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Book Review

Thermodynamics and Kinetics of Water–Rock Interaction

Geofluids (2010) EH Oelkers and J Schott. eds 2009. Reviews in Mineralogy and Geochemistry, 70, 569 pp.

Several factors motivating the preparation of the volume *Thermodynamics and Kinetics of Water–Rock Interactions* are underscored in the preface by Eric H. Oelkers and Jacques Schott. I completely agree with the Editors on the

… compelling societal need to resuscitate the field of the thermodynamics and kinetics of natural processes. This field is essential to quantify and predict the response of the Earth's surface and crust to the disequilibria caused by the various natural and anthropogenic inputs of energy to our planet. As such, it serves as the basis for sustainable development and assuring the quality of life on the Earth; it serves as the key to understanding the long term future of radioactive waste storage, toxic metal mobility in the environment, the fate of CO_2 injected into the subsurface as part of carbon sequestration efforts, quantifying the quality of petroleum reservoirs and generating novel methods of petroleum extraction, and the identification of new ore deposits. The recent interest in the weathering of continental surfaces and its impact on global elemental cycles and climate evolution has also brought new attention to the thermodynamics and kinetics of water–rock interactions as it has become evident that only a true mechanistic approach based on robust thermodynamic and kinetic laws and parameters can accurately model these processes. Yet this field has, in many ways, atrophied over the past two decades. …Some of this atrophy was also caused by past successes in this field; the development and success of computer generated thermodynamic databases, for example, giving the illusion that the work of scientists in this field was complete.

The book is aligned with these purposes, as the reader receives several messages on the importance of thermodynamics and kinetics as theoretical foundations for unraveling water–rock interaction. Another message transmitted to the reader concerns the considerable amount of work to be done to improve, for example: (i) the quality of presently available thermodynamic and kinetic databases, (ii) the modeling and understanding of processes occurring at the mineral–water interface, (iii) the role and fate of organic matter in water–rock interaction, and (iv) the nucleation and growth of secondary solid phases. The effort needed to achieve these goals is huge, but geochemists will be able to accomplish them, as long as they rely on thermodynamics and kinetics. This is certainly a very reassuring perspective.

Chapter 1 is devoted to the thermodynamic databases needed to investigate water–rock interaction, chiefly incorporating the thermodynamic properties of minerals and aqueous species. Eric H. Oelkers, Pascale Bénézeth, and Gleb S. Pokrovski focus mainly on the limitations of presently available thermodynamic databases, which were obtained through the use of a comparatively small amount of experimental data and several empirical correlations. According to Oelkers, Bénézeth, and Pokrovski (and I agree with them), users of computer codes for geochemical modeling must be aware of these limitations of thermodynamic databases – in spite of the surprising success of the empirical schemes and theoretical models adopted to derive the thermodynamic properties of a relatively large number of minerals and aqueous species, chiefly based on the groundbreaking scientific research of Harold Helgeson and coworkers. They also emphasize that data obtained through empirical correlations must be considered provisional until suitably planned experiments are executed. Recent advances in experimental techniques allowing the acquisition of thermodynamic properties of minerals and co-existing aqueous fluids are also presented and discussed (*e.g.*, *in situ* X-ray absorption fine-structure spectroscopy, *in situ* calorimetric and volumetric measurements, and the hydrogen-electrode concentration cell).

Chapter 2, written by Manuel Prieto, provides a clear and rigorous presentation on how the thermodynamics of aqueous solution-solid solution equilibria can be described through a graphical approach (based on Rozeboom and Lippmann plots) which is reminiscent of the classical treatment of solid-melt equilibria in systems of petrological interest. Several examples are considered, comprising ideal solid solutions, non-ideal solid solutions, solid-solution systems involving ordered phases, metastable equilibrium, and supersaturation in aqueous solution-solid solution systems. Relevant implications (*e.g.*, the transport and fate of toxic metals in the environment) are drawn and goals of future research are briefly reviewed.

