Interpretation of REE patterns in natural aquifer based on the stability constants of REE with humic substances

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Conditional stability constants of all rare earth elements (REE) with fulvic and humic acids were determined using solvent extraction method coupled with inductively coupled plasma mass spectrometry (ICP-MS), except for Ce and Pm. The stability constants of REE were determined under the conditions: pH 3.87-5.44, ionic strength 0.10 M with NaClO4, 10-160 pg/L REE, and 10-200 mg/L humic substances (HS). The stability constants of REE depend on pH, ionic strength, and the degree of site occupation (DSO) defined as the ratio of REE-HS complexes to dissociated ligands of HS. The stability constants of REE decreased with increase of DSO at lower DSO range under all pH conditions, but at higher DSO range the stability constants of REE were almost constant. The stability constants of REE ranged from 5.12 to 8.05 at higher DSO range and from 5.14 to 8.21 at lower DSO range under the experimental conditions. REE patterns of the stability constants of fulvate and humate were similar to that of isolated carboxylic groups like diacetate at lower DSO range, but these patterns become similar to those chelating agents like EDTA, asparate, malonate and lactate. It is suggested that these binding sites are responsible for the complexation of REE with HS, since the binding sites can be estimated from REE pattern of stability constants of REE-HS complexes as a spectrum. On the other hand, the stability constants of REE-HS complexes can be used for the modeling of REE behavior in natural aquifer. REE pattern of partitioning ratio between surface complexes sorbed on particulate matters and dissolved complexes depends only on a pair of the stability constants of main ligands in each phase. These patterns in seawater can be explained by the equilibrium between dissolved carbonate complexes and surface complexes sorbed on the mixture of Fe-Mn hydroxides and humic substances as the end-components. Our results enable us to estimate REE speicies in natural aquifer in details through the interpretation of natural REE patterns based on the stability constants of all REE with humic substances.