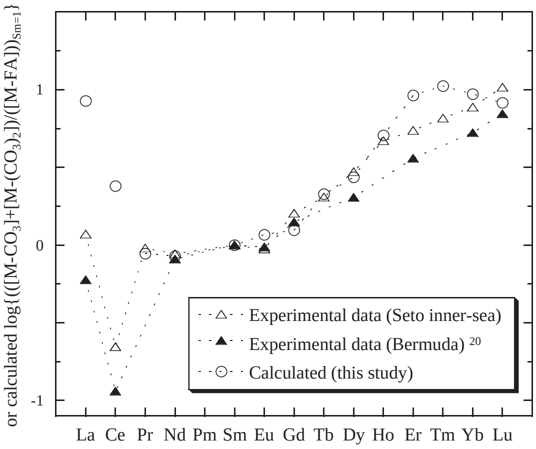

Figure 2. Comparison of the REE pattern between the model calculations and experimental data of partitioning ratio of REE between particulate matters and seawater. By selective leaching methods, REE sorbed on particulate mattes were obtained for the experimental data, where REE fractions in detrital components were excluded. M: REE, sw: seawater, and pm: particulate matters. Experimental data of Seto inner-sea were obtained in our laboratory (unpublished data).

methods such as NEXAFS (near edge X-ray absorption fine structure), the binding site was estimated to be carboxylic group.[18] This study provides another evidence for the binding site in HS based on the systematics of REE.

Moreover, if the relative differences of β_{MA} among REE do not change with pH and ionic strength, β_{MA} determined here can be used for the modeling of REE behavior in natural aquifer.[19] In seawater, for example, partitioning ratios between dissolved REE and REE sorbed on particulate matters were obtained from natural observations (Figure 2).[20] Theses patterns can be simulated by assuming the formation of REE–carbonate complexes in the seawater[21] and HS complexes on the particulate matters using β_{MA}. The estimated REE pattern normalized to the values of Sm can explain the patterns in natural system, except for La and Ce, which supports that organic complex is important on particulate matter for REE, as suggested in other studies of REE abundances in seawater.[12,22,23] It is expected that more results on the stability constants of HS–REE in wider pH range and ionic strength will enable us to estimate REE species in natural aquifer in details through the interpretation of natural REE pattern based on the stability constants of HS–REE.

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