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Structure and reactivity of environmental interfaces: Application of grazing angle X-ray spectroscopy and long-period X-ray standing waves

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Abstract

Chemical processes occurring at environmental interfaces (e.g. mineral–fluid, mineral–organic matter and mineral–biofilm interfaces) have a profound impact on the environmental fate and bioavailability of aqueous metals and other contaminant species. However, the direct analysis of molecular scale structure and properties of environmental interfaces, particularly under "high-pressure" or "wet" conditions is highly challenging. Synchrotron based X-ray scattering and spectroscopic approaches offer numerous advantages, such as the high penetrating power and molecular scale information inherent to X-ray techniques. Yet, the ability to localize information content to environmental interfaces requires challenging experimental configurations. Here, the application of grazing angle X-ray fluorescence techniques is reviewed, including the presentation of a model formalism that allows for quantitative analysis of fluorescent yield profiles and discussion of the experimental setup. Illustrative examples are discussed, particularly in the context of combining results of GI measurements with the results of other complementary interface probes such as crystal truncation rod diffraction and X-ray microprobe spectroscopic studies.

Keywords: Grazing-angle X-ray absorption; Long-period X-ray standing wave; Total reflection X-ray fluorescence; Environmental interface

1. Introduction

The chemistry of aquatic systems is markedly influenced by processes occurring at the interface between environmental solids and aqueous solutions. Natural waters are typically characterized by a large mass fraction of high surface area solids, making sorption processes a dominant factor controlling aqueous phase concentrations of trace species [1]. The surfaces of environmental solids also serve as substrates for heterogeneous transformation reactions including the oxidation/reduction of aqueous metal(loids), nucleation of mixed metal precipitates and the mineralization or polymerization of organic compounds. Furthermore, the rates of chemical weathering, precipitation of secondary phases and the transport of charged colloids are all influenced by the chemistry of the solid solution interface [2–6]. Therefore, consideration of surface chemical processes is critical to the study of water quality, the chemical fate and bioavailability of environmental contaminants and trace element biogeochemistry.

Inclusion of surface chemical processes in models used to predict the composition and speciation of aquatic systems is complicated by the difficulty of characterizing the relevant surface reactions and surface properties within the (often highly) heterogeneous assemblages of environmental solids associated with natural waters. Furthermore, the extent, rate and ultimate products of interfacial reactions are, in general, a sensitive function of solution pH and composition [7,8]. The extent to which these variables influence interfacial reactions depends on the particular aqueous phase species under consideration, as well as the structure, composition and physicochemical history of the reactive substrate(s). Therefore, there is a strong desire to develop a mechanistic understanding of the predominant surface processes in order to constrain macro-scale models and provide quantitative estimates of model parameters when direct characterization is not feasible.

A great deal of effort has gone into characterizing surface reactions on Al-, Fe-, Mn- and Si-(hyrd)oxides since they are among the most abundant reactive minerals in aquatic systems

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[1,9,10], and sorption reactions on these substrates play a particularly important role in the chemical speciation of trace metals and metalloids. In modeling applications, a hydrated metal-(hydr)oxide surface is typically represented as a fixed set of amphoteric hydroxyl groups [4,11–13]. These surface functional groups serve as reactive ligands for direct inner-sphere binding of Lewis acids, exchangeable sites for binding of Lewis bases and physisorption sites for the formation of outer-sphere complexes through either Coulomb or hydrogen-bonding interactions. Furthermore, mono-nuclear adsorption complexes may serve as nucleation centers for the formation of multi-nuclear clusters or surface precipitates. Therefore, partitioned solutes can be differentiated into several modes of "sorption" that reflect the molecular level structure of the reaction products and association with a mineral surface. The extent of solute partitioning and stability of the sorption products are related to these sorption modes, and thus have direct implications for the mobility and bioavailability of chemical species in aqueous systems.

