

REVIEWS IN MINERALOGY
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GEOCHEMISTRY OF
NON-TRADITIONAL
STABLE ISOTOPES

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FRONT COVER: Periodic Table of the Elements (lanthanides and actinides omitted) illustrating elements that have two or more stable isotopes (light blue background), including those that have very long half-lives. Geochemistry of the stable isotopes of H, B, C, O, and S have been discussed in RIMG volumes 16, 33, and 43.

Series Editor: Jodi J. Rosso

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DEDICATION

Dr. William C. Luth has had a long and distinguished career in research, education and in the government. He was a leader in experimental petrology and in training graduate students at Stanford University. His efforts at Sandia National Laboratory and at the Department of Energy's headquarters resulted in the initiation and long-term support of many of the cutting edge research projects whose results form the foundations of these short courses. Bill's broad interest in understanding fundamental geochemical processes and their applications to national problems is a continuous thread through both his university and government career. He retired in 1996, but his efforts to foster excellent basic research, and to promote the development of advanced analytical capabilities gave a unique focus to the basic research portfolio in Geosciences at the Department of Energy. He has been, and continues to be, a friend and mentor to many of us. It is appropriate to celebrate his career in education and government service with this series of courses in cutting-edge geochemistry that have particular focus on Department of Energy-related science, at a time when he can still enjoy the recognition of his contributions.

GEOCHEMISTRY OF NON-TRADITIONAL STABLE ISOTOPES

55

Reviews in Mineralogy and Geochemistry

55

FROM THE SERIES EDITOR

The review chapters in this volume were the basis for a two-day short course on non-traditional stable isotopes held prior (May 15–16, 2004) to the spring AGU/CGU Meeting in Montreal, Canada. The editors (and conveners of the short course) Clark Johnson, Brian Beard and Francis Albarède and the other chapter authors/presenters have done an exceptional job of familiarizing us with the cutting edge of this exciting field of study.

Errata (if any) can be found at the MSA website www.minsocam.org.

Jodi J. Rosso, Series Editor
West Richland, Washington
March 2004

FOREWORD

Until only a few years ago, I would never have imagined that a volume on the stable isotope geochemistry of elements like Mg, Fe or Cu would be written. In fact, a comic book of blank pages entitled “The Stable Isotope Geochemistry of Fluorine” would have been a more likely prospect. In volume 16 of this series, published in 1986, I wrote: *Isotopic variations have been looked for but not found for heavy elements like Cu, Sn, and Fe. ... Natural variations in isotopic ratios of terrestrial materials have been reported for other light elements like Mg and K, but such variations usually turn out to be laboratory artifacts.* I am about ready to eat those words.

We have known for many years that large isotopic fractionations of heavy elements like Pb develop in the source regions of TIMS machines. Nonetheless, most of us held fast to the conventional wisdom that no significant mass-dependent isotopic fractionations were likely to occur in natural or laboratory systems for elements that are either heavy or engaged in bonds with a dominant ionic character. With the relatively recent appearance of new instrumentation like MC-ICP-MS and heroic methods development in TIMS analyses, it became possible to make very precise measurements of the isotopic ratios of some of these non-traditional elements, particularly if they comprise three or more isotopes. It was eminently reasonable to reexamine these systems in this new light. Perhaps atomic weights could be refined, or maybe there were some unexpected isotopic variations to discover. There were.

Around the turn of the present century, reports began appearing of biological fractionations of about 2–3 per mil for heavy elements like Fe and Cr and attempts were made to determine the magnitude of equilibrium isotope effects in these systems, both by experiment and semi-empirical calculations. Interest emerged in applying these effects to the study of environmental problems. Even the most recalcitrant skeptic now accepts the fact that measurable and meaningful variations in the isotopic ratios of heavy elements occur as a result of chemical, biological and physical processes.

Non-Traditional Stable Isotopes – Foreword, Preface

Most of the work discussed in this volume was published after the year 2000 and thus the chapters are more like progress reports rather than reviews. Skepticism now focuses on whether isotopic variations as small as 0.1 per mil are indeed as meaningful as some think, and the fact that measured isotopic fractionations of these non-traditional elements are frequently much smaller than predicted from theoretical considerations. In fact the large fractionations suggested by the calculations provide much of the stimulus for working in this discipline. Clearly some carefully designed experiments could shed light on some of the ambiguity. My optimism for the future of this burgeoning new field remains high because it is in very good hands indeed.

James R. O'Neil

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PREFACE & ACKNOWLEDGMENTS

Approximately three-quarters of the elements in the Periodic Table have two or more isotopes. RiMG volumes 16 and 43 were devoted to H, C, O, and S isotope variations, and B isotope variations were discussed in RiMG volume 33. The importance of these elements to geochemistry may be illustrated by a *GeoRef* search of O isotope publications, which yields over 25,000 papers, theses, and abstracts spanning over five decades. Isotopic variations of the remaining 56 elements that have two or more isotopes, however, remains relatively little explored, but is gaining rapid attention, in part driven by advances in analytical instrumentation in the last 5–10 years. Our goal for this volume was to bring together a summary of the isotope geochemistry of *non-traditional* stable isotope systems as is known through 2003 for those elements that have been studied in some detail, and which have a variety of geochemical properties. In addition, recognizing that many of these elements are of interest to workers who are outside the traditional stable isotope fields, we felt it was important to include discussions on the broad isotopic variations that occur in the solar system, theoretical approaches to calculating isotopic fractionations, and the variety of analytical methods that are in use. We hope, therefore, that this volume proves to be useful to not only the isotope specialist, but to others who are interested in the contributions that these *non-traditional* stable isotopes may make toward understanding geochemical and biological cycles.

