

Chemical Weathering Rates of Silicate Minerals

TABLE OF CONTENTS, VOLUME 31

	<i>Page</i>
Foreword.....	iii
Acknowledgments.....	iii

Chapter 1

A. F. White & S. L. Brantley

CHEMICAL WEATHERING RATES OF SILICATE MINERALS: AN OVERVIEW

Introduction.....	1
Historical beginnings.....	1
Recent advances.....	2
Practical Importance of Chemical Weathering.....	3
Sources of inorganic nutrients in soils.....	3
Role of chemical weathering in buffering watershed acidification.....	5
The impact of chemical weathering on long term climate change.....	6
Purpose and Content of Present Volume.....	7
Fundamental approaches in describing mineral dissolution and precipitation rates.....	8
Silicate mineral dissolution as a ligand-exchange reaction.....	8
Chemical weathering rates of pyroxenes and amphiboles.....	9
The weathering of sheet silicates.....	10
Controls on silica reactivity in weathering environments.....	11
Dissolution rates of feldspars.....	11
Microscopic approaches to weathering.....	12
Weathering rates in soils.....	13
Weathering rates in catchments.....	14
Methods for reconciling experimental and soil and catchment weathering rates.....	14
Chemical versus physical weathering.....	15
Chemical weathering and its effect on atmospheric CO ₂ and climate.....	16
Weathering at Different Scales.....	17
Philosophy of kinetics models.....	17
Relating models at different scales.....	18
Mineral surface area.....	18
Coupling of transport and reaction.....	19
Transient versus steady state.....	20
Conclusions.....	20
References.....	21

Chapter 2

A. C. Lasaga

FUNDAMENTAL APPROACHES IN DESCRIBING MINERAL DISSOLUTION AND PRECIPITATION RATES

Introduction.....	23
A simple rate model.....	27
Kink sites.....	27
Kinetic model.....	29

Caveat—Test Forms of the Function	31
Other Forms of $f(\Delta G_r)$	32
Surface Area.....	33
Activation Energies.....	35
pH Dependence.....	36
Ionic Strength and Solution Composition.....	37
<i>Ab Initio</i> Approaches.....	39
<i>Ab initio</i> applications.....	44
<i>Ab initio</i> studies and dissolution/precipitation rates.....	54
Dissolution under acid conditions.....	56
Dissolution under basic conditions.....	56
Effect of hydration layers	61
Reaction Mechanisms and Rate Laws.....	63
Monte Carlo Methods and Rate Laws.....	70
Summary.....	80
Acknowledgments.....	80
References.....	81

Chapter 3

W. H. Casey & C. Ludwig

SILICATE MINERAL DISSOLUTION AS A LIGAND-EXCHANGE REACTION

Introduction.....	87
Ligand-Exchange Kinetics.....	88
What is a ligand-exchange reaction?	88
Solvent exchange rates vary with M-O bond strengths.....	92
Brønsted reactions commonly proceed to equilibrium and affect rates.....	94
Ligands can promote reaction.....	95
Ligands have acid-base properties that affect reactivities.....	95
M-O bond dissociation can control rates of chelation.....	97
Mineral Surface Reactions	98
General comments.....	98
Rate laws for surface reactions	98
Solute adsorption/desorption is usually faster than dissolution	101
Brønsted reactions on mineral surfaces.....	102
Proton-promoted dissolution.....	104
Ligand-promoted dissolution.....	105
Orthosilicate Minerals	108
Experimental dissolution of orthosilicates.....	109
Orthosilicate mineral dissolution in nature.....	112
Conclusions and Predictions	113
Acknowledgments.....	114
References.....	114

Chapter 4

S. L. Brantley & Y. Chen

CHEMICAL WEATHERING RATES OF PYROXENES AND AMPHIBOLES

Introduction.....	119
Mineralogy of Common Soil Inosilicates.....	120
Laboratory Chemical Reactors	121
Batch reactors	121

