

Reactivity of natural heterogeneous nanoparticles

RAEWYN M. TOWN¹

¹Institute for Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense, Denmark. E-mail:((raewyn.town@sdu.dk

The chemodynamics of metal complexation by humic acid (HA) is not well predicted by molecular concepts. HAs are small permeable particles with radius of a few nm. They carry a significant negative charge at ambient pH and are important complexants of metal ions in the environment. HAs are physically and chemically heterogeneous with distributed thermodynamic and kinetic properties. Recently developed theory for permeable charged nanoparticles [1-3] is applied to interpretation of metal ion binding by HA. Two opposing electric effects are operational with respect to the overall rate of association, namely (i) acceleration of metal ion diffusion from the bulk medium by the negative electrostatic field of the humic particle, and (ii) accumulation of metal ions in the negatively charged particle body by Boltzmann partitioning. The rate-limiting step in the metal-humic complex formation process is identified by comparing theoretical values of the rate constants for outer-sphere and inner-sphere complexation with those derived from measurements of the thermodynamic stability constant (K) and the dissociation rate constant (k_d). The experimentally derived association rate constant, k_a , is found to be practically independent of the degree of metal ion complexation, which confirms previous assumptions that the distribution in K is reflected in that of k_d . For the rapidly dehydrating Cu^{2+} , at an ionic strength of 0.1 mol dm^{-3} , the rate of diffusive supply of metal ions towards the humic particles is comparable to the rate of inner-sphere complex formation, indicating that both processes are significant for the observed overall rate. As the ionic strength decreases, the rate of diffusive supply becomes the predominant rate-limiting process, in contrast with the general assumption made for complexes with small ligands that inner-sphere dehydration is the rate-limiting step. The results are highly significant for interpretation of chemodynamics of metal complexation by HA.

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Halogen ratios in kimberlites and their xenoliths related to their origin

CHIAKI TOYAMA^{1*}, YASUYUKI MURAMATSU¹,
HIROCHIKA SUMINO², JUNJI YAMAMOTO³
AND ICHIRO KANEOKA²

¹Gakushuin University, Tokyo, 171-8588, Japan

(*correspondence: chiaki.toyama@gakushuin.ac.jp,
yasuyuki.muramatsu@gakushuin.ac.jp)

² University of Tokyo, Tokyo, 113-0032, Japan

(sumino@eqchem.s.u-tokyo.ac.jp, ikaneoka@aol.com)

³Hokkaido University, Hokkaido, 060-0810, Japan,

Recently, halogens are revealed to be one of the powerful tracers for water cycling in subduction zones [e.g., 1]. In the previous conference, we reported analytical method and some data for Cl, Br and I in kimberlites from South Africa, Greenland, Canada, Brazil, Russia and China, and found that the I/Br ratios of kimberlites are classified into two groups. In this study, additional samples of kimberlites and mantle-derived xenoliths collected from South Africa and Russia were analyzed to investigate the halogen characteristics and their origins in the kimberlite source regions. We analyzed halogens by using the pyrohydrolysis method [2] combined with ICP-MS and ion chromatography.

The kimberlite and xenolith samples from South Africa, Greenland, Canada and Brazil (Group S) showed high I/Br ratios (about 1×10^{-1}). The value is fairly similar to that of CI chondrite (I/Br ratio: about 1×10^{-1} [3]), suggesting these kimberlites preserve the characteristics of primordial halogen in the mantle from which the kimberlite magmas were formed. In contrast, both Chinese and Russian kimberlite and xenolith samples (Group C) showed low I/Br ratios (about 6×10^{-3}). Similarly low I/Br ratios have been observed in fluid inclusions in eclogites derived from seawater-altered oceanic crust [4] and in seawater associated with halite precipitation [5]. This suggests an involvement of seawater-derived halogens having low I/Br ratios in the source regions of the Group C kimberlites. Low I/Br ratios found in xenoliths also indicate possible subduction-related metasomatism on the halogen composition of the subcontinental lithospheric mantle.

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