

# Molecular Geochemistry: systematic understanding of geochemical behaviors of various elements based on XAFS

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State-of-the-art spectroscopic methods on the chemical speciation developed in a recent quarter-century has provided various atomic-scale information even for trace elements in natural samples. The information includes oxidation state and local structural information of elements of interest, and interactions among atoms and molecules. This information in turn allows us to compare behaviors and cycles of various elements from chemical properties. Professor V. M. Goldschmidt defined that geochemistry is the study of the distribution and amounts of the chemical elements in minerals, rocks, soils, water, and the atmosphere, and the study of the circulation of the elements in nature on the basis of the properties of their atoms and ions.<sup>1</sup> In particular, systematic understanding of various elements based on physico-chemical information and periodic table is important. To achieve comparison of any elements in periodic table, speciation that can be applied to trace elements with high sensitivity is essential. For this purpose, X-ray absorption fine structure (XAFS) can be an ideal method, which consists of XANES and EXAFS, good tools to identify the oxidation state and local structure of the particular ion, respectively. If we could establish such systematic understanding based on such methods, we can predict behaviors of various elements based on the physico-chemical laws. Thus, I here focus on (i) the systematic understanding of various elements (ions) in natural systems and (ii) new XAFS tools in terms of the sensitivity and information on the atomic scale interaction.

(i) Systematic understanding of various elements: One important process, which remains poorly understood, is adsorption of various ions on various adsorbents in water, which controls dissolved concentrations of ions and isotopic fractionation in water. For example, adsorption reactions on iron oxides and clay minerals are very different: the former is chemical interaction with hydroxyl group at the solid surface,<sup>2</sup> whereas the latter, in particular for smectites, is characterized by electrostatic interaction (except of the reaction to the edge sites). Consequently, the stability of adsorbed species on iron oxides strongly depends on the ionic potential of each ion, whereas larger ions can be preferentially stabilized within the interlayer of smectites. These processes can explain retention of various toxic elements by the reaction in soils and sediments, enrichment of metal ions as resources and optimization of extraction procedure, and isotopic fractionation that can be geochemical tools. As for smectites, for example, caesium, or a largest cation, forms stable inner-sphere complex within the interlayer which makes it fixed at the surface of soil that contains smectites.<sup>3</sup> However, smaller ion that forms stable hydrated complex is adsorbed as outer-sphere complex within the interlayer that makes the ion readily exchanged with other cations in coexistent water.<sup>4</sup> This property makes clay minerals very effective mineral resources for rare earth elements (REE) called ion-adsorption type ore.<sup>5</sup> Here, the materials are same, but its macro-scale application is totally different that depends on the properties of elements, which can be systematically understood based on their ionic radii, or hard and soft acids and bases (HSAB) concept, or more quantitatively by nucleophilic constant ( $E_n$ )<sup>6</sup>.

(ii) New XAFS tools: One important issue in (i) is the interaction of caesium ion with tetrahedral layer of clay minerals related to the formation of inner-sphere complex, since only the size (ionic radius) cannot be a cause for the formation of the inner-sphere complex. There should be some specific interaction between the cation and the tetrahedral layer, but such information cannot be given only by EXAFS, which only tells static structural information. For this purpose, XANES can be important, and a new technique using high energy resolution fluorescence X-ray detection system for XANES better than lifetime broadening effect (HERFD-XANES) has made XANES more important than before. For this purpose, the HERFD system using Bragg-type crystal analyzer (energy resolution better than 1-2 eV) is useful.<sup>7</sup> According to our recent studies using HERFD-XANES and its interpretation by hard and soft acids and bases (HSAB) concept, caesium has covalent-type interaction with tetrahedral layer to form stable inner-sphere complex for this soft cation. The HERFD system is also important to achieve sensitive analysis of XAFS for trace elements which can avoid interferences by fluorescence X-rays from other elements. For this purpose, a new detector, transition-edge sensor (TES), can be another powerful tool for fluorescence XAFS.<sup>9</sup> Various examples will be given in my presentation.

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