Many people have contributed to bringing this volume to fruition. The editors thank the authors of the individual chapters for their contributions. In addition, many scientists provided reviews of the chapters, including Francis Albarède, Ariel Anbar, Brian Beard, Tom Bullen, Don Canfield, Rick Carlson, Tom Chacko, Lui Chan, Robert Clayton, Max Coleman, Robert Criss, Susan Glasauer, Gideon Henderson, James Hogan, Clark Johnson, Mark Kurz, Peter Larson, Jean-Marc Luck, Brian Marshall, Peter Michael, Eta Mullane, Thomas Nägler, James O'Neil, Olivier Rouxel, Sara Russell, Edwin Schauble, John Valley, Ed Young, and six anonymous reviewers. Alex Speer and others at the MSA business office helped us greatly with the logistics of both the volume and the accompanying Short Course. We gratefully acknowledge the financial support provided by the U.S. Department of Energy. And finally, we are indebted to Jodi Rosso, series editor, for all of her work - she was a joy to work with, and it is through her dedication that the RiMG volumes continue to flourish.

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TABLE OF CONTENTS

1

Overview and General Concepts

*Clark M. Johnson, Brian L. Beard
and Francis Albarède*

INTRODUCTION	1
ISOTOPIC ABUNDANCES AND NOMENCLATURE	2
ISOTOPIC FRACTIONATIONS	6
The isotope fractionation factor and mass-dependency of fractionation.....	7
Predicted and measured isotopic variations	9
Processes that may produce isotopically distinct reservoirs.....	12
DETERMINATION OF ISOTOPIC FRACTIONATION FACTORS	15
Fluid-mineral fractionation factors.....	16
Evaluating approach toward isotopic equilibrium in experiments	17
CONCLUSIONS.....	20
ACKNOWLEDGMENTS	20
REFERENCES	22

2

An Overview of Isotopic Anomalies in Extraterrestrial Materials and Their Nucleosynthetic Heritage

Jean Louis Birk

INTRODUCTION	25
Historical background	26
The definition of isotopic anomalies	26
THE MEASUREMENT OF ISOTOPIC ANOMALIES	27
Large isotopic variations	27
Two isotope elements and small effects	27
Three isotope elements and small effects	27
Elements having 4 and more isotopes	28
Units	28
STELLAR EVOLUTION AND NUCLEOSYNTHESIS.....	28
Massive stars	29
p-r-s-processes	30
THE ISOTOPIC HETEROGENEITY IN THE REFRACTORY	
COMPONENTS OF THE EARLY SOLAR-SYSTEM.....	30
Refractory inclusions of the CV3 carbonaceous chondrites (CAIs)	31
Hibonite rich inclusions of the CM2 and oxide grains in carbonaceous chondrites ..	39
“Presolar” stardust grains: diamond, graphite, carbides and oxides	40
THE ISOTOPIC HETEROGENEITY IN NON-REFRACTORY EARLY	
SOLAR SYSTEM MATERIALS.....	43
Oxygen	45

Non-Traditional Stable Isotopes – Table of Contents

Chromium.....	45
Molybdenum	47
EXTINCT RADIOACTIVITIES.....	47
10-Beryllium - 10-Boron ($T_{1/2} = 1.5$ m.y.).....	49
26-Aluminum - 26-Magnesium ($T_{1/2} = 0.7$ m.y.).....	49
41-Calcium - 41-Potassium ($T_{1/2} = 0.1$ m.y.).....	51
53-Manganese - 53-Chromium ($T_{1/2} = 3.7$ m.y.)	51
60-Iron - 60-Nickel ($T_{1/2} = 1.5$ m.y.)	52
92-Niobium - 92-Zirconium ($T_{1/2} = 36$ m.y.).....	52
107-Palladium - 107-Silver ($T_{1/2} = 6.5$ m.y.)	52
129-Iodine - 129-Xenon ($T_{1/2} = 16$ m.y.).....	53
146-Samarium - 142-Neodymium ($T_{1/2} = 103$ m.y.)	53
182-Hafnium - 182-Tungsten ($T_{1/2} = 9.4$ m.y.).....	53
244-Plutonium spontaneous fission ($T_{1/2} = 81$ m.y.).....	54
Other nuclides.....	54
OPEN QUESTIONS AND FUTURE DIRECTIONS	54
Mass independent fractionation in physico chemical-processes	54
Early proton irradiation within the solar system	54
Presolar silicates.....	55
Instrumentation.....	55
CONCLUSION.....	55
ACKNOWLEDGMENTS	56
REFERENCES	56

3 Applying Stable Isotope Fractionation Theory to New Systems

Edwin A. Schauble

INTRODUCTION	65
Overview	66
History	66
General rules governing equilibrium stable isotope fractionations	67
Fractionation factors	68
EQUILIBRIUM FRACTIONATION THEORY	69
Fractionation in molecules	69
Fractionation in crystalline materials and solutions	75
The chemistry of stable isotope fractionation	77
Other causes of equilibrium isotopic fractionation	77
APPLYING STABLE ISOTOPE FRACTIONATION THEORY	78
Estimating unknown vibrational frequencies	78
Vibrational force-field modeling	79
Empirical force fields	81
Transferable empirical force fields (interatomic potentials).....	86
<i>Ab initio</i> force-field modeling	86
Theoretical applications of Mössbauer spectroscopy.....	90
Integrating theoretically estimated fractionations with measurements	91
BASIC KINETIC STABLE ISOTOPE FRACTIONATION THEORY	92