However, the concept of an environmental interface as a static array of binding sites is limited. For example, the reactivity of surface functional groups depends to a large extent on their coordination environments. Therefore, sorption affinity can be expected to vary among different surface orientations of a crystalline substrate, with the density of surface defects (e.g. steps and kink sites), as well as the extent of surface hydroxylation. Many interfacial processes also involve a dynamic variation in interfacial structure and composition, such as solid solution and diffusion as an incorporation mechanism, dissolution and re-precipitation and the non-stoichiometric (incongruent) dissolution of solids. Such processes may lead to the formation of new surface phases or surface leached layers that differ substantially in structure and composition from the bulk substrate. Furthermore, the surfaces of inorganic materials that comprise the bulk of environmental solids are often modified by attached natural organic matter or bacterial biofilms. The formation of such mineral/organic composites may significantly alter the apparent reactivity of the mineral surface due to competition between reactive surface sites and the organic functional groups for binding of dissolved species.

Thus, the ability to accurately account for the role of interfacial processes in the composition and speciation of natural waters requires detailed knowledge of the molecular scale structure of the solid-solution interface. Traditional batch (or column) measurements have been used to infer the products of interfacial reactions through analysis of changes in the aqueous phase composition after contact with a (typically high surface area) solid substrate. While such measurement have provided a great wealth of information about the overall reactivity trends among classes of solutes and substrates, this approach provides no direct molecular level information about the modes of sorption, distribution of species at the mineral–solution interface or mechanisms involved in dissolution and surface precipitation processes [8,12,14–16].

Therefore, high resolution spectroscopic and microscopic techniques have found widespread use for studying the chemical and structural properties of environmental interfaces [17,18]. A primary goal of such studies is to provide the experimental constraints necessary to develop an accurate picture of the molecular structure and spatial association of surface reaction products and surface associated species. Such information is needed to constrain the stoichiometry of surface reactions used in macro-scale modeling applications, as well as providing direct experimental comparison to theoretical approaches of predicting surface reactivity and reaction parameters (e.g. sorption free energies) based on molecular properties of the interface [5,6,19–25].

The detailed molecular scale analysis of environmental interfaces, however, poses several challenges. Of paramount importance is the role of water, making it preferable to utilize techniques that can provide in situ (environmentally relevant pressure and temperature) results. In addition, direct analysis of natural solids is complicated by the physical and chemical heterogeneity inherent in the sample matrix, and interpretation of results may be hampered by the lack of constraints for the range of physicochemical variations that lead to the observed speciation. Thus, many studies have focused on the use of simplified model system analogs, in which the systems are carefully controlled to provide a maximum level of detail on reaction products and the conditions under which they form. Furthermore, model system investigations allow the study of individual reactive components such as specific mineral surface orientations, and increasing complexity, such as competition between a specific surface and overlying organic films, can be added in a controlled fashion.

2. Synchrotron based X-ray techniques

X-ray spectroscopic and scattering techniques have found widespread application in the study of environmental and geochemical interfacial phenomena (cf. [26]). The large penetration depth and inherent molecular scale sensitivity of X-rays make them ideal probes for investigating the structural details of environmental materials under in situ conditions. Furthermore, the advent of high brilliance third generation synchrotron sources has made techniques with high spatial resolution and sensitivity widely available.

X-ray absorption fine structure (XAFS) spectroscopy has been used in numerous investigations to characterize the speciation of metals and metalloids associated with a variety of environmental media, including mineral surfaces, natural organic matter and bacterial cell walls and associated exo-polymers [9,16,17,27–35]. XAFS provides information on the local structure surrounding a central absorbing element including the distance, coordination number and identity of near neighbor atoms (first, second and in some cases more distant coordination shells). In conjunction with oxidation state determinations through analysis of the X-ray absorption near-edge structure (XANES), these techniques provide relatively complete characterization of the speciation of trace levels of heavy elements in natural or model system samples without the need for substantial pre-treatment (e.g. samples can typically be analyzed under wet or ambient conditions for transition metal and heavier elements).

The majority of XAS studies have been performed using a conventional "bulk" geometry, in which the incident X-rays intersects the sample at a large angle ($\sim$45°) and either trans-