

GEOCHEMICAL AND BIOGEOCHEMICAL REACTION MODELING

An indispensable primer and reference textbook, the third edition of *Geochemical and Biogeochemical Reaction Modeling* carries the reader from the field's origins and theoretical underpinnings through to a collection of fully worked examples. A clear exposition of the underlying equations and calculation techniques is balanced by real-world example calculations. The book depicts geochemical reaction modeling as a vibrant field of study applicable to a wide spectrum of issues of scientific, practical, and societal concern. The new edition offers a thorough description of surface complexation modeling, including two- and three-layer methods; broader treatment of kinetic rate laws; the effect of stagnant zones on transport; and techniques for determining gas partial pressures. This handbook demystifies and makes broadly accessible an elegant technique for portraying chemical processes in the geosphere. It will again prove to be invaluable for geochemists, environmental scientists and engineers, aqueous and surface chemists, microbiologists, university teachers, and government regulators.

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Third Edition

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For Abby, Henry, Gabrielle, and Claire

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Preface

When in 1995 I sent my editor the typescript for the first edition of this book—by parcel post, of course—I remember thinking, “Well, I’ll never do that again!” Writing such a detailed, technical monograph had proved all-consuming. Lacking further insight I felt I could contribute, I was anxious to leave reaction modeling behind and try new things.

And I did. The microbiological revolution swept over the geosciences shortly following the first edition’s debut. Colleagues and I quickly found a place for ourselves at the interface between aqueous geochemistry and environmental microbiology. Computers were traversing their own wild revolution, doubling and redoubling in capability on intervals measured in months. The work a privileged few of us were doing in the early 1990s using enormous, vastly expensive computers became possible at any scientist’s or engineer’s desk. Simulations that seemed out of reach became almost routine.

A decade after its publication, as a result, the first edition no longer seemed complete. The modern geochemist needed to understand redox disequilibrium, the foundation of chemolithotrophic life. The kinetics of mineral dissolution and precipitation remained important, but the rates at which redox reactions proceed and at which microbes catalyze chemical transformation, and the dynamics of microbial communities seemed just as central to the field. As I prepared the first edition I suspected only a handful of my hardest colleagues would care about the ins and outs of constructing reactive transport models of geochemical systems, an endeavor impractical for most. But microprocessors replaced supercomputers and an obscure field of study lurched into the mainstream. Buoyed by my editor’s enthusiasm, the second edition I had not expected to write emerged page by page, example by example. This time a mouse click sent the finished typescript, now ten chapters longer, on its way to publication.

History repeated itself, as it is apt to do, and a decade on the text once again seemed inadequate. Surface complexation theory had expanded as a field and its treatment needed to be generalized: polydentate complexes, single and double pK_a paradigms, electrically charged complexing sites, and the triple-layer and CD-MUSIC formalisms all demanded full consideration. Activity coefficient theory had evolved, especially in light of wider adoption of the SIT method. The relationship between partial pressure and gas fugacity could no longer remain implied, but had to be set out in a quantitative sense. The modern modeler wanted to account for the kinetics of the formation and breakdown of aqueous and surface complexes, and the transfer of gas species between aqueous and gaseous phases. The discussion of reactive transport modeling needed to better convey the nature of numerical dispersion, and to introduce the role of stagnant zones within the domain—the dual-porosity effect.

None of this work would have been possible had it not been for the good fortune of being able to benefit from the expert, good-spirited, and untiring assistance of my most valued colleagues. Brian Farrell and Melika Sharifironizi spent countless months sifting through the latest developments in surface complexation theory.

Melika took the lead in deciphering three-layer modeling; I remain pleasantly bemused to see our work on the subject laid out in only a dozen book pages. Brian and Jia Wang similarly sorted through SIT electrolyte theory and helped translate literature pages into lines of computer code. Helge Moog and Frank Bok blazed the way as we implemented and documented three methods for computing fugacity coefficients, work that once again was improbably distilled into a few book pages.

Wolfgang Voight, Pat Brady, Jon Chorover, Blaine McCleskey, Bill Casey, and Nita Sahai all stepped in at just the right moment with thoughts I could build upon, or the perfect literature reference. The work Brian, Melika, Jia, Frank, Helge, Blaine, and Pat proffered as they reviewed and proofread revision after revision contributed more than I can describe to the final product. Neither my editors, Cambridge University Press, nor the University of Illinois ever wavered in their support. Finally, I thank the community of more than 10,000 users of our codes for letting us know the moment anything seemed confusing or off-kilter: You are the ultimate quality control on everything we do.