In Chapter 3, Andrew Putnis focuses on mineral-replacement reactions, from high-temperature metamorphic and metasomatic processes to low-temperature weathering in near-surface environments. Through a series of examples referring to laboratory experiments and natural occurrences, interface-coupled dissolution-precipitation is recognized as the main mechanism controlling mineral replacement, thus deempha-

sizing the occurrence and role of solid-state diffusion and pressure-dissolution. In this way, emphasis is given to the role of fluids, and more specifically fluid transport through minerals and rocks, in mineral-replacement reaction. The work of Putnis underlines once again what was already recognized by the early geochemist George Bauer (1494–1555), who Latinized his name into Agricola: *corpora non agunt nisi soluta* (substances do not interact unless dissolved). The implications of interface-coupled dissolution-precipitation are huge, not only in Earth sciences but also in material sciences for the synthesis of new materials with specific physical and chemical properties.

In Chapter 4, Dmitrii A. Kulik deals with the thermodynamic concepts needed for modeling sorption processes at the aqueous solution–mineral interface. He presents and explains the classical adsorption isotherm equations, including the linear isotherm, Langmuir isotherm, Langmuir isotherm with site mole balance, competitive Langmuir isotherm, generalized Langmuir isotherm for n-dentate adsorption, Langmuir isotherm for multi-site adsorption, Frumkin isotherm, BET isotherm, and Freundlich isotherm. A large section of this chapter is devoted to surface-complexation models such as the Diffuse Layer model, Constant Capacitance model, Triple Layer model, Basic Stern model, and Charge Distribution three-plane model. Much attention is paid to mutual consistency between thermodynamic concepts and approaches adopted to describe sorption phenomena on mineral–water interfaces. As recognized by the author, neither methods and computer programs for surface-speciation modeling nor the surface-chemistry data needed to develop internally consistent thermodynamic databases are covered in this chapter.

Chapter 5, written by David M. Sherman, is also devoted to sorption processes, and aims to show how a molecular-scale picture of the mineral–water interface, chiefly obtained from computational quantum chemistry, can be used to develop surface-complexation models. Topics discussed are the nature of oxide surfaces, acid-base chemistry of oxide surfaces, electrostatic potential at the mineral–water interface, computational methods in surface-complex modeling, and surface complexation of metals and oxyanions.

Chapter 6 represents a logical continuation of the topics treated in the two previous sections. Jacques Schott, Oleg S. Pokrovsky, and Eric H. Oelkers review the mechanisms governing the kinetics of mineral dissolution and precipitation reactions, showing that accurate knowledge of water chemistry and distance from equilibrium are essential prerequisites for quantification of available rate data on different mineral-water systems. First, they recall the role of the stoichiometry and stability of the precursor surface complex to describe rates as a function of solution composition, in the framework of the Transition State Theory and Surface Coordination Chemistry. Brucite, quartz, boehmite, and gibbsite are discussed as examples of single oxide minerals, whose dissolution requires breaking one kind of bond only. The dissolution mechanisms and rates of multi-oxides minerals are then taken into account, including aluminum-silicate minerals and glasses and basic silicates, both under far-from-equilibrium and close-to-equilibrium conditions. The carbonate–solution interface is introduced to describe the dissolution and precipitation kinetics of carbonate minerals. Finally, the temperature dependence of mineral dissolution rates is discussed.

Chapter 7 is voluminous, comprising 111 pages, roughly one-fifth of the whole book. Indeed, the role and fate of organic substances in water–rock interaction is a rather large topic. Although it is extensively covered by Jiwchar Ganor, Itay J. Reznik, and Yoav O. Rosenberg, they acknowledge that they still have not represented all the important aspects of this field. The chapter begins with an introduction on the classification, distribution, and origin of organic compounds, followed by their effects on solution chemistry and a short introduction to characterization of the mineral–water interface. Most of the chapter is organized into three large sections dealing with the three main processes of water–rock interaction: sorption onto mineral surfaces, mineral dissolution, and mineral precipitation. This chapter represents a sort of separate book within the book, but it is certainly very informative.

