

# Geochemistry

## An Introduction



Introducing the essentials of modern geochemistry for students across the Earth and environmental sciences, this new edition emphasizes the general principles of this central discipline. Focusing on inorganic chemistry, Francis Albarède's refreshing approach is brought to topics that range from measuring geological time to the understanding of climate change. The author leads the reader through the quantitative aspects of the subject in a manner that is easy to understand.

The early chapters cover the principles and methods of physics and chemistry that underlie geochemistry, to build the students' understanding of concepts such as isotopes, fractionation, and mixing. These are then applied across many of the environments on Earth, including the solid Earth, rivers, and climate, and then extended to processes on other planets.

Three new chapters have been added – on stable isotopes, biogeochemistry, and environmental geochemistry. Student exercises are now included at the end of each chapter, with solutions available online.

**Francis Albarède** is Professor of Geochemistry at the Ecole Normale Supérieure de Lyon and a member of the Institut Universitaire de France. He had held visiting professorships at universities in the USA, Australia, and Japan. He has been President of the European Association of Geochemistry, Chief Editor of *Earth and Planetary Science Letters*, and the *Journal of Geophysical Research*. He has received numerous awards, including the Norman Bowen Award of the American Geophysical Union, the Arthur Holmes Medal of the European Union of Geosciences, and the Goldschmidt Award of the Geochemical Society. He is also author of *Introduction to Geochemical Modeling* (Cambridge University Press, 1995).

Cambridge University Press  
978-0-521-88079-4 - Geochemisry: An Introduction: Second Edition  
Francis Albarède  
Frontmatter  
[More information](#)

---

Cambridge University Press  
978-0-521-88079-4 - Geochemistry: An Introduction: Second Edition  
Francis Albarède  
Frontmatter  
[More information](#)

# Geochemistry

## An Introduction

Second Edition

Francis Albarède  
Ecole Normale Supérieure de Lyon  
Institut Universitaire de France



Cambridge University Press  
978-0-521-88079-4 - Geochemistry: An Introduction: Second Edition  
Francis Albarède  
Frontmatter  
[More information](#)

---

**CAMBRIDGE**  
UNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom

Cambridge University Press is part of the University of Cambridge.  
It furthers the University's mission by disseminating knowledge in the pursuit of  
education, learning and research at the highest international levels of excellence.

[www.cambridge.org](http://www.cambridge.org)

Information on this title: [www.cambridge.org/albarède](http://www.cambridge.org/albarède)

© F. Albarède 2003, 2009

This publication is in copyright. Subject to statutory exception  
and to the provisions of relevant collective licensing agreements,  
no reproduction of any part may take place without  
the written permission of Cambridge University Press.

First published 2003

Second Edition 2009

Reprinted with corrections 2011

6th printing 2015

Printed in the United Kingdom by TJ International Ltd, Padstow, Cornwall

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

ISBN 978-0-521-88079-4 Hardback

ISBN 978-0-521-70693-3 Paperback

Cambridge University Press has no responsibility for the persistence or  
accuracy of URLs for external or third-party internet websites referred to  
in this publication, and does not guarantee that any content on such  
websites is, or will remain, accurate or appropriate.

## Contents

<i>Preface to the second edition</i>	<i>page</i> ix
<i>Foreword to the first English edition</i>	x
<i>Foreword to the French edition</i>	xii
<i>Acknowledgments</i>	xiv
<b>Introduction</b>	<b>1</b>
<b>1 The properties of elements</b>	<b>5</b>
1.1 The periodic table	7
1.2 Chemical bonding	11
1.3 States of matter and the atomic environment of elements	15
1.4 Geochemical classifications	17
1.5 The different reservoirs and their compositions	19
1.6 The nucleus and radioactivity	20
Exercises	22
<b>2 Mass conservation and elemental fractionation</b>	<b>25</b>
2.1 Conservation of mass	26
2.2 Elemental fractionation	31
2.3 Films and interfaces	36
2.4 Distillation processes	37
Exercises	41
References	44
<b>3 Fractionation of stable isotopes</b>	<b>45</b>
3.1 Principles of stable isotope fractionation	46
3.2 Delta notation and stuff	56
3.3 Hydrogen	59
3.4 Oxygen	60
3.5 Carbon	64
3.6 Sulfur	66
3.7 Nitrogen	67
3.8 Other elements	68
Exercises	68
References	70

