

Andreas Bauer · Bruce D. Velde

# Geochemistry at the Earth's Surface

Movement of Chemical Elements

 Springer

Andreas Bauer · Bruce D. Velde

# Geochemistry at the Earth's Surface

Movement of Chemical Elements

 Springer

# Geochemistry at the Earth's Surface



Andreas Bauer • Bruce D. Velde

# Geochemistry at the Earth's Surface

Movement of Chemical Elements

 Springer

Andreas Bauer  
Karlsruher Institut für Technologie (KIT)  
Institut für Nukleare Entsorgung (INE)  
Eggenstein-Leopoldshafen  
Germany

Bruce D. Velde  
Ecole Normale Supérieure  
Laboratoire de Géologie  
Paris CEDEX 5  
France

ISBN 978-3-642-31358-5      ISBN 978-3-642-31359-2 (eBook)  
DOI 10.1007/978-3-642-31359-2  
Springer Heidelberg New York Dordrecht London

Library of Congress Control Number: 2014939512

© Springer-Verlag Berlin Heidelberg 2014

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. Exempted from this legal reservation are brief excerpts in connection with reviews or scholarly analysis or material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work. Duplication of this publication or parts thereof is permitted only under the provisions of the Copyright Law of the Publisher's location, in its current version, and permission for use must always be obtained from Springer. Permissions for use may be obtained through RightsLink at the Copyright Clearance Center. Violations are liable to prosecution under the respective Copyright Law.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

While the advice and information in this book are believed to be true and accurate at the date of publication, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Printed on acid-free paper

Springer is part of Springer Science+Business Media ([www.springer.com](http://www.springer.com))

# Introduction

Geochemistry is a frequently used term in geological studies that defines a discipline which has developed in importance over the past 40 years. The meaning of this term and the substance of the discipline is the relationship between the chemical properties of elements found in the geological sphere and their expression as minerals or other phases found in rocks. Essentially the elements that are the most common and abundant in surface materials are limited in number, such as Na, K, Mg, Ca, Al, Si, and Fe (called the major elements) with concentrations of elements such as Mn, P, S, C, Cl present in smaller amounts and considered as minor elements. The elements of industrial importance, such as the transition metals Cu, Cd, Co, Ni, Ti, and Au, among others, are of yet lesser abundance in rocks and most often occur as inclusions in phases dominated by major elements or as isolated concentrations due to special geological conditions. Other elements of low overall abundance in rocks such as As, Sb, and Sn are more difficult to classify in that their occurrence is limited to small and sporadic concentrations in rocks. In the classical geological chemical framework the elements found as gases in the atmosphere such as Ar, N, Ne, He, and others are little present. Some atmospheric elements such as C and O are present in both the realm of geological occurrence and the sphere of the surface atmosphere. Geochemistry is the study of the occurrence and reasons for these occurrences of different elements.

A further direction of investigation, used with great success to solve some specific problems, is the determination of the relative abundance of the isotopes of the elements present. Isotope geochemistry has proved to be a powerful tool in the determination of many geological processes of rock formation.

Our proposition in the present study is to use the available published information concerning elemental abundances at the surface of the earth, in the zone of atmosphere and rock interaction, to follow the selection and segregation of elements during the surface chemical processes which are dominated by the interaction of atmospheric and biologically determined chemical processes with rocks that have formed and attained chemical equilibrium under other conditions of temperature and pressure.

One fundamental point to remember is that rocks are composed roughly of half oxygen atoms and the atmosphere is still more oxygen rich. Water, the agent of change, is composed of oxygen and hydrogen atoms. Oxygen is the major element of the geological realm and especially that of surface geochemistry. Interactions of cations with oxygen are the dominant modes of chemical interaction. The geochemical actions initiated at the surface are essentially those of hydrogen exchange for cations in rock minerals which creates “hydrated” minerals such as the silicate clay minerals or hydroxy oxides of Fe or Al. Geochemistry at the earth’s surface is initiated by phase change through the interaction of water with rocks which sets the stage for geochemical exchange throughout the erosion, transportation, and deposition processes. The activity of oxygen and ensuing oxidation of metal elements are another fundamental constraint on surface geochemical reactions. Since most multi-oxidation state elements are in a more or less reduced state in rocks, oxidation disrupts the former chemical interactions in the minerals and this produces the destabilization of these phases and eventual formation of new minerals. However, biological activity at the interface of surface materials and the atmosphere creates variations in oxidation state of materials in many cases which reorganizes some of the material present and changes the chemical relations among ions and solids. Thus hydration and oxido-reduction are the key concepts to keep in mind when considering earth surface geochemistry. These are the chemical variables or active forces present.