Non-Traditional Stable Isotopes – Table of Contents

Effects of isotopic mass on molecular and atomic velocities and diffusivity	93
Effects of isotopic mass on rates of activation	94
MASS-DEPENDENCE OF EQUILIBRIUM AND KINETIC ISOTOPE	
FRACTIONATIONS.....	96
CONCLUSIONS.....	97
ACKNOWLEDGMENTS	97
REFERENCES	97
APPENDIX: ANNOTATED BIBLIOGRAPHY OF THEORETICAL	
EQUILIBRIUM FRACTIONATIONS	102

4

Analytical Methods for Non-Traditional Isotopes

Francis Albarède and Brian L. Beard

INTRODUCTION	113
INSTRUMENTATION USED FOR ISOTOPE RATIO ANALYSIS.....	113
Gas source machines	114
TIMS	115
MC-ICP-MS	118
A PHENOMENOLOGICAL DESCRIPTION OF THE MASS-DEPENDENT	
INSTRUMENTAL BIAS	124
STANDARD BRACKETING METHODS.....	129
DOUBLE-SPIKE ANALYSIS.....	130
THE EFFECT OF PEAK SHAPE	132
COUNTING STATISTICS	132
IMPLEMENTATION OF THE MASS BIAS CORRECTION FOR MC-ICP-MS	134
MATRIX EFFECT	136
Spectral (isobaric) effects.....	136
Non-spectral effects.....	137
INSTRUMENTAL BIAS: MEMORY EFFECTS	140
ABUNDANCE SENSITIVITY	141
CORRECTION OF THE NON-MASS DEPENDENT INSTRUMENTAL	
BIAS IN STATIC MODE.....	142
CORRECTION OF THE INSTRUMENTAL BIAS IN DYNAMIC MODE	143
A FEW SIMPLE RULES FOR PRECISE AND ACCURATE	
MC-ICP-MS MEASUREMENTS	146
ACKNOWLEDGMENTS	147
REFERENCES	147
APPENDIX A: TABLE OF SYMBOLS	151
APPENDIX B: EXAMPLE OF DOUBLE-SPIKE CALCULATION	
USING A NEWTON-RAPHSON ITERATION	152

5 Developments in the Understanding and Application of Lithium Isotopes in the Earth and Planetary Sciences

Paul B. Tomascak

INTRODUCTION	153
BACKGROUND: LITHIUM ISOTOPES IN THE SCIENCES	154
Experiments in Li isotope fractionation	154
Lithium isotopes in fields outside geochemistry	154
LITHIUM ISOTOPIC ANALYSIS	155
From early Li isotope measurement to the “modern era” of analysis	155
Plasma-source mass spectrometry	156
Requirements in chemical separation	157
<i>In situ</i> analysis	158
Precision and accuracy	158
INTERNAL-PLANETARY SYSTEMS	159
Mass fractionation in igneous systems	159
Mantle processes	160
Crustal processes	165
PLANETARY SURFACE SYSTEMS	168
Mass fractionation in hydrologic cycle of Li	168
Primarily clastic sediments and sedimentary rocks	169
Lithium isotopic fractionation in the oceans	170
Lithium isotopic fractionation on the continents	180
SIGNIFICANCE OF LITHIUM ISOTOPES IN THE BULK EARTH	185
CONCLUSIONS AND FUTURE DIRECTIONS	187
ACKNOWLEDGMENTS	188
REFERENCES	189

6 The Isotope Geochemistry and Cosmochemistry of Magnesium

Edward D. Young and Albert Galy

INTRODUCTION	197
REFERENCE MATERIALS, NOMENCLATURE, AND ANALYTICAL CONSIDERATIONS	198
Reference material	198
Nomenclature	199
Analytical considerations	200
MAGNESIUM ISOTOPE RESERVOIRS	202
RESOLVING MECHANISMS OF ISOTOPE FRACTIONATION WITH THREE ISOTOPE DIAGRAMS	205
Mass-dependent fractionation laws	206
Mass-fractionation in three-isotope space	208
The definition of $\Delta^{25}\text{Mg}'$	211
Uncertainties in $\Delta^{25}\text{Mg}'$	211
$\Delta' - \delta'$ Diagrams	212

TERRESTRIAL MAGNESIUM ISOTOPE RESERVOIRS	
IN THREE-ISOTOPE SPACE: IMPLICATIONS FOR	
MECHANISMS OF FRACTIONATION	213
EXTRATERRESTRIAL MAGNESIUM ISOTOPE RESERVOIRS IN	
THREE-ISOTOPE SPACE	217
ISOTOPIC COSMOBAROMETRY	223
<i>IN SITU</i> LASER ABLATION.....	225
SUMMARY	228
REFERENCES	229

7

The Stable-Chlorine Isotope Compositions of Natural and Anthropogenic Materials

Michael A. Stewart and Arthur J. Spivack

INTRODUCTION	231
CHLORINE ISOTOPE NOMENCLATURE	232
STABLE-CHLORINE ISOTOPE ANALYSES.....	232
CHLORINE ISOTOPE FRACTIONATION.....	233
RESULTS AND IMPLICATIONS OF THE STABLE-CHLORINE ISOTOPIC	
COMPOSITION OF GEOLOGIC AND ANTHROPOGENIC MATERIALS	233
Meteorites.....	233
Igneous and metamorphic rocks and minerals	235
Fluids	239
Summary of terrestrial chlorine isotope distributions	246
Sea-salt aerosols	247
Environmental chemistry.....	247
ACKNOWLEDGMENTS	249
REFERENCES	250

8

Calcium Isotopic Variations Produced by Biological, Kinetic, Radiogenic and Nucleosynthetic Processes

