

Advances in elucidating biogeochemical processes in soils: It is about scale and interfaces

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Received 24 March 2005; accepted 19 August 2005

Available online 27 December 2005

Abstract

Contributions in biogeochemical research have immensely benefited humankind, including enhanced food production and the quality of our environment. This overview paper focuses on recent breakthroughs in elucidating biogeochemical processes in soils and other natural materials and delineates frontiers for the present decade and beyond. Frontiers will undoubtedly involve multiple spatial and temporal scale investigations, elucidation of reactions at biological, chemical, and physical interfaces, and the use of advanced in situ technologies in combination with interdisciplinary research.

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Keywords: Molecular scale; Macroscopic scale; Temporal scale; Biogeochemical processes; Surface spectroscopy

1. Introduction

The critical zone is “the heterogeneous, near surface environment in which complex interactions involving rock, soil, water, air and living organisms regulate the natural habitat and determine the availability of life sustaining resources” (NRC, 2001). The critical zone is an interfacial region of mass and energy flux comprising terrestrial, lacustrine, and marine components of the continental crust and is one of the two primary loci of life on Earth and for most of human activity. The critical zone is comprised of an array of spatial scales, ranging from the atomic to the global, and temporal scales, ranging from seconds to eons. The physical, chemical, and biological processes within the critical zone mediate exchange of mass and energy which is required for

biomass productivity, chemical recycling, and water storage. The critical zone is the most heterogeneous and abstruse portion of the entire Earth (NRC, 2001). If we are going to sustain the planet for human habitation we must understand the physical, chemical, and biological processes and reactions in the critical zone over a range of spatial and temporal scales (NRC, 2001; Hochella, 2002; Sparks, 2004).

With the advent of state-of-the-art analytical techniques, some of which are synchrotron-based (e.g., X-ray absorption fine structure spectroscopy, XAFS), one can elucidate reaction mechanisms at small scale. This has been one of the major advances in the earth and environmental sciences over the past decade. Undoubtedly, the molecular characterization of microenvironments and interfacial reactions will become increasingly significant in understanding the interactions between chemistry, physics, and biology in natural environments.

The use of small-scale techniques in environmental research has resulted in a new multidisciplinary field of

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study that geoscientists are actively involved in—molecular environmental science. Molecular environmental science can be defined as the study of the chemical and physical forms and distribution of contaminants in soils, sediments, waste materials, natural waters, and the atmosphere at the molecular level (Sparks, 2002, 2004). There are a number of areas in the geosciences where the application of molecular environmental science is resulting in major frontiers. These include: speciation of contaminants, which is essential for understanding release mechanisms, spatial resolution, chemical transformations, toxicity, bioavailability, and ultimate impacts on human health; mechanisms of microbial transformations; development of predictive models; effective remediation and waste management strategies; and risk assessment. Some of these frontier areas will be discussed in the paper.

2. Results and analysis

Over the past 15 years, major advances have occurred in elucidating sorption mechanisms at the mineral/water interface. From these studies one can conclude that sorption of alkali and alkaline earth elements primarily occurs via outer-sphere complexes

while for most other cations and anions, such as most heavy metals and oxyanions, inner-sphere sorption complexes result. Sorption of metals such as Co, Cr, Mn, Ni, and Zn on mineral components and soils can result in the formation of metal hydroxide precipitate phases (Scheidegger et al., 1997). The formation of these phases could be an important mechanism for sequestering metals in soil and water environments such that they are less mobile and bioavailable.

In the remaining section of this paper, I will focus on the use of advanced micro-focussed synchrotron-based techniques to speciate metals in contaminated soils. Other frontier topics that will be covered in the oral presentation will include mineral/microbe and plant/soil interfacial reactions. Standard XAS techniques probe an area of several square mm. However, the most reactive sites in soils have particle sizes in the micrometer range and metal speciation may vary over regions of a few $100 \mu\text{m}^2$. Therefore, the derived structural information may be only an average of several contaminant species. With the advent of third generation synchrotron radiation facilities, which afford enhanced spatial resolution ($<5 \mu\text{m}$) and sensitivity, one can speciate metals in soils using micro-XAS and determine elemental distributions and asso-