Preface to Second Edition

In the decade since I published the first edition of this book,¹ the field of geochemical reaction modeling has expanded sharply in its breadth of application, especially in the environmental sciences. The descriptions of microbial activity, surface chemistry, and redox chemistry within reaction models have become more robust and rigorous. Increasingly, modelers are called upon to analyze not just geochemical but biogeochemical reaction processes.

At the same time, reaction modeling is now commonly coupled to the problem of mass transport in groundwater flows, producing a subfield known as reactive transport modeling. Whereas a decade ago such modeling was the domain of specialists, improvements in mathematical formulations and the development of more accessible software codes have thrust it squarely into the mainstream.

I have, therefore, approached preparation of this second edition less as an update to the original text than an expansion of it. I pay special attention to developing quantitative descriptions of the metabolism and growth of microbial species, understanding the energy available in natural waters to chemosynthetic microorganisms, and quantifying the effects microorganisms have on the geochemical environment. In light of the overwhelming importance of redox reactions in environmental biogeochemistry, I consider the details of redox disequilibrium, redox kinetics, and effects of inorganic catalysts and biological enzymes.

I expand treatment of sorption, ion exchange, and surface complexation, in terms of the various descriptions in use today in environmental chemistry. And I integrate all the above with the principles of mass transport, to produce reactive transport models of the geochemistry and biogeochemistry of the Earth's shallow crust. As in the first edition, I try to juxtapose derivation of modeling principles with fully worked examples that illustrate how the principles can be applied in practice.

In preparing this edition, I have drawn on the talents and energy of a number of colleagues. First and foremost, discussion of the kinetics of redox reactions and microbial metabolism is based directly on the work my former graduate student Qusheng Jin undertook in his years at Illinois. My understanding of microbiology stems in large part from the tireless efforts of my colleague Robert Sanford. In modeling the development of zoned microbial communities, I use the work of my students Qusheng Jin, Jungho Park, Meng Li, Man Jae Kwon, and Dong Ding. Tom Holm found in the literature he knows so well sorption data for me to use, and Barbara Bekins shared data from her biotransformation experiments. Finally, I owe a large combined debt to the hundreds of people who have over the years reviewed our papers, commented on our software, sent email, talked to us at meetings, and generally pointed out the errors and omissions in our group's thinking.

I owe special thanks to colleagues who reviewed draft chapters: Patrick Brady at Sandia National Laboratories; Glenn Hammond, Pacific Northwest National Laboratory; Thomas Holm, Illinois Water Survey;

¹ *Geochemical Reaction Modeling*, Oxford University Press, 1996.

Qusheng Jin, University of Oregon; Thomas McCollom, University of Colorado; David Parkhurst, US Geological Survey; Robert Sanford, University of Illinois; Lisa Stillings, US Geological Survey; and Brian Viani, Lawrence Livermore National Laboratories.

Finally, the book would not have been possible without the support of the institutions that underwrote it: the Centre for Water Research at the University of Western Australia and UWA's Gledden Fellowship program, the Department of Geology at the University of Illinois, the US Department of Energy (grant DE-FG02-02ER15317), and a consortium of research sponsors (Chevron, Conoco Phillips, Exxon Mobil, Idaho National Engineering and Environmental Laboratory, Lawrence Livermore Laboratories, Sandia Laboratories, SCK CEN, Texaco, and the US Geological Survey).

Preface to First Edition

Geochemists have long recognized the need for computational models to trace the progress of reaction processes, both natural and artificial. Given a process involving many individual reactions (possibly thousands), some of which yield products that provide reactants for others, how can we know which reactions are important, how far each will progress, what overall reaction path will be followed, and what the path's endpoint will be?

These questions can be answered reliably by hand calculation only in simple cases. Geochemists are increasingly likely to turn to quantitative modeling techniques to make their evaluations, confirm their intuitions, and spark their imaginations.

Computers were first used to solve geochemical models in the 1960s, but the new modeling techniques disseminated rather slowly through the practice of geochemistry. Even today, many geochemists consider modeling to be a “black art,” perhaps practiced by digital priests muttering mantras like “Newton–Raphson” and “Runge–Kutta” as they sit before their cathode ray altars. Others show little fear in constructing models but present results in a way that adds little understanding of the problem considered. Someone once told me, “Well, that’s what came out of the computer!”