Donald J. DePaolo

INTRODUCTION	255
CALCIUM ISOTOPE ESSENTIALS	256
Analysis methods and issues for radiogenic ^{40}Ca	257
Analysis methods and issues for mass dependent Ca isotope fractionation.....	258
Ca isotope standards and reference materials.....	260
CALCIUM ISOTOPES IN METEORITES AND LUNAR SAMPLES	262
TERRESTRIAL STUDIES OF RADIOGENIC CALCIUM	263
Effects of radiogenic calcium ^{40}Ca on measured $\delta^{44}\text{Ca}$ values	266
STUDIES OF TERRESTRIAL CALCIUM STABLE ISOTOPE FRACTIONATION.....	267
Igneous and metamorphic rocks and petrogenetic processes	267

Non-Traditional Stable Isotopes – Table of Contents

Biological fractionation through food chains	268
Model for Ca isotope fractionation in vertebrates.....	270
Ca isotope fractionation in marine shelled organisms.....	271
Calcium in the weathering cycle	275
Ca isotopic variations in the paleo-oceans	279
Paleoclimatology	281
CONCLUSIONS AND IMPLICATIONS	284
ACKNOWLEDGMENTS	284
REFERENCES	285

9

Mass-Dependent Fractionation of Selenium and Chromium Isotopes in Low-Temperature Environments

Thomas M. Johnson and Thomas D. Bullen

INTRODUCTION	289
Se geochemistry.....	290
Cr geochemistry.....	291
Reduction of sulfate, nitrate, selenate and chromate: Analogous isotopic behavior	292
ANALYTICAL METHODS	293
Selenium mass spectrometry	293
Selenium sample preparation	294
Chromium mass spectrometry and sample preparation.....	295
Standards currently in use	296
NOTATION.....	296
KINETIC ISOTOPE EFFECTS: THEORETICAL CONSIDERATIONS AND INSIGHTS FROM THE SULFUR ISOTOPE LITERATURE	297
Dominance of kinetic effects at earth-surface temperatures	297
Dependence of kinetic isotope effects on reaction mechanisms and rates	297
SELENIUM ISOTOPE SYSTEMATICS	299
Theoretical estimates of equilibrium isotope fractionation	300
Se(VI) reduction: abiotic	301
Se(IV) reduction: abiotic	302
Se(VI) reduction: microbial.....	302
Se(IV) reduction: microbial.....	303
Se oxidation.....	304
Se(VI) and Se(IV) uptake by algae and plants	304
Volatilization.....	305
Lack of isotopic fractionation between adsorbed and dissolved species	305
SELENIUM ISOTOPE APPLICATIONS AND DATA FROM NATURAL MATERIALS	306
Meteorites and igneous rocks	306
Wetlands	306
Hydrothermal sulfides	306
Marine sediments.....	306
CHROMIUM ISOTOPE SYSTEMATICS.....	308

Non-Traditional Stable Isotopes – Table of Contents

Equilibrium isotope fractionation.....	308
Fractionation during Cr(VI) reduction	308
Lack of isotopic fractionation between adsorbed and dissolved Cr(VI)	309
Other processes.....	310
Cr isotope data from igneous rocks, reagent Cr, and Cr plating baths	310
Cr isotope data from groundwater systems	311
Need for field calibration.....	312
FUTURE DIRECTIONS	313
ACKNOWLEDGMENTS	313
REFERENCES	313

10A

Fe Isotope Variations in the Modern and Ancient Earth and Other Planetary Bodies

Brian L. Beard and Clark M. Johnson

INTRODUCTION	319
NOMENCLATURE AND ANALYTICAL METHODS	321
Nomenclature	321
Analytical methods.....	323
ORIGIN OF Fe ISOTOPE VARIATIONS.....	324
Calculated fractionation factors.....	324
Experimental determination of fractionation factors.....	326
Composite effects of equilibrium and kinetic fractionations in an experiment	329
Summary observations on Fe isotope fractionation factors	335
IRON ISOTOPE VARIATIONS IN HIGH TEMPERATURE ENVIRONMENTS.....	336
Fe isotope fractionation produced by vaporization	339
High-temperature inter-mineral Fe isotope fractionation.....	340
IRON ISOTOPE VARIATIONS IN LOW TEMPERATURE ENVIRONMENTS.....	344
Fe isotope variations in clastic sediments	344
Fe isotope variations in MOR hydrothermal fluids.....	347
Iron isotope variations in Fe-Mn nodules.....	348
Banded iron formations.....	351
CONCLUSIONS.....	352
ACKNOWLEDGMENTS	353
REFERENCES	353

10B

Isotopic Constraints on Biogeochemical Cycling of Fe

*Clark M. Johnson, Brian L. Beard, Eric E. Roden
Dianne K. Newman and Kenneth H. Nealson*

INTRODUCTION	359
Nomenclature	360
BIOLOGICAL PROCESSING OF IRON.....	361
Fe(II) oxidation.....	361

Non-Traditional Stable Isotopes – Table of Contents

Fe(III) reduction	363
Implications for Fe isotope fractionations	364
ISOTOPIC FRACTIONATION DURING DISSOLUTION AND PRECIPITATION OF MINERALS	365
Congruent dissolution.....	365
Incongruent dissolution	367
Isotopic fractionations among aqueous species and minerals in abiologic systems	369
ISOTOPIC MASS BALANCE	369
ISOTOPIC FRACTIONATION PRODUCED DURING DISSIMILATORY Fe(III) REDUCTION	371
Calculation of Fe isotope compositions	374
Temporal changes in reservoir sizes and isotopic compositions	376
Sorption effects.....	377
Solid products of DIR.....	379
Summary of Fe isotope fractionations produced during DIR	383
ANAEROBIC PHOTOSYNTHETIC Fe(II) OXIDATION	383
Proportions of reacting species.....	386
Constraints on isotopic variations	388
The Fe(III)aq–ferrihydrite fractionation factor	390
Comparison with abiologic Fe(II) oxidation	391
ISOTOPIC VARIATIONS PRODUCED DURING BIOGEOCHEMICAL CYCLING OF IRON	392
Redox cycling of Fe by bacteria	392
Isotopic variations in marine settings	395
CONCLUSIONS.....	399
ACKNOWLEDGMENTS	401
REFERENCES	402

