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Book Review

THERMODYNAMICS AND KINETICS OF WATER-ROCK INTERACTION, Eric H. Oelkers and Jacques Schott, Editors. (2009) Reviews in Mineralogy and Geochemistry, vol. 70, 569 pages. ISBN 978-0-939950-84-3. $40 (U.S.). (http://www.minsocam.org/MSA/RIM/Rim70.html)

Migration of fluids from one geochemical reservoir to another may bring about disequilibria and drive reactions that ultimately control the mineralogical and chemical composition of the Earth's crust and surface. Understanding water-rock interaction is mandatory in solving a wide variety of academic and societal problems such as assessing environmental hazards, optimizing oil recovery, identifying and exploiting mineral and ore deposits, and reconstructing past environments and climate.

This volume collects contributions from different disciplines within the earth sciences and presents reviews on a wide spectrum of topics that are relevant in understanding water rock systems. It gives a comprehensive account of the well-established fundamentals on the thermodynamics and kinetics of water-rock interaction including basic thermodynamic and kinetic principles and also introduces more recent developments, such as the atomistic view on sorption and chemical reactions in water rock systems and reactive transport modeling. The subjects are treated at a relatively advanced level and the volume is not necessarily suitable as an introduction to the topic of water-rock interaction for beginners. It is, however, without doubt a comprehensive source of relevant information and guide to the dedicated literature for advanced students and for researchers in the field.

The initial two chapters are concerned with the thermodynamics of water-rock systems. Chapter 1 on "Thermodynamic Databases for Water-Rock Interaction" by Eric H. Oelkers, Pascale Benezeth, and Gleb S. Pokrovski presents basic thermodynamic relations and gives a brief overview of the thermodynamic properties of minerals, aqueous species, and the solvent water. Necessarily the presentation of the thermodynamic formalism is very condensed, and the non-expert reader may need to consult a thermodynamics textbook to appreciate the larger context behind the formalism. Chapter 2 on the "Thermodynamics of Solid Solution-Aqueous Solution Systems" by Manuel Prieto introduces the important aspect of element distribution among mineral phases and an aqueous fluid. It introduces mass-action relations, equilibrium constants, and distribution coefficients with a particular focus on systems containing solid solutions. Both the presentation of the formalism as well as the graphical representations (Lippmann and Rozeboom diagrams) are very instructive. Considerable attention is given to solid solutions with non-ideal mixing properties and the effect of ordering.

In chapter 3 on "Mineral Replacement Reactions" by Andrew Putnis the phenomenon of mineral replacement is presented from various natural environments and from experiment. A strong case is made for the pivot role of aqueous fluids in mineral replacement, and dissolution-reprecipitation is identified as the prime mechanism for reequilibration in fluid-saturated systems. The arguments supporting this view are stated very clearly. The discussion is mainly qualitative, which makes it easy to follow also for non-expert readers. Several questions that are raised with regard to the interplay of interface reactions and chemical mass transfer are taken up and developed further in chapters 6 and 8.

The following two chapters deal with thermodynamic and mechanistic models of sorption at mineral surfaces. Chapter 4 on "Thermodynamic Concepts in Modeling Sorption at the Mineral-Water Interface" by Dmitrii A. Kulik discusses the various mechanisms that may be responsible for sorption of aqueous species on mineral surfaces and compares thermodynamic models with different degrees of complexity. In this chapter, many technical terms and acronyms are introduced that are explained only briefly. It may be expedient to first read chapter 5 on "Surface Complexation Modeling: Mineral Fluid Equilibria at the Molecular Scale" by David M. Sherman, where models of surface complexation are described in more detail. In this latter chapter, it is argued convincingly that classical distribution coefficients need to be replaced by mass action relations, which account for the nature of the mineral-water interface on the molecular scale. This implies that considerations of crystal chemistry are combined with computational models of surface complexation.

The next three chapters deal with the links between solution chemistry and the kinetics of mineral dissolution and precipitation. In chapter 6 on "The Link Between Mineral Dissolution/Precipitation Kinetics and Solution Chemistry" by Jacques Schott, Oleg S. Pokrovsky, and Eric H. Oelkers, the saturation index is introduced as a measure of the departure from equilibrium, and kinetic rate laws are developed for interface reactions based on transition-state theory. The contribution of coordination surface chemistry and surface complexation modeling to the identification of the activated complex, which plays a pivot role in determining reaction rates, is nicely demonstrated. Moreover, an instructive discussion is presented on the phenomenon of leached layer formation, which is typical for dissolution of multi-oxide minerals. In chapter 7 on "Organics in Water-Rock Interactions" by Jiwchar Ganor, Itay J. Reznik, and Yoav O. Rosenberg, the

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role of organic compounds as potential ligands and their influence on the speciation of an electrolyte solution as well as the effects of the adsorption of organic molecules on mineral surfaces are addressed. In particular, the various effects of organic molecules on mineral dissolution and precipitation are discussed in a systematic manner. In chapter 8 on "Mineral Precipitation Kinetics" by Bertrand Fritz and Claudine Noguera, a succinct and very clear summary is given of the formalism used to describe mineral-fluid equilibria and nucleation of a solid phase from a supersaturated solution. In particular, the complexities that arise from the nucleation and growth of solid-solutions are presented. The corresponding formalism is developed in a very instructive way and applications of kinetic modeling of mineral precipitation are discussed based on several worked examples.

The following two chapters put the concepts on water-rock interaction that were developed in the previous chapters into the context of weathering and its role in global element cycles and interplay with climate. In chapter 9 on "Towards an Integrated Model of Weathering, Climate, and Biospheric Processes" by Yves Godderis, Caroline Roelandt, Jacques Schott, Marie-Claire Pierret, and Louis M. Francois, a reaction-transport model describing the dissolution/precipitation of minerals in the soil and a model of continental biospheric activity are combined to assess the influence of environmental factors such as climate and vegetation on continental weathering. In chapter 10 on "Approaches to Modeling Weathered Regolith" by Susan L. Brantley and Art F. White, analytical and numerical models are presented that describe the evolution of soil profiles. Six case studies are described in some detail, and interesting inferences are made with respect to the significance of the advance and the width of reaction fronts for the extent of chemical mass transfer and the relative rates of transport and mineral-fluid reactions.

The last two chapters address the coupling between chemical mass transfer and mineral-fluid reactions. In chapter 11 on "Fluid-Rock Interaction: A Reactive Transport Approach" by Carl I. Steefel and Kate Maher, the basic processes of chemical mass transport in fluid-rock systems are reviewed and the governing equations for modeling transport reaction systems are presented in a very instructive manner. Reactive transport modeling and in particular the influence of the relative rates of chemical mass transport and mineral-fluid reactions on the resulting geochemical and mineralogical patterns is discussed, based on several worked examples. Finally, in chapter 12 on "Geochemical Modeling of Reaction Paths and Geochemical Reaction Networks" by Chen Zhu, reaction path modeling in the traditional geochemical sense, i.e., the tracing of the sequence of states of an aqueous solution and mineral parageneses during irreversible reactions in water-rock systems is illustrated.

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