A large body of existing literature describes either the formalism of numerical methods in geochemical modeling or individual modeling applications. Few references, however, provide a perspective of the modeling specialty, and some that do are so terse and technical as to discourage the average geochemist. Hence, there are few resources to which someone wishing to construct a model without investing a career can turn.

I have written this book in an attempt to present in one place both the concepts that underpin modeling studies and the ways in which geochemical models can be applied. Clearly, this is a technical book. I have tried to present enough detail to help the reader understand what the computer does in calculating a model, so that the computer becomes a useful tool rather than an impenetrable black box. At the same time, I have tried to avoid submerging the reader in computational intricacies. Such details I leave to the many excellent articles and monographs on the subject.

I have devoted most of this book to applications of geochemical modeling. I develop specific examples and case studies taken from the literature, my experience, and the experiences over the years of my students and colleagues. In the examples, I have carried through from the initial steps of conceptualizing and constructing a model to interpreting the calculation results. In each case, I present complete input to computer programs so that the reader can follow the calculations and experiment with the models.

The reader will probably recognize that, despite some long forays into hydrologic and basin modeling (a topic for another book, perhaps), I fell in love with geochemical modeling early in my career. I hope that I have communicated the elegance of the underlying theory and numerical methods as well as the value of calculating models of reaction processes, even when considering relatively simple problems.

I first encountered reaction modeling in 1980 when working in Houston at Exxon Production Research Company and Exxon Minerals Company. There, I read papers by Harold Helgeson and Mark Reed and experimented with the programs EQ3/EQ6, written by Thomas Wolery, and PATH, written by Ernest Perkins and Thomas Brown.

Computing time was expensive then (about a dollar per second!). Computers filled entire rooms but were slow and incapacious by today's standards, and graphical tools for examining results almost nonexistent. A modeler sent a batch job to a central CPU and waited for the job to execute and produce a printout. If the model ran correctly, the modeler paged through the printout to plot the results by hand. But even at this pace, geochemical modeling was fun!

I returned to modeling in the mid 1980s when my graduate students sought to identify chemical reactions that drove sediment diagenesis in sedimentary basins. Computing time was cheaper, graphics hardware more accessible, and patience generally in shorter supply, so I set about writing my own modeling program, GT, which I designed to be fast enough to use interactively. A student programmer, Thomas Dirks, wrote the first version of a graphics program GTPLOT. With the help of another programmer, Jeffrey Biesiadecki, we tied the programs together, creating an interactive, graphical method for tracing reaction paths.

The program was clearly as useful as it was fun to use. In 1987, at the request of a number of graduate students, I taught a course on geochemical reaction modeling. The value of reaction modeling in learning geochemistry by experience rather than rote was clear. This first seminar evolved into a popular course, "Groundwater Geochemistry," which our department teaches each year.

The software also evolved as my group caught the interactive modeling bug. I converted the batch program GT to REACT, which was fully interactive. The user entered the chemical constraints for his problem and then typed "go" to trigger the calculation. Ming-Kuo Lee and I added Pitzer's activity model and a method for tracing isotope fractionation. Twice I replaced GTPLOT with new, more powerful programs. I wrote ACT2 and TACT to produce activity–activity and temperature–activity diagrams, and RXN to balance reactions and compute equilibrium constants and equations.

In 1992, we bundled these programs together into a package called "The Geochemist's Workbench[®]" which is owned by The Board of Trustees of the University of Illinois and can be licensed inexpensively for educational or commercial purposes. Within a few months of its completion the software was in use at dozens of universities and companies around the world.

We find that the programs allow us to try fresh approaches to teaching aqueous geochemistry. Once a student can reliably balance reactions by hand, the task quickly becomes a chore. After calculating a few Eh–pH diagrams, what does one learn by manually producing more plots? For many students, trees quickly come to obscure a beautiful forest. The computer can take over the mechanics of basic tasks, once they have been mastered, freeing the student to absorb the big picture and find the broad perspective. This approach has proved popular with students and professors. Many examples given in this book were developed originally as class assignments and projects.