This is the chemical framework. Then the first part of the term “geochemistry” must be considered. In many texts, treatises, and scientific papers, the concept of geological forces at play is not taken into account. Chemistry is essentially static, where the electronic configuration of the elements present is arranged as quickly as possible to create an assemblage of phases that are in chemical equilibrium. Geology by contrast is the realm of movement dynamics driven by the forces of tectonics (mountain building) and the forces of gravity which drive water movement, the major transport vector. The earth is a restless object, especially at its surface. Movement of matter in solid or dissolved form is the general rule.

Then the “geo” part of geochemistry is the study of the chemical accommodation to the dynamic forces of geological energy. However, the inherent instability generated by the earth processes is such that chemical equilibrium is often not attained and materials of contrasting chemistry are found together in the same environment. The work of the geochemist is then that of sorting out the nature of materials in a given sample and their origins in order to understand where they came from and what will happen to them as they approach a chemical equilibrium in a given setting. As a simple example, if one considers the sediments carried in a river and its load of dissolved elements, one must look at the relief and erosion rate of the drainage basin, its climatic variation, and geomorphologic characteristics in order to interpret the chemical variations of materials found in the river load and river water. These will be reflected in the sediment that is eventually deposited by the river along an inland lake or ocean shelf. Surface geochemistry is the interrelationship between chemistry and geology.



In the text that follows we have purposefully left out any reference to isotopic variations of the different chemical species in that there is not a great abundance of such information available and the changes and instability of surface materials render the interpretation of isotopic variation very difficult in many instances. If one studies the isotopic variation of an element in a given stable context, things can often be worked out to a satisfying degree, but such studies are not generally available and using them to interpret the overall variations of chemical isotopic abundance throughout a geological sequence is very difficult indeed. Hence we attempt to find the underlying relations between elements, of major and minor abundance depending upon the local chemical context and the dynamics of the geological setting.

It is clear in reading the following studies that there is much to be done yet in order to understand the many aspects of surface geochemistry; however, we hope to lay out some general principles and relationships that can be used as a basis for further work.



# Contents

<b>1</b>	<b>Geology and Chemistry at the Surface . . . . .</b>	<b>1</b>
1.1	The Geological Framework of Surface Geochemistry . . . . .	1
1.1.1	Movement of Materials . . . . .	3
1.1.2	Physical Constraints . . . . .	4
1.1.3	Chemical Effects . . . . .	13
1.1.4	Alteration: Rock to Soil Transformation . . . . .	14
1.1.5	Alteration Profile . . . . .	18
1.1.6	Plant and Soil . . . . .	23
1.2	Chemical Elements and Associations in Surface Environments . . . . .	30
1.2.1	Affinities of the Major Elements and Surface Geochemistry . . . . .	30
1.2.2	Agents of Change . . . . .	32
1.2.3	Bonding Between Elements . . . . .	33
1.2.4	Cation Substitutions . . . . .	36
1.2.5	Chemical Types of Atoms and Multi-element Units . . . . .	38
1.2.6	Reduction of Oxoanions . . . . .	39
1.2.7	Metals . . . . .	41
1.2.8	Special Elemental Groups . . . . .	42
1.2.9	Association of the Elements in Phases (Minerals) at the Surface . . . . .	43
1.2.10	Elements in Surface Phases . . . . .	46
1.2.11	Silicates . . . . .	47
1.2.12	Oxides and Hydroxides . . . . .	48
1.2.13	Carbonates . . . . .	48
1.2.14	Phosphates . . . . .	48
1.2.15	Sulfates . . . . .	49
1.2.16	Substitutions of Ions in Mineral Structures . . . . .	49
1.2.17	Mineral Surface Reactions . . . . .	53
1.2.18	Summary . . . . .	54
1.3	Useful Source Books . . . . .	55