11

The Stable Isotope Geochemistry of Copper and Zinc

Francis Albarède

INTRODUCTION	409
THE CHEMICAL PROPERTIES OF Cu AND Zn	410
THE GEOCHEMICAL PROPERTIES OF Cu AND Zn.....	411
THE BIOCHEMICAL USE OF Cu AND Zn.....	412
ANALYTICAL TECHNIQUES	413
NATURAL ISOTOPIC VARIATIONS.....	415
Meteorites and igneous rocks	416
Sedimentary rocks: zinc	416
Sedimentary rocks: copper	419
Biological products.....	420
Cu and Zn ores.....	420
EXPERIMENTAL PARTITIONING.....	420
ACKNOWLEDGMENTS	424
REFERENCES	425

12

Molybdenum Stable Isotopes: Observations, Interpretations and Directions

Ariel D. Anbar

INTRODUCTION	429
MOLYBDENUM IN THE ENVIRONMENT AND IN BIOLOGY:	
SETTING THE STAGE	430
Molybdenum environmental geochemistry	430
Molybdenum in biology	433
Isotopic expectations	434
ANALYTICAL CONSIDERATIONS	434
Data reporting conventions.....	434
Historical perspective	435
Chemical separations.....	436
Analytical mass fractionation.....	436
OBSERVATIONS	437
Igneous rocks.....	438
Marine sediments.....	439
Waters	440
Laboratory experiments.....	440
INTERPRETATIONS	441
Mo isotope fractionation in the oceans.....	442
Mo isotope mass balance in the oceans.....	446
POTENTIAL APPLICATIONS	447
Mo stable isotopes and global ocean paleoredox	447
Other potential applications.....	449
CONCLUSIONS.....	450
ACKNOWLEDGMENTS	450
REFERENCES	450

Overview and General Concepts

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INTRODUCTION

Of the eighty-three naturally occurring elements that are not radioactive or have half lives long enough to be considered stable ($\geq 10^9$ yrs), nearly three-quarters have two or more isotopes. Variations in the isotopic ratios of a number of these elements, including H, C, N, O, and S, provide the foundation for the field of *stable isotope geochemistry*. Investigations of variations in the isotopic compositions of these *traditional* elements have provided important constraints on their sources in natural rocks, minerals, and fluids. These studies have focused on a range of problems including planetary geology, the origin and evolution of life, crust and mantle evolution, climate change, and the genesis of natural resources. Much less attention, however, has been paid to stable isotope variations of other elements that are also geochemically important such as certain metals and halogens. In part this has been due to analytical challenges, although first-order variations for several systems have been constrained using long-standing analytical methods such as gas- and solid-source mass spectrometry. With the advent of analytical instrumentation such as multi-collector, inductively-coupled plasma mass spectrometry (MC-ICP-MS), large portions of the Periodic Table are now accessible to stable isotope studies.

In this volume, the geochemistry of a number of *non-traditional* stable isotopes is reviewed for those elements which have been studied in some detail: Li, Mg, Cl, Ca, Cr, Fe, Cu, Zn, Se, and Mo. This volume is intended for the non-specialist and specialist alike. The volume touches on the multiple approaches that are required in developing new isotopic systems, including development of a theoretical framework for predicting possible isotopic fractionations, perfecting analytical methods, studies of natural samples, and establishment of a database of experimentally-determined isotope fractionation factors to confirm those predicted from theory. In addition to the systems discussed in this volume, we expect that more elements will be subject to isotopic studies in the next several years, significantly broadening the field that is known as *stable isotope geochemistry*.

Chapter 1 is intended to provide an overview of basic concepts of stable isotope geochemistry that are applicable to the chapters that follow on specific topics and isotopic systems. There are a number of excellent reviews of stable isotope geochemistry that have tended to focus on H, C, O, and S, including two prior volumes of Reviews in Mineralogy and

Geochemistry (Valley et al. 1986; Valley and Cole 2001), and a few texts (e.g., Criss 1999; Hoefs 2004). The concepts discussed in these works are entirely applicable to the isotopic systems discussed in the present volume. Because our discussion here is restricted to essential concepts, we refer the reader who is interested in more depth to the works above.

ISOTOPIC ABUNDANCES AND NOMENCLATURE

There are many sources for information on the distribution of the elements and isotopes (e.g., Lide 2003), as well as discussions that are pertinent to stable isotope geochemistry (e.g., Criss 1999). In Chapter 2 Birck (2004) reviews in detail the isotopic distribution and nucleosynthetic origin of many elements that are of geochemical interest. He highlights the fact that isotopic variations for many elements are greatest for extraterrestrial samples, where evidence for a variety of fractionation mechanisms and processes are recorded, including mass-dependent and mass-independent fractionation, radioactive decay, and incomplete mixing of presolar material. Below we briefly review a few general aspects of isotope distribution that are pertinent to isotopic studies that bear on nomenclature, expected ranges in isotopic fractionation, and analytical methodologies.