<b>4</b>	<b>Geochronology and radiogenic tracers</b>	<b>71</b>
4.1	Dating by radioactive nuclides	78
4.1.1	Carbon-14	78
4.1.2	Beryllium-10	79
4.1.3	The thorium-230 excess method	81
4.2	Systems with high parent/daughter ratios	83
4.2.1	The potassium–argon method	83
4.2.2	Dating zircons by the uranium–lead method	84
4.3	The isochron method	86
4.4	Radiogenic tracers	90
4.5	Helium isotopes	93
	Exercises	94
	References	99
<b>5</b>	<b>Element transport</b>	<b>101</b>
5.1	Advection	102
5.2	Diffusion	103
5.2.1	Closure temperature: chronometers, thermometers, and barometers	106
5.2.2	Other applications	110
5.3	Chromatography	110
5.4	Reaction rates	113
5.5	Adsorption	115
	Exercises	116
	References	118
<b>6</b>	<b>Geochemical systems</b>	<b>120</b>
6.1	Single-reservoir dynamics	120
6.2	Interaction of multiple reservoirs and geochemical cycles	127
6.3	Mixing and stirring	131
	Exercises	134
	References	137
<b>7</b>	<b>The chemistry of natural waters</b>	<b>138</b>
7.1	Basic concepts	138
7.2	Dominance diagrams	141
7.3	Speciation in solutions	143
7.4	Water–solid reactions	144
7.5	Electrolyte chemistry	146
7.6	Biological activity	147
7.7	The carbonate system	148
7.8	Precipitation, rivers, weathering, and erosion	152
7.9	Elements of marine chemistry	156

	Exercises	163
	References	167
<b>8</b>	<b>Biogeochemistry</b>	<b>168</b>
8.1	The geological record	168
8.2	Some specifics of biological activity	170
8.3	The chemistry of life	172
8.4	Biominerals	176
8.5	Biological controls on the ocean–atmosphere system	177
8.6	Diagenetic transformation of organic material	178
8.7	Biomarkers	181
8.8	Metals in organic matter	182
	References	183
<b>9</b>	<b>Environments</b>	<b>184</b>
9.1	Phanerozoic climates	185
	9.1.1 Quaternary climates	186
	9.1.2 Mesozoic and Cenozoic climatic trends	187
	9.1.3 Biogeochemical catastrophes in the Phanerozoic	191
9.2	The rise of atmospheric oxygen	193
	9.2.1 The 2.1 Ga crisis	193
	9.2.2 The Snowball Earth and the emergence of Metazoans	196
9.3	The geochemical environment of the origin of life	198
	Exercises	200
	References	201
<b>10</b>	<b>Mineral reactions</b>	<b>202</b>
10.1	Early diagenesis	204
10.2	Hydrothermal reactions	205
10.3	Metamorphism	211
10.4	Water/rock ratios	214
	Exercises	215
	Reference	217
<b>11</b>	<b>The solid Earth</b>	<b>218</b>
11.1	The geochemical variability of magmas	221
	11.1.1 Melting of the mantle and crust	221
	11.1.2 Differentiation of magmatic series	225
11.2	Magmatism of the different tectonic sites	229
11.3	Mantle convection	237
11.4	The growth of continental crust	241
	References	246

