



Preface

From micro to molecular scale investigations in geochemistry

Geochemical processes can be examined at widely variable spatial scales. Some of these processes may entail phenomena that occur along very large scales and thus produce such global consequences as soil or mineral deposit formation, to name a few examples. However, the geochemical reactions involved in these phenomena can be tracked down to molecular and microscopic scale mechanisms and may be represented by chemical reactions, which often multiply along large spatial (and variable temporal) scales. For example, the production of acid drainage in mine settings begins with oxidation reactions of sulfide minerals at molecular sites on their surfaces. These reactions release protons that trigger a series of subsequent catalytic oxidation reactions, often involving microorganisms, and which are multiplied by the large masses of sulfide source material removed from the underground and exposed to air and water. This can produce highly deleterious environmental consequences, often affecting large geographical areas in relatively short time-scales if in contact with sufficient water.

The ultimate goal of investigating fundamental geochemical reactions at small scales is to explain many large-scale phenomena, in what has been termed a “bottom-up” approach. Although not widely popular among field geochemists, small-scale investigations, including atomic, molecular, nanometric, and colloidal scales, is being undertaken increasingly by geochemist communities worldwide. That, especially as microscopies and X-ray spectroscopic and other probing techniques are developed or improved to increase their respective spatial resolutions. High-resolution electron microscopies (*e.g.*, TEM, SEM, AFM, STM, etc.) allow imaging of geochemical materials at ever-increasing magnifications, often revealing crucial details that were previously undetectable and that may have important consequences for explaining their larger-than-predicted reactivity. Such is the case, for example, of the very small but widespread steps and kinks found on mineral crystal faces that used to be considered as entirely flat. X-ray Absorption Spectroscopy (XAS) is one of the atomic-scale resolution techniques of choice to probe the near-neighbor atoms around a central atomic identity of interest, and is highly useful when investigating the mineral-water interfacial configuration, or the structural details of natural nanoparticles.

In Mexico, the bottom-up approach has yet to be adopted by a critical number of geochemists, especially in the environmental subdiscipline. The goal of the present Special Issue of the BSGM is to showcase geochemical

investigations approached from the point of view of small spatial scales, through seven research articles.

The paper by Tamura and Kunz offers an overview of the potentials of X-ray microdiffraction from synchrotron sources to analyze geological samples at resolutions between 100 nm and a few microns, emphasizing two techniques: powder (monochromatic) microdiffraction and Laue (polychromatic) microdiffraction. These are respectively used to map the nanocrystallized and microcrystallized phases in samples where a full diffraction pattern can be collected in subseconds up to a few seconds with negligible instrumental downtime. It is noteworthy that despite the powerful nature of microdiffraction it is as yet an underutilized tool for geological and environmental materials.

Precisely, X-ray micro-diffraction from synchrotron sources, together with other techniques were used by Castillo *et al.* to identify a calcium arsenate mineral responsible for the very high arsenic levels found in an aquifer in San Luis Potosí, Mexico. Although these arsenates were not unequivocally identified, many other experimental evidences point to these minerals as the source of the arsenic contamination in the water, which is explained by the fact that in the investigated area the contents of iron oxides, to which arsenic normally binds, are very low, in contrast to calcium.

In the work by Loredó-Portales *et al.* a combination of micro-X-ray fluorescence and absorption techniques were used to help determine the speciation of copper in mine tailings and contaminated soils from an abandoned mine in Guanajuato, Mexico. Using a multianalytical approach, they found a large percentage of highly-mobile Cu(II) present, but also some less mobile phases, such as Cu(II) arsenates.

In larger-scale investigations, Otero *et al.* determined the surface reactivity of nanoparticulate and colloidal iron oxide phases from two acid mine drainage-affected environments, towards copper and arsenate ions. The adsorption behavior of these two chemically different species, a cation and an oxyanion, respectively, was adequately modeled using thermodynamic surface complexation considerations derived from synthetic iron oxide phases on the same types of surface sites for both sorbates.

The mineral-water interface was also probed by Vaca-Escobar and Villalobos for the adsorption behavior towards arsenic of the iron oxide mineral, goethite, in conjunction (and competition) with precipitation of arsenic as Pb(II) and Cu(II) arsenates. The mobility behavior of arsenic was described in a thermodynamic surface complexation

modeling approach coupled to an aqueous/solid speciation model. The investigation was applied to a relatively simple synthetic system, in a “bottom-up” approach to approximate the complexity of natural systems.

A practical work was presented by Villacís-García *et al.* to show how the synthesis of the iron oxide minerals of nanometric and colloidal sizes, goethite and ferrihydrite, can be achieved with controlled specific surface areas, which is analogous to producing them in controlled particle sizes. This type of controlled-size syntheses can be very useful in fundamental investigations of the surface structure and reactivity of minerals.

Finally, a more macroscopic approach was adopted by Tevez and Dos Santos Afonso to describe the adsorption of the pesticide glyphosate on different soil horizons, and its

dependence with pH, and soil particle sizes and composition. They described the behavior using the more empirical approaches of Freundlich and Langmuir adsorption isotherm models, and found a strong retention as soil pH decreased, but also with soil contents of small particle sizes (humics and other clay-like fractions).

Although the large majority of articles presented in this Special Issue pertain to the environmental geochemical subdiscipline, we hope to convey that the micro to molecular scale investigations can be applied and are very useful to all areas within geochemistry. The article by Tamura and Kunz certainly provides an example of this, through one of the many microscopic-scale techniques available.

Mario Villalobos