Flow-through reactors	121
Interpreting reactor experiments.....	122
Laboratory Dissolution Rates.....	123
Measurement of true steady state	123
Rate discrepancies	126
Run duration	130
Mineral chemistry or structure.....	130
Aging of powders.....	130
Surface area	131
Chemical affinity.....	131
Effects of varying solution composition.....	132
Mineral surface area	133
Surface area of starting material	133
Relationships between surface area and dissolution.....	133
Surface roughness.....	137
Etch pits.....	137
Relative elemental release rates	140
Early observations.....	140
Enstatite, bronzite, diopside, tremolite	140
Wollastonite.....	141
Rhodonite	141
Hornblende.....	142
Surface Analysis of Fe-free Inosilicates	142
Spectroscopy of laboratory-dissolved surfaces.....	142
Enstatite.....	142
Diopside	142
Wollastonite.....	143
Rhodonite	143
Tremolite	144
Surface Analysis of Naturally Weathered Minerals.....	145
Coupled Oxidation-Reduction of Fe-containing Inosilicates	145
Rate Laws for Dissolution	148
pH dependence.....	148
Best estimates of empirical rate laws.....	151
Trends in dissolution rates	152
Temperature Dependence of Dissolution	155
Mechanism of Dissolution	157
Armoring surface layers.....	157
Interface-controlled models.....	158
Steady state leached layers	158
Helgeson model.....	158
Rimstidt and Dove model for wollastonite.....	159
Stumm's surface protonation model.....	159
Surface charging of inosilicates	161
Alkaline dissolution of inosilicates.....	162
Point of minimum dissolution rate	162
Natural Inosilicate Weathering Rates	162
Quantitative evaluation of etching rates.....	162
Mean maximum etch depth.....	163
Pit size distributions.....	164
Rate control in natural systems	165
Conclusions.....	167
Acknowledgments.....	168
References.....	168

DISSOLUTION AND PRECIPITATION KINETICS OF SHEET SILICATES

Introduction	173
Bonding in Sheet Silicates	174
Sheet and layer structures	175
Composition	177
Cations	177
Anions	177
Interlayer bonding	178
Surface chemistry, bonding, and reaction pathways	178
Dissolution Kinetics	181
Introductory comments	181
The dissolution reaction	182
Acid-leaching experiments	183
Dissolution data from solubility experiments	184
Ion exchange and early dissolution experiments	185
Far-from-equilibrium rates and pH-dependence	186
Aluminum hydroxide phases	188
Al-oxide phases	189
Brucite	190
Kaolinite	190
Chrysotile	192
Antigorite	196
Talc	196
Muscovite	196
Illite	197
Montmorillonite	198
Biotite	198
Phlogopite	199
Chlorite	199
Effect of temperature	199
Gibbsite	200
Brucite	200
Kaolinite	201
Muscovite	201
Phlogopite	201
Chrysotile	201
Stoichiometry versus nonstoichiometry of dissolution	202
Rate catalysts and inhibitors	205
Aluminum and silicon	205
Other metals and anions	205
Organic ions and molecules	207
Role of biota	209
Dependence on reaction affinity or Gibbs free energy of reaction	209
Surface defects	211
Oxidation of octahedral Fe	212
Experimental approaches and caveats	212
Type of experiment	212
Solution composition	213
Solids pretreatment	214
Nucleation Kinetics	214
Introductory comments	214
Nucleation	214
Topotaxy	215

Epitaxy.....	215
Role of adsorption.....	217
Gel recrystallization.....	217
Organic templates.....	218
Precipitation (Growth) Kinetics.....	218
Introductory comments.....	218
Precipitation data.....	218
Al phases.....	218
Kaolinite.....	219
Sepiolite, palygorskite, and brucite.....	220
pH-dependence.....	220
Rate catalysts and inhibitors.....	221
Inorganic ions.....	221
Organic ions.....	221
Dependence on reaction affinity or Gibbs free energy of reaction.....	222
Gibbsite.....	223
Kaolinite.....	223
Surface defects.....	223
Summary Remarks.....	224
Acknowledgments.....	225
References.....	225