<b>12 The Earth in the Solar System</b>	<b>248</b>
12.1 The formation of elements	249
12.2 The formation of the Solar System	255
12.3 Condensation of planetary material	258
12.4 The composition of the Earth and its core, and the origin of seawater	261
12.5 The early Solar System	265
12.6 The Moon	272
12.7 Mars	276
12.8 Venus	278
12.9 Planetary atmospheres	279
Exercises	283
References	287
<b>13 The element barn</b>	<b>288</b>
13.1 Silicon	288
13.2 Aluminum	290
13.3 Potassium	291
13.4 Sodium	292
13.5 Magnesium	293
13.6 Calcium	294
13.7 Iron	295
13.8 Sulfur	298
13.9 Phosphorus	299
13.10 Carbon	300
References	302
<i>Appendix A Composition of the major geological units</i>	303
<i>Appendix B The mixing equation for ratios</i>	306
<i>Appendix C A refresher on thermodynamics</i>	308
<i>Appendix D The geological time scale</i>	315
<i>Appendix E An overview of analytical methods</i>	316
<i>Appendix F Physical and geophysical constants</i>	322
<i>Appendix G Some equations relative to residence time</i>	323
<i>Appendix H The adiabatic atmosphere</i>	325
<i>Further reading</i>	327
<i>Index</i>	330

## Preface to the second edition

The material of several chapters has been deeply revised and rewritten for better intelligibility and to account for some major recent scientific developments. Many figures have been redrawn. I stuck to the black-and-white option to make it easier for teachers to distribute photocopied material for educational purpose: with due credit, I will gladly provide the figures as eps files that can be dressed with colors for classes. New chapters have been added, one on stable isotope fractionation, one on biogeochemistry, and one on paleoenvironments; and existing chapters have been complemented with new material. Overall, the new edition is 50 percent longer than the first one.

Although I used graphic analogies whenever I thought it could spare the reader a difficult mathematical derivation without losing the substance of basic concepts, some of this new material will certainly be felt as a turn-off and I apologize for that. Boxes have been added for very specific material, such as the derivation of some equations, common misconceptions, or more anecdotal material, all of which can be left out without interrupting the main flow of the presentation. Quoting too much old work is pedantic but we can't really ignore the papers that created the basic concepts we use every day. I have marked as "must read" with a ♠ sign some references which laid the groundwork of entire fields.

Finally, at the end of most chapters I have incorporated an additional section of exercises, which have been found previously only on my website. In addition, the References and Further reading sections have been comprehensively updated.

**Francis Albarède**  
*Ecole Normale Supérieure, Lyon*

## Foreword to the first English edition

Modern geochemistry is a discipline that pervades nearly all of Earth science, from measuring geological time through tracing the origin of magmas to unravelling the composition and evolution of continents, oceans and the mantle, all the way to the understanding of environmental changes. It is a comparatively young discipline that was initiated largely by Goldschmidt in the 1930s, but its modern development and phenomenal growth started only in the 1950s. Although there are many journals dedicated to geochemical research, there have been remarkably few general geochemical textbooks that cover more than a limited segment of the full scope of modern geochemistry. This is one reason why Francis Albarède's new book is most welcome. It is written by the author of the authoritative and widely acclaimed *Introduction to Geochemical Modeling* (Cambridge University Press, 1995), and it is intended as an undergraduate introductory course in geochemistry. Its scope is large, though not all-inclusive, concentrating on the inorganic chemistry of the condensed part of our planet. Although it started out as a translation from the original French book, the new English-language edition is much more than just a translation. The entire text has been substantially revised and in some parts expanded, and it is really a new book. Yet it retains a distinctly French flavor, particularly in the way many subjects are addressed via mathematical description. This approach is entirely normal for a student of the French Ecole Normale or a French university, but it will surprise many American teachers and students of geology alike. So if you are teaching or taking a course in "Rocks for Jocks," this book is not for you. But if you are interested in an introduction to modern geochemistry as a quantitative science, this book is definitely for you. Francis Albarède often uses a light touch, not taking the subject (or himself) excessively seriously, he uses refreshingly surprising analogs to approach important principles or processes, and his style is often informal. Look, for example, at the "Further reading" list. The books are classified into three categories, A, armchair reading, B, for students, and C, serious stuff, and each book is given a one- or two-line thumbnail characterization. Very nice. And by the way, the book itself, while clearly aimed at B, does contain material in all three categories!