<b>2</b>	<b>Elements in Solution</b> . . . . .	57
2.1	Ions and Water . . . . .	57
2.1.1	Ions . . . . .	58
2.1.2	Ions in Water . . . . .	60
2.1.3	Inner Sphere: Outer-Sphere Attractions . . . . .	61
2.1.4	Attraction of Ions to Solids: Absorption–Adsorption . . . . .	61
2.2	Absorption (Outer-Sphere Attraction and Incorporation Within the Mineral Structures) . . . . .	62
2.2.1	Dynamics of Interlayer Absorption of Hydrated Cations in Clay Minerals . . . . .	64
2.3	Adsorption (Inner-Sphere Surface Chemical Bonding) . . . . .	69
2.3.1	Edge Surface Sites and their Interactions with Cations and Anions . . . . .	69
2.3.2	Origin of the Surface Charge of Soil Minerals . . . . .	71
2.3.3	Acid–Base Reactions at the Surface of Minerals and the Notions of Points of Zero Charge . . . . .	73
2.3.4	What Is the Significance of PZCs? . . . . .	76
2.3.5	Ions and Factors Affecting their Attraction to Solids . . . . .	77
2.4	Eh–pH Relations: The Effects of Redox Reactions . . . . .	80
2.4.1	Eh and pH in Weathering . . . . .	81
2.5	Observation of Absorption Phenomena for Some Specific Elements in Solution . . . . .	83
2.5.1	Transuranium Elements . . . . .	83
2.5.2	Lanthanides . . . . .	85
2.5.3	Transition and Other Metals . . . . .	86
2.5.4	Oxides and Oxyhydroxides: Complex Cases . . . . .	87
2.5.5	Summary . . . . .	87
2.5.6	Soils and Cation Retention: Clays Minerals Versus Organic Material . . . . .	88
2.5.7	Surface Precipitation of New Phases . . . . .	94
2.6	Summary . . . . .	95
2.6.1	Controlling Factors . . . . .	96
2.7	Useful References . . . . .	97
	Glossary . . . . .	97
<b>3</b>	<b>Weathering: The Initial Transition to Surface Materials and the Beginning of Surface Geochemistry</b> . . . . .	101
3.1	Alteration Processes: Oxidation, Hydration, and Dissolution . . . . .	103
3.1.1	Air and Water: Interaction of the Atmosphere and Aqueous Solutions . . . . .	104
3.1.2	Oxidation . . . . .	105
3.1.3	Hydrolysis . . . . .	105
3.1.4	Hydration . . . . .	106
3.1.5	Biological Weathering . . . . .	106
3.1.6	Rocks and Alterite Compositions . . . . .	107

- 3.2 Weathering (Water–Rock Interaction) . . . . . 108
  - 3.2.1 Initial Stages of Weathering: Major Elements . . . . . 108
  - 3.2.2 Silicate Mineral Transformations: The Origins of Alteration . . . . . 112
  - 3.2.3 Rock Alteration: Gain and Loss of Major Elements . . . . . 113
  - 3.2.4 Rock Types and Element Loss or Gain in the Alterite Material . . . . . 114
  - 3.2.5 Granite Alterite . . . . . 114
  - 3.2.6 Weathering Profiles and the Soil Zone . . . . . 119
  - 3.2.7 Alterite Chemical Trends . . . . . 121
  - 3.2.8 End Member Alterite Products: Laterites and Bauxites . . . . . 123
- 3.3 Rock Weathering: Minor Elements . . . . . 129
  - 3.3.1 Major, Minor, and Trace Element Affinities . . . . . 130
  - 3.3.2 K–Rb . . . . . 131
  - 3.3.3 Ca–Sr . . . . . 131
  - 3.3.4 Ca–Ba . . . . . 132
  - 3.3.5 Li . . . . . 133
  - 3.3.6 Cs . . . . . 135
  - 3.3.7 Transition Metal Elements . . . . . 136
  - 3.3.8 Oxides and Associations of Elements . . . . . 137
  - 3.3.9 Importance of Oxidation State (Solubility of Oxide) . . . . . 137
  - 3.3.10 Co . . . . . 140
  - 3.3.11 Ni . . . . . 140
  - 3.3.12 Zn . . . . . 140
  - 3.3.13 Cu . . . . . 144
  - 3.3.14 V and Cr . . . . . 144
  - 3.3.15 Some Heavy Trace Elements Bi, Cd, Sb, Sn, Pb, As, Hg . . . . . 146
  - 3.3.16 Elements in Refractory Phases (Very Low Solubility and High Chemical Stability) . . . . . 148
  - 3.3.17 Summary of Minor Element Relations . . . . . 152
- 3.4 Following the Elements . . . . . 153
- 3.5 Useful References . . . . . 156
- 4 Soils: Retention and Movement of Elements at the Interface . . . . . 157**
  - 4.1 Background Setting . . . . . 157
    - 4.1.1 Soil Development Types . . . . . 160
    - 4.1.2 Summary . . . . . 163
  - 4.2 Chemical Uplift by Plants . . . . . 164
    - 4.2.1 The Chemical Effects . . . . . 164
    - 4.2.2 Elements in Soils . . . . . 169
    - 4.2.3 Correlative Effects . . . . . 174
    - 4.2.4 Uplift Dynamics . . . . . 175
  - 4.3 Chemical Controls Engendered by Plants . . . . . 176
    - 4.3.1 Soil pH . . . . . 176