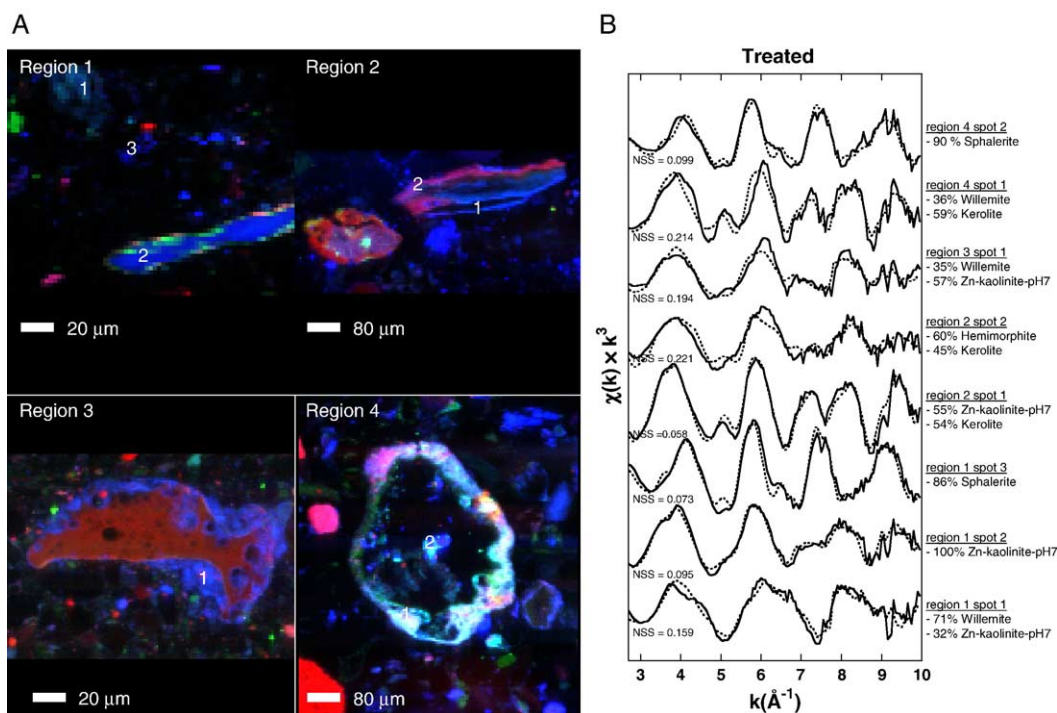


Fig. 1. (a) μ -SXRF tricolor maps for the treated soil samples. The numbers indicate the spots where μ -EXAFS spectra were collected. Red is indicative of the distribution of iron, green of copper and blue of zinc. (b) μ -EXAFS spectra from selected spots on thin sections from treated soil. The solid line indicates the raw $k^3\chi(k)$ data and the dotted line indicates the best fits obtained with a linear fitting approach. From Nachttegaal et al. (2005). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

ciations using micro-X-ray fluorescence (micro-XRF) spectroscopy. An example of the use of these techniques is shown in Fig. 1 from the research of Nachtegaal et al. (2005). They investigated the speciation, distribution, and association of Zn and its relation to mobility and bioavailability of Zn in a non-remediated and a remediated (treated) smelter contaminated soil from Belgium. Overall, the researchers found that there were no significant differences in Zn speciation between samples of the two soils. About 30 to 50% of Zn was in smelter related minerals (willemite, hemimorphite or gahnite), while 50 to 70% of Zn was incorporated into newly formed Zn precipitates (mixed Zn–Al layered double hydroxides (LDH) in the non-remediated and Zn-phyllosilicates in the remediated soil). Macroscopic desorption and biosensor studies were conducted on the soils to assess bioavailability of Zn. At the pH of the soils (6.4–6.7), these studies showed that the presence of the LDH phases greatly diminished the bioavailability of Zn in the soils. Desorption of Zn, and consequently bioavailability, was enhanced at lower pH levels. The results of this investigation indicate that at higher pHs the formation of (mixed) metal hydroxide precipitates could be an important means of sequestering toxic metals such as Zn, as well as Co and Ni, in the soil environment.

3. Summary and conclusions

To successfully address and fund the major research needs that have been alluded to, and others that were not mentioned, multidisciplinary and interdisciplinary and multifaceted approaches must be carried out. Geoche-

mists, soil scientists, chemists, physicists, biologists, and engineers must and will increasingly collaborate. I predict that one of the major leitmotifs in the geosciences in the 21st century will be the study of biological effects on geochemical reactions and processes. This provides geoscientists with a unique opportunity to combine their expertise with that of molecular biologists. We must also employ an array of multiple, molecular-scale techniques over a range of temporal scales in combination with macroscopic approaches and computational modeling to solve complex questions concerning biogeochemical properties and processes.

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