Chapter 6

P. M. Dove

KINETIC AND THERMODYNAMIC CONTROLS ON SILICA REACTIVITY IN WEATHERING ENVIRONMENTS

Introduction.....	235
Biogeochemistry of silica in terrestrial weathering environments.....	235
Intent of this review.....	237
Silica Polymorphs in Weathering Environments.....	237
Occurrence and forms.....	237
Macroscopic to Microscopic: Grain textures and surfaces in weathering.....	239
Fragmentation.....	239
Grain surface shapes.....	239
Etch pits.....	240
Correlation of grain textures and weathering histories.....	240
Silica polymorphs as coatings on other mineral constituents.....	240
Reactivity in Silica-Saturated Environments: Solubility.....	242
The dissolution reaction.....	242
Solubility of silica phases.....	242
Effect of pH.....	244
Effect of solution species.....	245
Apparent solubility.....	246
Solubility as a function of particle size.....	247
The Silica-Water Interface.....	247
Surface structures and properties.....	250
Electrical double layer of the silica-water interface.....	250
Ionization and surface charge.....	253
Reactivity in Non-Equilibrium Environments: Kinetics.....	254
Basic principles.....	254
Aqueous diffusion.....	254
Dissolution and precipitation.....	255
Nucleation.....	260
Etch pit development.....	262
Controls of solution composition and temperature on reactivity.....	263
Temperature dependence in deionized water.....	264

Catalysis by alkali cations.....	265
Solution pH	266
Combined temperature, electrolyte, and pH relations	268
Modifiers: Effects of sorbates and coatings on reactivity.....	268
Organic acids.....	268
Aluminum	269
Ferrous-ferric iron.....	272
Coatings on silica surfaces in natural settings	273
Surface and mechanistic controls on reactivity.....	274
Development of surface complexation models of dissolution	274
Solvent-surface controls on reactivity	277
Theoretical mechanistic models	280
Regional Scale Weathering: Siliceous Fracture Kinetics.....	280
Concluding Remarks.....	282
Acknowledgments.....	282
References.....	282

Chapter 7

A. E. Blum & L. L. Stillings

FELDSPAR DISSOLUTION KINETICS

Introduction.....	291
Feldspar Mineralogy	292
Feldspar Surface Chemistry during Dissolution.....	292
H ⁺ /OH ⁻ sorption and H ⁺ /cation exchange reactions on the feldspar surface.....	293
Surface titrations.....	293
Exchange and/or sorption reactions involving the interstitial cations.....	294
Adsorption and desorption reactions at dangling oxygens at the surface.....	296
Adsorption at bridging oxygens at the surface	297
Alteration of the Al-Si tetrahedral framework.....	299
Experimental Determination of Feldspar Dissolution Kinetics.....	303
Experimental techniques.....	303
Feldspar surface areas.....	303
Rapid initial dissolution rates.....	304
Steady-state feldspar dissolution rates.....	305
Albite dissolution kinetics.....	305
Potassium-feldspar dissolution kinetics.....	305
Plagioclase dissolution kinetics	306
Reproducibility of feldspar dissolution rates.....	308
Effects of aluminum concentration and saturation state	308
Effects of ionic strength on feldspar dissolution	310
Acidic pH solutions.....	310
Basic pH solutions.....	311
Temperature dependence of feldspar dissolution.....	312
Effects of organic acids upon feldspar dissolution.....	316
Models of Feldspar Dissolution Kinetics.....	324
Leached-layer/diffusion models.....	324
Atomistic models	325
Surface speciation models	326
Applications of surface speciation models to feldspar dissolution kinetics.....	327
Macroscopic models.....	331
Surface nucleation models	331
Dissolution at dislocations.....	331

