

Chemical homologue speciation in natural systems: A key to understand the anthropogenic RN fate

F. CLARET¹ C. LEROUGE S. GRANGEON¹ T. SATO²
T. SCHÄFER³ E. GIFFAUT⁴ AND C. TOURNASSAT¹

¹BRGM, 3 avenue C. Guillemin, BP 36009, 45060 Orléans
Cedex 2-France

²Laboratory of Environmental Geology, Hokkaido University
Kita 13 Nishi 8, Sapporo 060-8628, Japan

³Institute for Nuclear Waste Disposal (INE), KIT Campus
Nord, D-76021 Karlsruhe, Germany

⁴RA, 1 rue Jean-monnet, Châtenay-Malabry 92298, France

Anthropogenic radionuclides (RN) are generated by a wide range of industrial, medical and military activities. In a context of storage in deep geological formations or after their release in terrestrial environments by accidents, it is of paramount importance to quantify their mobility, which is partly ruled by their interaction with the solid surfaces. Usually, experiments are conducted using radiotracers at various scale from laboratory to the field in order to measure retention and retardation parameters. Although this kind of experiment is fundamental to tackle this issue, understanding the natural speciation of stable isotopes as chemical homologues to RN brings useful additional information. In particular, it sheds light on RN isotopic exchange and “irreversible” trapping mechanisms. This approach has already been used successfully to gain a better comprehension of iodine fate in the far-field of geological disposals (Claret *et al.*, 2010), which was debated in the literature, due to conflicting experimental results (from no retardation to significant retardation, depending on the study). By careful quantification of iodine reservoirs in the Callovian-Oxfordian clay rock, it was possible to provide new insights into this aspect of the iodine problem. The relevance of such approach for Sr (Lerouge *et al.*, 2010), Se and Ni, three elements with contrasted chemical behaviours and of interest for radwaste storage will be discussed based on new experimental results.

Claret, F., *et al.*, 2010. Natural iodine in a clay formation: Implications for iodine fate in geological disposals. *GCA* 74, 16-29.

Lerouge, C., *et al.* 2010. Strontium distribution and origins in a natural clayey formation (Callovian-Oxfordian, Paris Basin, France): A new sequential extraction procedure. *GCA* 74, 2926-2942.

Interfacial chemistry viewed through the lens of network analysis

A. E. CLARK*¹ A. OZKANLAR² AND M. KELLEY³

Department of Chemistry, Washington State University
(¹a uclark@wsu.edu)

² (abdullah.ozkanlar@wsu.edu)

³ (m.kelly@wsu.edu)

In prior work we have utilized a combination of density functional theory, classical molecular dynamics, and time-resolved laser-induced fluorescence to probe the surface sorption of trivalent lanthanides to various silicate minerals.[1-3] Those studies illustrated the utility and predictive capability of DFT and MD to obtain accurate bulk observable properties and average molecular scale speciation. However, interrogation of interfacial dynamics and time-dependent correlations between surface organization and reactivity have proven more difficult to quantify. Toward this end, we have recently demonstrated that the hydrogen bond network of water has many similarities to the complex and distributed networks found in computer science, and is thus amenable to new types of network information analyses that include degree distributions, network neighborhoods, and geodesic pathways.[4 – 7] Structural motifs can be elucidated within the network. The distribution of defect states and their evolution in time, in addition to a network entropy of the fluid can be also determined. Finally, hydrogen bond dynamics at the molecular and intermediate length scales (1-100's of Å) are readily quantified. In this work we re-analyze our prior MD studies of trivalent sorption to quartz through the lens of modern network analysis methods, deriving new insight into the role that interfacial organization and hydrogen bond dynamics has upon interfacial reactivity.

[1] Wander & Clark (2008), *Journal of Physical Chemistry C* 112, 8233-8241. [2] Kuta, Wander, Wang, Jian, Wall & Clark (2011), *Journal of Physical Chemistry C* 115, 21120-21127. [3] Kuta, Wang, Wisuri, Wander, Wall & Clark (2013), *Geochimica Cosmochimica Acta* 136, 204104. [4] Mooney, Corrales & Clark (2012), *Journal of Computational Chemistry* 33, 853-860. [5] Mooney, Corrales & Clark (2012), *Journal of Physical Chemistry B* 116, 4263. [6] Hudelson, Mooney & Clark (2012), *Journal of Mathematical Chemistry* 50, 2342. [7] Ozkanlar & Clark (2013), *Journal of Physical Chemistry B*, submitted.