Chapter 8 is dedicated to one of the most challenging topics in water–rock interaction, namely mineral-precipitation kinetics. First, Bertrand Fritz and Claudine Noguera present and discuss the theoretical background of nucleation and growth processes, for solid particles of both fixed and variable composition. They then introduce the NANOKIN computer code. Finally some applications are developed, including precipitation of a single mineral phase of fixed composition, the competition between two mineral phases with the same composition in an initially supersaturated aqueous solution, precipitation in response to granite dissolution, and the precipitation of mineral phases of variable composition. The authors recognize the need to actually measure the variables entering the nucleation and growth model, such as surface energies, parameters related to the nucleation rate, and evolution of particle size for several minerals of interest.

The last four chapters of the book are dedicated to geochemical modeling. In Chapter 9, Yves Goddéris and coauthors apply a coupling strategy, using the mechanistic weathering model WITCH with either the regional-scale biospheric productivity

model ASPECTS or the continental-scale global dynamic vegetation model LPJ. In this way, they estimate the role of silicate weathering and related cation export in the large tropical drainage basin of the Orinoco River.

In Chapter 10, Susan L. Brantley and Art F. White concentrate on the weathered regolith. They first provide a theoretical framework for modeling soil profiles. They then present several models which have been proposed to interpret the composition of aqueous solutions and solids in the regolith. Next, numerical modeling is addressed through two different approaches: relatively simple spreadsheet calculators and then more sophisticated multi-component, multi-phase reactive-transport computer programs; in this way, kinetic and transport parameters as well as hydrological, chemical, and physical soil data are taken into account. Finally, the outputs of this hierarchical approach to the study of soil profiles are compared, and generalizations are drawn.

In Chapter 11, Carl I. Steefel and Kate Maher review the transport processes (advection, molecular diffusion, hydrodynamic dispersion, electrochemical migration) influencing and governing gas–water–rock interaction, as well as the variations in transport properties caused by chemical reactions. They then introduce the equations governing reactive transport and related parameters (e.g., the Péclet and Damköler numbers) and discuss specific research foci. The three different types of models that are presently used for describing reactive transport in porous media are briefly discussed: (i) continuum models, (ii) pore-scale models, and (iii) multi-continuum or hybrid models involving a combination of different scales. To highlight the power and flexibility of reactive-transport models, some case studies are considered. In particular, reactive-transport models are used to estimate the rates of (i) anaerobic methane oxidation in marine sediments; (ii) chemical weathering; and (iii) reactions occurring in a permeable reactive barrier used for remediation treatment for acid mine drainage. Finally, incorporation of isotopes in multi-component models is investigated.

In the final Chapter 12, Chen Zhu deals with geochemical modeling of reaction paths and reaction networks and, in particular, with the dynamic evolution, feedback, and coupling of reactions in a given network. First, the field evidence for reaction network is considered, with examples from carbon sequestration, seawater injection for secondary recovery of oil and gas, and CO_2 injection for enhanced oil recovery. Applications of chemical kinetics to model reaction networks are then presented.

Throughout the book, topics are treated in a rigorous, complete, and up-to-date way. One might question why only a minimal part of the book (i.e., the example presented from Chapter 11) was dedicated to isotopes and their integration in geochemical models, but I suspect this to be a deliberate choice of the editors.

The main item missing from this book is a subject index. Indexes are absent from all of the volumes of *Reviews in Mineralogy & Geochemistry* (formerly *Reviews in Mineralogy*) that I have had the opportunity to read (about 15). Without a subject index, it is impossible to search for a specific topic or word in these large volumes. This severely limits their use. Ideally, a global subject index should be placed at the end of each book, but a subject index for each individual chapter could be a good alternative. This improvement should be taken into serious consideration by the Series Editor.

I strongly recommend this book to everybody who wants to know the latest developments in the geochemistry of water–rock interaction, with special emphasis on thermodynamics and kinetics, which are the pillars of geochemistry.

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