Limitations to modeling natural systems with experimentally-derived rates .	333
References.....	335
Appendix I. Dissolution studies of feldspar minerals in the presence of organic acid solutions.....	343
Appendix II. Dissolution rates of feldspars in organic acid solutions.....	346

Chapter 8

M. F. Hochella, Jr. & J. F. Banfield

CHEMICAL WEATHERING OF SILICATES IN NATURE: A MICROSCOPIC PERSPECTIVE WITH THEORETICAL CONSIDERATIONS

Introduction.....	353
Precursors to Weathering: Mineral Surfaces.....	355
General characteristics of mineral surfaces.....	355
Mineral surface areas.....	357
Measuring surface areas.....	357
Working definitions of external versus internal surfaces.....	359
Evidence for the importance of internal surface area.....	361
Implications for laboratory-based dissolution studies.....	363
Reactive surface areas.....	364
Microscopic Observations: Rationale, Techniques, and Results.....	366
The need for microscopic characterization of reacted surfaces.....	366
The HRTEM approach.....	367
Evidence of microtextural and defect controls of silicate dissolution and weathering.....	368
Perthitic alkali feldspars.....	369
Plagioclase feldspars.....	373
The incipient stages of silicate mineral alteration.....	377
Characteristics of Internal Weathering Fronts in Minerals.....	383
Some physical properties of water in confined spaces.....	384
The structure of water near silicate surfaces.....	386
Water at the quartz/water interface.....	386
Water at the kaolinite/water interface.....	387
The structure of aqueous solutions near silicate surfaces.....	388
Aqueous solutions at the quartz/water interface.....	388
Aqueous solutions at the smectite/water interface.....	388
The solvent properties of water in confined spaces.....	389
Bronsted acidity.....	390
Aqueous solution saturation states and nucleation/crystallization.....	390
Consequences of Internal Weathering Front Characteristics on Reaction Mechanisms and Rates.....	391
A qualitative model for weathering at internal surfaces.....	391
Applications to stagnant water in the vadose zone.....	395
Beyond Internal Weathering Fronts: More Advanced Stages of Mineral Alteration.....	396
Summary, Conclusions, and Final Thoughts.....	397
A word about modeling.....	400
Acknowledgments.....	400
References.....	401

CHEMICAL WEATHERING RATES OF SILICATE MINERALS IN SOILS

Introduction	407
Weathering Environments Based on Soil Classification	409
Mineralogical Mass Balances in Soils	411
Mass balance approaches	411
Required assumptions for mass balance calculations	412
Use of mass balance equations	413
Elemental losses as functions of time	415
Mineral losses as functions of time	416
Volumetric analysis and rates of soil formation	418
Soil Surface Areas	419
Surface areas of silicate minerals in soils	420
Surface area and particle size	422
Surface areas of weathered silicates	422
Internal porosity	426
Calculation of combined surface roughness and internal porosity	426
Mineral Dissolution Rates Based on Primary Silicate Losses	428
Coupling mineral surface area and dissolution rates	429
Interactive approaches	431
Calculation of dissolution rates	432
Rates constants calculated from geometric and BET surface area estimates	433
Weathering Rates Based on Etch Pit Formation	434
Mineral Dissolution Rates Based on Solute Fluxes	435
Soil solution chemistry	438
Comparison of soil solution and watershed chemistry	438
Equilibrium controls on soil solution chemistry	440
Role of solute chemistry and reaction affinity	444
Soil water hydrology	445
Estimating rates of fluid flow	445
Example of estimation of soil water flux	447
Soil mineral weathering rates based on solute fluxes	449
Interpretation of Weathering Rate Constants in Soils	450
Surface area	451
Soil age	452
Solute chemistry	453
Hydrologic heterogeneity	453
Role of biological activity	454
Climate	455
Conclusion	457
Acknowledgments	457
References	458

WEATHERING RATES IN CATCHMENTS

Introduction	463
Measurement of Weathering Rates	463
By solute budgets	463
Solute in outflow	464
Solute from the atmosphere	465
Changes in the exchange pool	466
Changes in the biomass	466