I should not, however, give the impression that geochemical modeling is of any greater value in education than in scientific and practical application. The development of our modeling software, as evident in the case studies in this book, reflects the practical needs of petroleum geology and environmental geochemistry expressed to us over nearly a decade by a consortium of industrial and governmental affiliates to the Hydrogeology Program. These affiliates, without whom neither the software nor this book would exist, are: Amoco Production Research; ARCO Oil and Gas Company; British Petroleum Research; Chevron Petroleum Technology Company; Conoco, Incorporated; Du Pont Company; Exxon Production Research; Hewlett Packard, Incorporated; Illinois State Geological Survey; Japan National Oil Company; Lawrence Livermore National

Laboratory; Marathon Oil Company; Mobil Research and Development; Oak Ridge National Laboratory; Sandia National Laboratories; SiliconGraphics Computer Systems; Texaco, Incorporated; Union Oil Company of California; and the United States Geological Survey.

I can thank just a few of my colleagues and students who helped develop the case studies in this book. John Yecko and William Roy of the Illinois State Geological Survey first modeled degradation of the injection wells at Marshall, Illinois. Rachida Bouhlila provided analyses of the brines at Sebkhath El Melah, Tunisia. Amy Berger helped me write Chapter 10 (Surface Complexation), and Chapter 35 (Acid Drainage) is derived in part from her work. Edward Warren and Richard Worden of British Petroleum's Sunbury lab contributed data for calculating scaling in North Sea oil fields, Richard Wendlandt first modeled the effects of alkali floods on clastic reservoirs, and Kenneth Sorbie helped write Chapter 34 (Petroleum Reservoirs). I borrowed from Elisabeth Rowan's study of the genesis of fluorite ores at the Albigeois district, Wendy Harrison's study of the Gippsland basin, and a number of other published studies, as referenced in the text.

The book benefited enormously from the efforts of a small army of colleagues who served as technical reviewers: Stephen Altaner, Tom Anderson, and Amy Berger (University of Illinois); Greg Anderson (University of Toronto); Paul Barton, Jim Bischoff, Neil Plummer, Geoff Plumlee, and Elisabeth Rowan (US Geological Survey); Bill Bourcier (Livermore); Patrick Brady and Kathy Nagy (Sandia); Ross Brower and Ed Mehnert (Illinois State Geological Survey); David Dzombak (Carnegie Mellon University); Ming-Kuo Lee (Auburn University); Peter Lichtner (Desert Research Institute); Benoit Madé and Jan van der Lee (Ecole des Mines); Mark Reed (University of Oregon); Kenneth Sorbie (Heriot-Watt University); Carl Steefel (Battelle); Jim Thompson (Harvard University); and John Weare (University of California, San Diego). I learned much from them. I also thank Mary Glockner, who read and corrected the entire manuscript; my editor Joyce Berry, and Lisa Stallings at Oxford for their unwavering support; and Bill Bourcier and Randy Cygan, who have always been willing to lend a hand, and often have.

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A Note About Software

The geochemical modeler's milieu is software and the computer on which it runs. A number of computer programs have been developed over past decades to facilitate geochemical modeling; Appendix A lists the availability of current versions of a number of popular applications. Each program has its own capabilities, limitations, and indeed, personality. There is no best software, only the software that best meets a modeler's needs.

No discussion of geochemical modeling would be fully useful without specific examples showing how models are configured and run. In setting up the examples in this book, I employ a group of interactive programs that my colleagues and I have written over the past thirty-five or so years. The programs, RXN, ACT2, TACT, SPECE8, REACT, GTPLOT, X1T, X2T, XTPLOT, PHASE2, P2PLOT, TEDIT, and GSS, are known collectively as The Geochemist's Workbench[®], or simply the GWB. The GWB is available in a versatile Community Edition as a free download, as well as in several paid packages; the latter options will be needed to reproduce the more advanced examples in latter sections of the book.

I chose to use this software for reasons that extend beyond familiarity and prejudice: the programs are interactive and take simple commands as input. As such, I can include within the text of this book scripts that in a few lines show the precise steps taken to calculate each result¹. Readers can, of course, reproduce a given calculation by using any of a number of other modeling programs, such as those listed in Appendix A. Following the steps shown in the text, they should be able to construct input in the format recognized by the chosen program.

¹ The input scripts developed in this text are installed along with the GWB 2022 and subsequent software releases, and available for download as an Online Resource from Cambridge University Press.