The number of stable isotopes for the naturally occurring elements tends to increase with increasing atomic number, to a maximum of 10 for Sn (Fig. 1). Elements with low atomic numbers tend to have the lowest number of stable isotopes, limiting the possible ways in which isotopic compositions can be reported. Both H and C have only two stable isotopes (Fig. 1), and therefore isotopic compositions are reported using one ratio, D/H and $^{13}\text{C}/^{12}\text{C}$, respectively. Single ratios can only be used for B and N, and data are reported as $^{11}\text{B}/^{10}\text{B}$ and $^{15}\text{N}/^{14}\text{N}$, respectively. Of the *non-traditional* stable isotope systems discussed in this volume, only three have just two stable isotopes (Li, Cl, and Cu; Fig. 1).

The choice of isotopic ratios for reporting data increases, of course, for elements with three or more isotopes. Although O isotope compositions are almost exclusively reported in terms

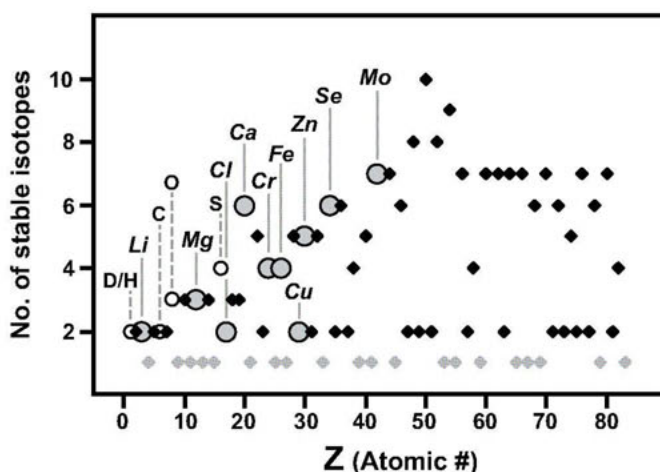


Figure 1. Number of stable isotopes relative to atomic number (Z) for the elements. Mono-isotopic elements shown in gray diamonds. Elements discussed in this volume are shown as large gray circles. Other elements that have been the major focus of prior isotopic studies are shown in small white circles, and include H, C, O, and S. Nuclides that are radioactive but have very long half-lives are also shown in the diagram.

of $^{18}\text{O}/^{16}\text{O}$ ratios, data for $^{17}\text{O}/^{16}\text{O}$ variations are reported, and are valuable in distinguishing mass-dependent and mass-independent isotopic variations (see Chapter 2; Birck 2004). The majority of S isotope data are reported using the ratio of the two most abundant isotopes, $^{34}\text{S}/^{32}\text{S}$, although studies of mass-independent isotope variations report data for three or all four stable isotopes of S (e.g., Farquhar et al. 2000). Magnesium, Ca, Cr, Fe, Zn, Se, and Mo all have three or more stable isotopes (Fig. 1), and therefore the isotopic compositions for these elements may be reported using a number of ratios. In some cases, isotopic abundances limit the isotopic ratios that can be measured with reasonable precision. For many elements, however, isotopic abundances are relatively high for a number of isotopes and, in these cases, data are reported using a number of ratios.

The vast majority of isotopic data are reported in “delta notation”, where the isotopic composition is cast as the deviation of an isotopic ratio relative to the same ratio in a standard (e.g., O’Neil 1986a):

$$\delta^i E_X = \left(\frac{R_X^{i/j} - R_{STD}^{i/j}}{R_{STD}^{i/j}} \right) 10^3 \quad (1)$$

where i and j are the specific isotopes used in ratio R of element E , X is the sample of interest, and STD is a standard reference material or reservoir. It is traditional to use isotope i in the δ value, and it is important to note the specific ratio $R^{i/j}$ that is used. The units for the δE_X value are in parts per thousand or “per mil”, which is commonly noted using the per mil sign (‰). In the case of the $\delta^{18}\text{O}$ value, $R = ^{18}\text{O}/^{16}\text{O}$, following the traditional protocol of expressing $R^{i/j}$ as the abundance ratio of the rare isotope to the major isotope (e.g., O’Neil 1986a). Similarly, δD , $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and $\delta^{34}\text{S}$ values are defined using the isotopic ratio of rare isotope over major isotope, that is, D/H , $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, and $^{34}\text{S}/^{32}\text{S}$, respectively. The conventional definitions of $R^{i/j}$ for H, C, N, and S correspond to *heavy over light* masses, leading to a consistent nomenclature where a positive δE_X value refers to a sample that is relatively enriched in the heavy isotope (a high $R^{i/j}$ ratio relative to the standard). Although some groups have reported isotopic compositions in parts per 10,000 using the ϵ unit (e.g., Rehkämper and Halliday 1999; Zhu et al. 2000), this nomenclature is not very common and should probably be discontinued to avoid confusion.

The standard reference used for reporting isotopic compositions of H and O is Standard Mean Ocean Water (SMOW), although the fossil marine carbonate PDB standard is also used for oxygen (O’Neil 1986a). For the new isotopic systems discussed in this volume, the choice of standard reference material or reservoirs has not been settled in many cases (Table 1), requiring careful attention when comparing δE values. Some groups have chosen a major geologic reservoir such as ocean water or bulk earth, following the convention used for some light stable isotope systems, as well as several radiogenic isotope systems such as Nd, Hf, and Os. Reporting δE values relative to a major geologic reservoir may be advantageous in interpretations, where relative enrichment or depletion in heavy isotopes are referenced to a geologic component. The disadvantage of using major geologic reservoirs as a reference is that they are not distinct substances that can be measured in the laboratory. In other cases, an international or other widely-available purified standard is used. For some isotopic systems, data are reported relative to in-house standards (Table 1), which may not allow easy cross-calibration with other laboratories. Data should be reported for several internationally-available standards whenever possible so that δ values may be compared using equivalent reference materials or reservoirs.