What I particularly like about this book is its scope and choice of subjects, combined with sometimes bold brevity, which I hope will leave the student with an appetite for more. The emphasis is always on general principles rather than specific geochemical results or observations, and this should give the book a long residence time and keep it from becoming outdated. We are led from an introduction to the atomic and nuclear properties of the chemical elements to the principles of chemical and isotopic fractionation and mixing, geochronology and the use of radiogenic tracers to characterize source reservoirs, geochemical transport by advection and diffusion, the concept of closure temperature, chromatography, reaction rates to the treatment of large-scale systems, such as the oceans,

the crust, and the mantle. The approach is initially mostly theoretical, focusing on the mathematical description of the behavior and interaction of single and multiple reservoirs. This is followed by a wide-ranging chapter on “Waters present and past,” which covers topics from solution chemistry, water–rock interactions, erosion, rivers and oceans, to climate development during the Pleistocene. From there, we move to the “solid Earth,” which deals with the evolution of mantle and crust, but also with the geochemistry of magmas. Finally, or almost finally, we are taken to phenomena of even much larger scale, the formation of the chemical elements in stars, the formation of the Solar System, the age and composition of Earth, Moon, and Mars.

The message the student should take from this is that geochemistry is a quantitative science that has made decisive contributions to the understanding of all these subjects. It has thus become one of the central disciplines of Earth science, a fact that is not always reflected in undergraduate curricula. This book should help to correct this common deficiency in the training of Earth scientists. It is an inspired book; I hope you will enjoy reading it as much as I did.

**Albrecht W. Hofmann**

*Max Planck Institute for Chemistry, Mainz*

## Foreword to the French edition

I am specially happy to preface this book. First, because it is always a pleasure to be able to speak well of a friend's work; and Francis Albarède is a friend of long standing! We both embarked on our academic careers at about the same time. After some solid grounding in geology at the University of Montpellier, we were fortunate enough to begin our doctoral research in geochemistry in the 1970s in Professor Claude Allègre's laboratory at the Paris Institut de Physique du Globe, at a time when the discipline was really taking off in France. We also helped set up degree courses in geochemistry at the recently founded University of Paris 7, where we were appointed Assistant Lecturers. Our work together resulted in the publication of a short book in 1976, primarily for students, which quickly sold out and curiously enough was never reprinted! Few universities in those days offered specialist courses in geochemistry.

Times have clearly changed since then! Geochemistry is now taught in most universities and it is needless to recall here the fundamental contribution that this discipline has made to all areas of Earth sciences and cosmochemistry. It is always helpful, though, for students and for non-specialist faculty to have a textbook that provides a review of the basic concepts and the most recent contributions to the discipline. And this is the second reason why I am happy to present this book; because Francis Albarède's work fulfills both these requirements. The basic principles of the use of the chemical elements and their isotopes are set out clearly, together with their major applications in such varied domains as cosmochemistry (the formation of the chemical elements, of the Solar System, and of the planets), the internal dynamics of the Earth (with its various reservoirs and interaction among them, convection within the mantle, etc.), and its surface processes (hydrosphere, atmosphere, and climate change). Francis Albarède is particularly well qualified to deal with the diversity of geochemical applications because his own research has covered most of these major fields. A number of aspects that are sometimes overlooked in geochemistry books feature here, such as the processes of transport of elements (Chapter 4) or the concepts of residence time (in Chapter 5 on geochemical systems), and there is an overview of analytical techniques, which have proved so fundamental to the development of geochemistry. Moreover, the presentation is often novel (e.g. the presentation of geochronology, which is not just a catalog of the different methods), and the text is copiously illustrated with instructive diagrams and graphs.

