

THEME 2: THE DYNAMIC INTERFACE

Session 2.2: Growth and dissolution of minerals – linear and non-linear processes

CONVENED BY:

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INVITED SPEAKER:

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This session addresses the full spectrum of rates, mechanisms, and consequences of mineral-fluid reactions, studied from field, laboratory and computational approaches. Some areas include: 1) Mineral growth: Application of surface-sensitive techniques to determine growth mechanisms, such as e.g. spiral growth and surface nucleation; trace element control on growth rate; field characterisation of precipitation rates; and first principle computation. 2) Inorganic dissolution: Quantification of weathering rates and mechanisms from laboratory studies; surface area rate control; numerical modelling; and links between surface speciation and adsorption or exchange reactions and mechanism. 3) Biotic weathering and growth: Microbe and organic acid influence on dissolution, growth and isotopic fractionation under various conditions, e.g pH, T, or Eh. 4) Coupled growth and dissolution: links between dissolution, leached layers and growth; reactions in confined volumes and in porous media. 5) Isotopic evolution: Field, laboratory and theoretical studies on fractionation mechanisms; application of fractionation to quantify growth rates in natural systems.

2.2.11

Impact of dissolved organics on mineral dissolution kinetics: Towards a predictive model for Ca- and Mg-bearing oxides, carbonates and silicates

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Quantification of the effect of inorganic and organic ligands on mineral dissolution rate is extremely useful to check the validity of kinetic models. In this regard, the pioneering studies of Stumm and co-workers have established a firm basis for modeling the catalyzing and inhibiting effects of ligands on metal oxide dissolution rate. However, if numerous studies have been devoted to the effect of organic and inorganic ligands on the dissolution rate of trivalent metal oxides, little is known on the effect of these ligands on the mobilization of alkaline-earths from mineral surfaces. Quantification of the ligand controlled dissolution of Ca- and Mg-bearing minerals is of crucial importance for modeling the weathering of basic rocks in the presence of natural organic ligands such as humic acids, root exudates and bacterial metabolites. This study, that leans on the data collected in our laboratory over the last five years, presents a synthesis of the effect of more than 35 different organic ligands on dolomite, brucite, wollastonite and diopside dissolution kinetics. The ligands selected in this study can be used as analogs of functional groups for dissolved organic matter, bacterial cell envelopes and their exometabolites. Experiments were performed at 25°C with calibrated mineral powders in mixed flow reactors as a function of pH (from 4 to 11) and organic ligand concentrations (from 10⁻⁶ M to 0.1 M).

The effect of investigated ligands on mineral dissolution rate can be modeled within the framework of the surface coordination approach taking into account the adsorption of these ligands on dissolution-active sites and the molecular structure of the surface complexes they form. The higher the value of the ligand sorption constant, the stronger will be its catalyzing or inhibiting effect. As for Fe and Al oxides, bi- or multidentate mononuclear complexes, that labilize Me-O bonds and water coordination to Me atoms at the surface, enhance dissolution whereas bi- or polynuclear complexes tend to inhibit dissolution by bridging two or more metal centers and extending the crosslinking at the solid surface. Overall, results of this study demonstrate that very high concentrations of organic ligands (0.01 – 0.1 M) are necessary to significantly affect dissolution rates. As a result, the effect of extracellular organic products on the weathering rate of Ca- and Mg-containing minerals in natural settings is expected to be weak which provides important constraints on the modeling of biota effect on carbon global cycle related to mafic rocks weathering.