The motivation for defining the δE_X value as *rare isotope over major isotope* lies in the fact that the mathematical forms of mixing relations and other physical processes are greatly simplified in cases where the rare isotope i is very low in abundance, which leads to the simplification that the abundance isotope j may be treated as invariant, particularly when the

Table 1. Nomenclature and standards for isotope systems.

Element	Ratio	Typical Precision	Standard Reference Material or Reservoir	Other Notation	Ratio	Other Standards	Isotopic Composition
$\delta^7\text{Li}$ (‰)	$^7\text{Li}/^6\text{Li}$	0.5–1.0‰	NIST SRM-8545	$\delta^7\text{Li}$ (‰)	$^6\text{Li}/^7\text{Li}$	IRMM-016	$\delta^7\text{Li} = 0$
$\delta^{26}\text{Mg}$ (‰)	$^{26}\text{Mg}/^{24}\text{Mg}$	0.1–0.2‰	DSM 3	$\delta^{26}\text{Mg}$ (‰) $\Delta^{26}\text{Mg}$ (non-mass-dependent variations)	$^{25}\text{Mg}/^{24}\text{Mg}$	SRM 980_O	$\delta^{26}\text{Mg} = -3.41$
$\delta^{37}\text{Cl}$ (‰)	$^{37}\text{Cl}/^{35}\text{Cl}$	0.1–0.3‰	Std. Mean Ocean Chloride (SMOC)				
$\delta^{44}\text{Ca}$ (‰)	$^{44}\text{Ca}/^{40}\text{Ca}$	0.1–0.2‰	UCB Ca std.			Seawater Ca Fluorite Ca	$\delta^{44}\text{Ca} = +0.9$ $\delta^{44}\text{Ca} = +0.5$
$\delta^{53}\text{Cr}$ (‰)	$^{53}\text{Cr}/^{52}\text{Cr}$	0.1–0.2‰	NIST SRM-979				
$\delta^{56}\text{Fe}$ (‰)	$^{56}\text{Fe}/^{54}\text{Fe}$	0.1–0.5‰	Bulk Earth (BE)	$\delta^{57}\text{Fe}$ (‰) $\delta^{57/56}\text{Fe}$ (‰) $\epsilon^{57}\text{Fe}$ $\epsilon^{56}\text{Fe}$	$^{57}\text{Fe}/^{54}\text{Fe}$ $^{57}\text{Fe}/^{56}\text{Fe}$ $^{57}\text{Fe}/^{54}\text{Fe}$ (parts per 10,000) $^{56}\text{Fe}/^{54}\text{Fe}$ (parts per 10,000)	IRMM-14	$\delta^{56}\text{Fe} = -0.09$
$\delta^{65}\text{Cu}$ (‰)	$^{65}\text{Cu}/^{63}\text{Cu}$	0.1–0.2‰	NIST SRM-976				
$\delta^{67}\text{Zn}$ (‰)	$^{67}\text{Zn}/^{64}\text{Zn}$	~0.1‰	NIST SRM-682	$\delta^{67}\text{Zn}$ (‰) $\delta^{68}\text{Zn}$ (‰) $\epsilon^{66}\text{Zn}$ $\epsilon^{67}\text{Zn}$ $\epsilon^{68}\text{Zn}$	$^{67}\text{Zn}/^{64}\text{Zn}$ $^{68}\text{Zn}/^{64}\text{Zn}$ $^{66}\text{Zn}/^{64}\text{Zn}$ (parts per 10,000) $^{67}\text{Zn}/^{64}\text{Zn}$ (parts per 10,000) $^{68}\text{Zn}/^{64}\text{Zn}$ (parts per 10,000)	NIST SRM-683	$\delta^{67}\text{Zn} = +2.4$
$\delta^{80}\text{Se}$ (‰)	$^{80}\text{Se}/^{76}\text{Se}$	0.2–0.3‰	CDT	$\delta^{82}\text{Se}$ (‰)	$^{82}\text{Se}/^{76}\text{Se}$	NIST SRM-3149	$\delta^{80}\text{Se} = 0$
$\delta^{97}\text{Mo}$ (‰)	$^{97}\text{Mo}/^{95}\text{Mo}$	0.1–0.2‰	Rochester JMC Mo	$\delta^{98}\text{Mo}$ (‰)	$^{98}\text{Mo}/^{95}\text{Mo}$	Seawater Mo	$\delta^{97}\text{Mo} = +1.5$

Note: Standard Reference Material or Reservoir refers to $R^{\text{ref}}_{\text{STD}}$ in equation 1 in the text.

range in isotopic compositions is relatively restricted. For example, the exact mixing relation for a single element between components A and B which differ in their isotopic compositions is given by:

$$\frac{M_A}{M_B} = - \left(\frac{C_B}{C_A} \right) \left(\frac{R_{MLX}^* - R_B^*}{R_{MLX}^* - R_A^*} \right) \quad (2)$$

where M_A and M_B are the masses of components A and B , respectively, C_A and C_B are the concentrations of the element in components A and B , respectively, and R^* is defined as the ratio of the mass of the rare isotope over the total mass of the element (Eqn. 1.14, p. 22-23, Criss 1999). In the case of O, where the abundances of ^{18}O and ^{16}O are 0.20% and 99.76%, respectively, R^* is very nearly equal to the $^{18}\text{O}/^{16}\text{O}$ ratio, allowing us to relate the exact mixing equation directly to the measured isotopic compositions. We may further simplify Equation (2) using δ notation as:

$$\delta^i E_{MLX} \approx \delta^i E_A f + \delta^i E_B (1 - f) \quad (3)$$

where f is the fraction of component A in the two-component mixture.