Chemical weathering	468
Rates Normalized to Mineral Surface Area	469
Catchments in the Czech Republic	469
Coweeta Basin, North Carolina	470
Bear Brooks, Maine	471
Rocky Mountain National Park, Colorado	472
Causes of discrepancies between field and laboratory rates	474
Rates Normalized to Land Surface Area	477
Effect of climate	478
Effect of lithology	478
Relief	480
Summary	480
References	481

Chapter 11

H. Sverdrup and P. Warfvinge

ESTIMATING FIELD WEATHERING RATES USING LABORATORY KINETICS

Introduction	485
The importance of models in geochemistry	485
Good and bad models	485
Soil and catchment models	486
Process-oriented models	487
Dynamic versus static models	488
Spatial and temporal resolution of dynamic models	488
Chemical weathering	489
Other model type	491
Theoretical and Experimental Kinetics	491
Introduction	491
A brief history of weathering kinetics	492
The long years of confusion	492
Early rate equations	492
Chemical dissolution reactions	493
The Transition State Theory applied to weathering	493
The reaction between H^+ -ions and a mineral	497
Organic acids	499
The transition state theory rate expression	500
Extension of the theoretical expression to field conditions	501
Determining the surface area on soil samples	503
Soil wetness and surface area	503
Considering the temperature	503
How rate coefficients were determined from data	504
The reaction with H^+ -ion	504
The reaction with organic acid and CO_2	506
The kinetic parameters	506
Modeling Kinetics of Field Weathering	507
Introduction	507
PROFILE and SAFE model description	508
Processes included	508
Mass balance equations	508
The pH-ANC relationship	510
Cation exchange	511
Nutrient uptake reactions	512
Weathering limits forest growth	512
Chemical feedback from soil chemistry	513
Integrated feedback from soil chemistry and weathering	513

Spatial structure.....	514
Hydrological structure.....	514
Computer appearance.....	514
The Gårdsjön Case Study.....	519
Site characteristics.....	519
Method.....	520
Results.....	520
Modelling the field weathering rate with PROFILE.....	520
Budget study method.....	522
Strontium isotope method.....	523
Total analysis correlation.....	525
The historic weathering rate.....	526
Historic weathering as reconstructed with the SAFE model.....	527
Comparing methods for estimating the weathering rate.....	528
Model Validation.....	529
Regional applications.....	531
Discussion.....	532
The important minerals.....	532
A simple model based on mineralogy.....	533
The difference disappeared!.....	534
The importance of product inhibition under field conditions.....	535
Taking away the difference step-by-step.....	538
Conclusions.....	538
References.....	539

Chapter 12

R. F. Stallard

RELATING CHEMICAL AND PHYSICAL EROSION

Introduction and Background.....	543
Sediments and the geologic record.....	543
The present is unusual.....	544
Providing a Framework: Steady-State Erosion.....	545
Working hypotheses.....	545
Collection of representative samples.....	546
Caveats and corrections.....	547
Steady-state denudation definitions.....	548
Hillslope processes.....	549
Erosion regimes.....	550
Roles of organisms in physical erosion.....	551
Deep erosion.....	551
Exceptional erosion.....	553
Clastics and carbonates.....	554
Solid yields and silicate rocks.....	557
Predicted solid yields.....	559
Summary Conclusions.....	561
References.....	562

Chapter 13

Robert A. Berner

CHEMICAL WEATHERING AND ITS EFFECT ON ATMOSPHERIC CO₂ AND CLIMATE

Introduction.....	565
Weathering as a Feedback Control on CO ₂	567
Factors Affecting Weathering over Geologic Time.....	569
Continental land area and lithology.....	569

Mountain uplift.....	570
Climate.....	571
Vegetation	574
Sensitivity of the GEOCARB Carbon Cycle Model to Some Weathering Parameters	578
Summary: Weathering, Climate, and CO ₂	581
Acknowledgments.....	581
References.....	581