

Aqueous Transport of Rare Earth, Alkaline and Alkaline Earth Elements with Organic Acids: Implications for Radionuclide Transport

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The transport of rare earth elements, alkaline and alkaline earth elements are of interest to many geochemists because the former represent a group which behave in a consistent manner in environmental as varied as melts to aqueous solutions. The latter are, on the other hand, mobile in aqueous solutions as diverse as surface waters to hydrothermal solutions. The aqueous geochemistry of REE has received a growing interest in recent years in relation to radioactive waste disposal because REE are both fission products (e.g. ^{154}Eu) and considered as chemical analogues for trivalent actinides (e.g. Ac^{3+}). ^{90}Sr and ^{137}Cs are also important components of radioactive waste. Radionuclides are present in contaminated surficial waters but their behaviour in the presence of natural organic acids is poorly known. Acetate is a common simple acid found in natural waters, basinal brines and hydrothermal. The formation of REE, strontium and cesium-organic complexes could thus significantly affect the transport of rare earth elements, Sr and Cs. Dissociation constants for Rare Earth element acetate (REE-Ac) complexes (La, Gd, Yb, Eu) (1,2,3), strontium acetate (Sr-Ac) and cesium acetate (Cs-Ac) (4) have recently been determined from 25°C to 80°C or 175°C, giving a new insight into how these elements will behave in the presence of organic ligands.

Results show that Logarithms of measured dissociation constants (log K) decrease with increasing temperature, showing that REE, Sr and Cs complexing increases as temperature rises. Log K for $\text{SrCH}_3\text{COO}^+$ decreases from -1.48 at 25°C to -1.97 at 175°C, whereas log K for $\text{CsCH}_3\text{COO}^0$ decreases from 0.35 at 25°C to -0.30 at 175°C. Similarly for the REE-Ac complexes the complex stability increases with temperature. The Rare Earths form both REE-Ac²⁺ and REE-Ac³⁺ and the first REE-Ac complexes increase in stability from La to Eu, then decreases to Yb. Log K for La-Ac, Eu-Ac, Gd-Ac and Yb-Ac dissociation constants vary from -2.20, -2.91, -2.52, and -2.32, respectively at 25°C and -2.80, -3.30, -3.04 and -3.06, respectively at 80°C. For Eu-Ac the Eu-Ac stability increases further to 170°C where the log K is measured to be -4.25. The stability of EU-Ac complexes therefore increases by one and a half orders of magnitude

from 25°C to 170°C. At 170°C the measured dissociation constants for the first Eu-Ac complex are as much as one and a half orders of magnitude lower than those predicted previously (5) based on 25°C data only, showing that the REE-acetate complexes are more important at high temperatures than thought previously. The logarithm of the second dissociation constant (Eu-Ac²⁺) decreases from -1.92 at 25°C to -3.14 at 170°C, showing that these complexes also become more stable as the temperature rises. Only (3) report the third constant RE-Ac complexes (Eu-Ac₃⁰). They also increase in stability with temperatures with log K ranging from -4.83 at 25°C to -7.39 at 170°C.

Species distribution calculations based on the experimentally determined dissociation constants indicate that acetate complexes may be significant for the transport of radionuclides such as ^{154}Eu and ^{90}Sr in contaminated surficial environments as well as future geological radioactive waste repositories where temperatures are expected to rise over 100°C. In contrast, ^{137}Cs transport appears to be affected in a minor way only by the presence of aqueous acetate. Evaluation of REE and Sr, and Cs transport in contaminated waters and in natural settings therefore needs to take organic ligands into account. These results demonstrate that the measurement of thermodynamic constants is very important for understanding the transport and deposition of a variety of elements in the Earth's crust as well as for environmental and radioactive waste geochemistry.

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