Sensitivity analysis for a multisurface geochemical modelling approach

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Geochemical models such as surface complexation have been used to successfully describe the leaching of trace metals from different waste matrices. As the model complexity increases different tools need to be used to understand the effect a given input parameter has on the model output. This work extended the multisurface geochemical modelling approach to predict trace metals leaching behaviour in sewage sludge. The NICA-Donnan model was used to incorporate organic matter as a sorbent. The generalized two layer model was used to incorporate iron, aluminium and manganese oxides. Selective chemical extractions were conducted to determine the concentration of available surface sites. The model was tested against pH dependent leaching experiments and isotherm studies.

A sensitivity analysis was conducted to rank the relevance the different input parameters have on the model outcome, as well as to test the model robustness and reliability. The sensitivity analysis was carried out by defining uniform distributions for the input parameters. New sets of input parameters were randomly obtained by sampling the input distributions with a Montecarlo method; and the model was evaluated. The uncertainty of the outcome was assessed by comparing the median, 5^{th}, 25^{th}, 75^{th} and 95^{th} percentiles from the output with the experimental values. There are different ways to evaluate the effects of the input parameters on the model outcome. One of them is to define best and worst set of inputs by comparing the output to the experimental value. The best and worst input sets were described in terms of probability distributions and the two probabilities were compared using the Kolmogorov-Smirnov test to determine how likely they are to be the same distribution. This sensitivity analysis shows that the most relevant parameters in this model are solid and dissolved organic matter concentrations, concentration of iron oxides available for sorption, amount of metal available for sorption. Background analytes have different levels of relevance.

Toward calculation of the thermodynamic stabilities of proteins in the deep biosphere

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Microbes that thrive in the deep subsurface and other extreme environments depend for their survival on proteins and other biomacromolecules that are chemically distinct from their counterparts in organisms on Earth's surface. Among the variables that characterize different geochemical environments are oxidation state, hydration state, temperature, pressure, and pH. Although the advantages of a chemical thermodynamic assessment of the relative stabilities of inorganic species as a function of physical chemical variables have long been recognized, such an approach generally has not been used to study systems of proteins and other biomacromolecules. Assessment of the relative metastabilities of proteins as a function of these variables can now be performed, owing to 1) generation of group additivity equations of state parameters for calculating the standard molal thermodynamic properties of ionized proteins at high temperatures and pressures, and 2) the development of a computer software package for calculating the chemical affinities of biomacromolecular formation reactions and displaying predominance diagrams consistent with metastability constraints in systems of biomacromolecules. In this communication we present the results of calculations of the relative metastabilities of orthologous proteins from organisms adapted to different geochemical environments. For example, diagrams representing the relative metastabilities of surface-layer proteins from mesophilic, thermophilic, and hyperthermophilic species of *Methanococcus* have been generated as a function of oxygen fugacity, temperature, pressure, and pH. The locations of the predominance fields of the proteins correspond with the temperature and other geochemical characteristics of the environments inhabited by these organisms. These findings support the notion that energy minimization in systems of representative proteins provides a thermodynamic driving force for the evolution of biological species, and also provide evidence that a thermodynamic assessment of the relative metastabilities of proteins can be used to predict the physical chemical limits on their occurrence in different environments. Because the current approach takes account of the relative metastabilities of different proteins, it permits explicit assessment of relations between different proteins and the physical chemical characteristics of geochemical environments. Hence, we also discuss calculations of the effects on protein metastability of potential biogeochemical oxidation-reduction buffers which may be composed of mineral or organic species, or both. Continued development of the thermodynamic calculations and integration with experimental observations may contribute significantly to our understanding of the fundamental forces involved in the interaction between microbes and their environments.