One last reason why I particularly like this book is the method that Francis Albarède has chosen for setting out the principles underlying the main geochemical models: most of the relations describing these principles are demonstrated here, and the argument is invariably accompanied and supported by mathematical equations that unquestionably help the reader follow the reasoning. Advancing from one equation to the next is not always effortless, but

the (slight) exertion required is well worth the trouble. Students need to discover or rediscover the satisfaction to be gained from working out the equations describing a particular process from what are often intuitive relationships and, above all, from understanding that such equations are a short-hand representation of an underlying physico-chemical model that it is often easy to symbolize through a simple diagram: in short, they need to call on their faculties of understanding and their aptitude for model-making rather than their memory. Reading this geochemistry textbook should encourage them to do just that. Readers may rest assured though, there is no need to know any advanced mathematics to understand this book; it is within the reach of any good college student. Nor is it devoid of humor: the allegory of dogs, and black and white cats to explain chemical fractionation and the absence of isotopic fractionation is a prime example! Through its resolutely model-based approach to processes and its concise and up-to-date explanations of the main contributions of the discipline, this book should become a standard text for college courses and a very valuable source of information for non-specialists eager to learn more about geochemistry. It comes out at a particularly fortunate time, just as new analytical instruments are about to widen the scope of geochemical tools substantially and give geochemistry a renewed impetus. I wish Francis Albarède's book swift and sustained success.

**Professor Michel Condomines**  
*Université de Montpellier II*

## Acknowledgments

I would like to thank those who made the first edition a success. Advice by Philippe Bonté, Dominique Boust, Hervé Cardon, Bill McDonough, Mireille Polvé, Yannick Ricard, Simon Sheppard, and Pierre Thomas is gratefully acknowledged. Careful reading of the original French manuscript by Janne Blichert-Toft, Frédéric Chambat, Michel Condomines, Don Francis, John Ludden, and Philippe Vidal, and by graduate students at ENS Lyon, has weeded out many errors of form and substance. Dave Manthey allowed me to reproduce graphics from his great Orbital Viewer. Agnès Ganivet kindly and effectively tidied up a first manuscript littered with syntactic errors. I would like to thank Nick Arndt, Edouard Bard, Janne Blichert-Toft, Marc Chaussidon, Al Hofmann, Dan McKenzie, Bruce Nelson, Simon Sheppard, and Jacques Treiner, for reviewing the English manuscript. Chris Sutcliffe did an immense and wonderful job with translation and editing. Lesley Thomas was a clear-headed and efficient copy-editor.

In addition, the second edition owes also a great deal to new friends and colleagues. Detailed reviews by Janne Blichert-Toft and Simon Sheppard led to significant corrections and improvements. Scientific and editorial comments on particular chapters by Vincent Balter, Gilles Dromart, Toshi Fujii, Stephane Labrosse, Bruno Reynard, and Doug Rumble were very much appreciated. Particular thanks for the second edition are due to Tsuyoshi Iizuka, Bruno Reynard, Doug Rumble, and Ivan Vlastelic, for making unpublished material available, and to Barry Bickmore, Fábio Dias, Peter Kolesar, Ran Qin, and John Rudge for pointing out errors in the first edition. Careful copy-editing by Zoë Lewin identified additional issues. Special thanks are due to the Educational Technology Clearinghouse (University of South Florida, <http://etc.usf.edu/clipart/>) for permission to use their clipart.

Working as a faculty at the Ecole Normale Supérieure in Lyon is good luck, both for the prevailing intellectual standard among scientists and students, and for the time saved by the liberal enforcement of academic chores by the Directeurs, Bernard Bigot, Philippe Gillet, and now Jacques Samarut. This book, like the previous ones, owes its existence to this luck. I would also like to express my gratitude to my wife, Janne Blichert-Toft, for letting such an inconsiderate intruder devour so much of our private life without complaining and for her steady encouragements. In writing this book, and in particular the first edition, I have also sought to express my gratitude to the Institut Universitaire de France: since my appointment has allowed me to devote more time to research, I felt it only right that this should be requited by some concrete contribution to the teaching of geochemistry.

Finally, special thanks are due to the Fondation des Treilles: nowhere on Earth can a book be prepared in such a magnificent environment worthy of Plato and Virgil surrounded by caring and friendly people. The last stretch was completed at Rice University in Houston, where Cin-Ty Lee and Alan Levander arranged a very fruitful and friendly time away from the daily troubles.