GEOCHEMICAL AND BIOGEOCHEMICAL REACTION MODELING

Geochemical reaction modeling plays an increasingly vital role in a number of areas of geoscience, ranging from groundwater and surface water hydrology to environmental preservation and remediation to economic and petroleum geology to geomicrobiology.

This book provides a comprehensive overview of reaction processes in the Earth's crust and on its surface, both in the laboratory and in the field. A clear exposition of the underlying equations and calculation techniques is balanced by a large number of fully worked examples. The book uses The Geochemist's Workbench® modeling software, developed by the author and installed at over 1000 universities and research facilities worldwide. The reader can, however, also use the software of his or her choice. The book contains all the information needed for the reader to reproduce calculations in full.

Since publication of the first edition, the field of reaction modeling has continued to grow and find increasingly broad application. In particular, the description of microbial activity, surface chemistry, and redox chemistry within reaction models has become broader and more rigorous. Reaction models are commonly coupled to numerical models of mass and heat transport, producing a classification now known as reactive transport modeling. These areas are covered in detail in this new edition.

This book will be of great interest to graduate students and academic researchers in the fields of geochemistry, environmental engineering, contaminant hydrology, geomicrobiology, and numerical modeling.

CRAIG BETHKE is a Professor at the Department of Geology, University of Illinois, specializing in mathematical modeling of subsurface and surficial processes. He won the O.E. Meinzer Award from the Geological Society of America and is a Fellow of the American Association for the Advancement of Science; he has worked in France and Australia, as well as in the United States.

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Second Edition

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CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo

Cambridge University Press
The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521875547

First edition published as Geochemical Reaction Modeling by Oxford University Press, 1996

Printed in the United Kingdom at the University Press, Cambridge

A catalog record for this publication is available from the British Library

ISBN 978-0-521-87554-7 hardback

For A., H., G., and C.

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Preface

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 principals 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

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

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; 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

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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.

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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 Sebkhat El Melah, Tunisia.

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Amy Berger helped me write Chapter 10 (Surface Complexation), and Chapter 31 (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 30 (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.

I thank the two institutions that supported me while I wrote this book: the Department of Geology at the University of Illinois and the Centre d'Informatique Géologique at Ecole Nationale Supérieure des Mines de Paris in Fontainebleau, France. I began writing this book in Fontainebleau while on sabbatical leave in 1990 and completed it there under the sponsorship of the Académie des Sciences and Elf Aquitaine in 1995.

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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 the past twenty years to facilitate geochemical modeling (sources of the current versions of popular programs are listed in Appendix 1). Each program has its own capabilities, limitations, and indeed, personality. Some programs work on personal computers, others on scientific workstations, and a few run best on supercomputers. Some provide output graphically, others produce printed numbers. 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 twenty or so years. The programs, RXN, ACT2, TACT, SPECE8, REACT, GTPLOT, X1T, X2T, XTPLOT are known collectively as "The Geochemist's Workbench®." To run all of the examples in this book, you will need to have installed version 7.0 or later.

The package, which runs on personal computers, can be licensed for educational and commercial use. This book is not intended to serve as documentation for these programs; a separate, comprehensive set of User's Guides is available for that purpose.

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 result. Readers can, of course, reproduce the calculations by using any of a number of other modeling programs, such as those listed in Appendix 1. Following the steps shown in the text, they should be able to construct input in the format recognized by the chosen program.