- 4.3.2 Modelling Cation Absorption to Describe Experimental Observation . . . . . 182
- 4.3.3 Profiles and Uplift of Minor Elements . . . . . 186
- 4.3.4 Cases of Minor Elements Retention in Soils . . . . . 190
- 4.3.5 Summary . . . . . 193
- 4.4 Useful Texts . . . . . 195
- 5 Transport: Water and Wind . . . . . 197**
  - 5.1 Water Transport Materials . . . . . 199
    - 5.1.1 Materials Present in Transport Waters . . . . . 199
    - 5.1.2 Alteration Products in Rivers . . . . . 202
    - 5.1.3 Dissolved Material and Colloidal Material . . . . . 202
    - 5.1.4 Suspended Matter . . . . . 208
    - 5.1.5 Comparison of Dissolved and Particulate Matter in a River . . . . . 213
    - 5.1.6 Rivers and Seawater: The Deltas . . . . . 217
    - 5.1.7 Summary: River Transport . . . . . 221
  - 5.2 Wind-Borne Materials . . . . . 222
    - 5.2.1 Types of Loess . . . . . 223
    - 5.2.2 Volcanic Ash . . . . . 227
    - 5.2.3 “Human Loess” . . . . . 231
    - 5.2.4 Summary . . . . . 234
  - 5.3 Geochemical Alteration of Loess and Volcanic Materials at the Surface and the Effect of Plants . . . . . 235
    - 5.3.1 Major Elements . . . . . 237
    - 5.3.2 Minor Elements . . . . . 240
    - 5.3.3 Soluble Elements . . . . . 243
    - 5.3.4 Transition Metals and Heavy Elements . . . . . 244
    - 5.3.5 Summary . . . . . 246
  - 5.4 Summary: Transport by Wind and Water . . . . . 247
  - 5.5 Useful References . . . . . 248
- 6 Sediments . . . . . 249**
  - 6.1 Introduction . . . . . 249
  - 6.2 Freshwater Sedimentation: Lakes and Streams . . . . . 251
    - 6.2.1 Fe Effect . . . . . 251
    - 6.2.2 The Ferrous Wheel . . . . . 253
    - 6.2.3 Diagenesis and Migration . . . . . 257
  - 6.3 Sedimentation in Saltwater and Salt Marshes . . . . . 258
    - 6.3.1 Fe and S in Salt Marsh Sediments: Oxidation Effects . . . 260
  - 6.4 Element Concentration . . . . . 270

6.4.1	Rare Earth Elements in the Alteration–Transportation– Deposition Cycle . . . . .	270
6.4.2	Sedimentary Iron Deposits . . . . .	271
6.5	Evaporites and Concentrated Saline Solutions . . . . .	272
6.5.1	Carbonates . . . . .	275
6.5.2	Silicates . . . . .	277
6.5.3	Phosphates . . . . .	278
6.5.4	Sulfates . . . . .	279
6.5.5	Salts . . . . .	280
6.5.6	Oxyanions in the Last Stages of Evaporite Mineral Formation . . . . .	280
6.5.7	Mineral Associations in Evaporite Deposits . . . . .	282
6.6	Summary . . . . .	282
6.6.1	Particulate Material Sediments . . . . .	283
6.6.2	Evaporites and Organically Precipitated Materials . . . . .	284
6.7	Useful References . . . . .	284
	<b>Summary . . . . .</b>	<b>285</b>
	<b>Bibliography . . . . .</b>	<b>299</b>