Although the simplicity of Equation (3) makes it quite useful, it is important to note that it is valid only for cases when the abundance of the isotope in the numerator of R is very low or when the difference between $\delta^i E_A$ and $\delta^i E_B$ is small. For example, use of Equation (3) for mixing two components that differ in their $^{18}\text{O}/^{16}\text{O}$ ratios by 50‰ produces an error of 0.0016‰ at 50:50 mixing (assuming equal oxygen abundances) relative to use of the exact mixing Equation (2). However, in the case of Fe isotopes, for example, where ^{56}Fe and ^{54}Fe have abundances of 91.76% and 5.84%, respectively, the assumption that ^{54}Fe is a rare isotope is not valid. Assuming that two components differ in their $^{56}\text{Fe}/^{54}\text{Fe}$ ratios by 50‰, use of the approximate Equation (3) produces an error of 0.61‰ at 50:50 mixing (assuming equal iron abundances) relative to use of the exact mixing Equation (2). If mixing relations are calculated using $^{57}\text{Fe}/^{54}\text{Fe}$ ratios, as is reported by a number of workers, isotope i is even closer in abundance to isotope j , and the error introduced using Equation (3) in the above example becomes larger, at 0.90‰. Fortunately, we will see that except for Li, isotopic variations in nature for the elements discussed in this volume are generally less than 10‰, and in most cases Equation (3) may be used without significant loss in accuracy. This may not be the case, however, for experiments that involve enriched isotope tracers.

It is not always possible to follow the convention of *rare isotope over major isotope* in the definition of $\delta^i E_X$ and maintain the convention *heavy over light* for elements across the Periodic Table. If we restrict R to be the ratio of the major isotope to the next-most-abundant isotope, it will be *heavy over light* for only half of the elements under consideration (Fig. 2). The combined definition of *rare over major* and *heavy over light* is satisfied for Mg, Cl, Ca, Cr, Cu, and Zn, but is *not* satisfied for Li, Fe, Se, and Mo (Fig. 2). If the *rare over major* definition of R is maintained, as has been the norm for over five decades of work in the *traditional* stable isotopes, then there will be inconsistencies in the sign of the $\delta^i E_X$ value, where, in some cases, a positive value will reflect a relative enrichment in the heavy isotope, and in others, a depletion. Given the fact that some nucleosynthetic processes produce values of R (as defined in Fig. 2) that approach unity with increasing atomic number (Fig. 2), we suggest that the isotope community should abandon the practice of *rare over major* in defining R for new isotopic systems at the intermediate- to heavy-mass range, because as R approaches unity, the simplifications of mixing and other equations become less accurate, regardless of defining isotopic ratios as *rare over major* or *major over rare*. Instead, defining R for new isotopic systems as *heavy over light* is probably preferred, because this will maintain the same convention used in *traditional* stable isotope systems, where a positive $\delta^i E_X$ value

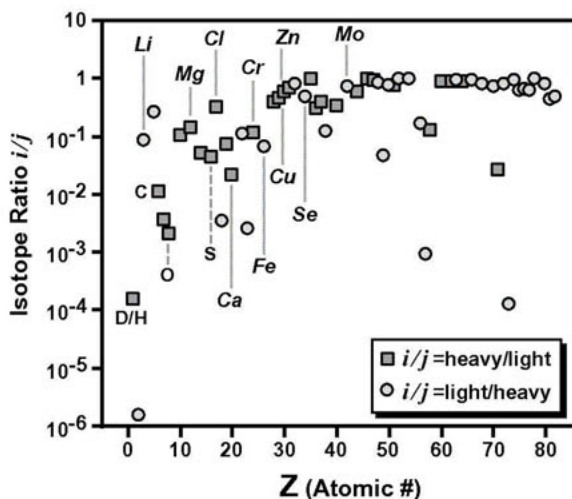


Figure 2. Variations in isotope ratio i/j for elements that have two or more isotopes relative to atomic number (Z), where j is the most abundant mass, and i is the next-most abundant mass. Elements where i/j , as defined here, reflects the ratio of a heavy mass i relative to that of j are shown in gray squares, whereas elements where i/j reflects a lighter mass i over heavy mass j are shown in gray circles. The lighter elements tend to have low i/j ratios, from $\sim 10^{-6}$ to $\sim 10^{-1}$, which simplify mixing relations in terms of δ plots. In the case of elements that have been extensively studied for their isotopic variations, such as H, C, O, and S, i/j is heavy over light, leading to the traditional convention that a high δ value reflects a relative enrichment of the heavy isotope. The convention i/j does not remain consistently *heavy over light* for a number of non-traditional stable isotopes, including those discussed here.

indicates a relative enrichment in the heavy isotope relative to a standard (or, more precisely, an enrichment in the heavy/light isotopic ratio, as discussed above), and a negative δE_x value indicates a relative depletion in the heavy isotope. The *heavy over light* convention is followed in this volume.

ISOTOPIC FRACTIONATIONS

As discussed by O'Neil (1986b), and also in Chapter 3 of this volume (Schauble 2004), isotopic fractionations between species or phases depend on a number of factors, including relative mass difference, the nature of the bonding environment, and redox state. Ignoring issues related to bonding and redox state, we generally expect that the range in isotopic variations will decrease with increasing atomic number (Z) because the relative mass difference also decreases (Fig. 3), generally following the relation of $1/Z$. The relatively large mass differences for the *traditional* stable isotopes such as H, C, O, and S, ranging from 66.7% for H to 3.0% for S (calculated as $\Delta m/m$; Fig. 3), are in part responsible for the large ranges in isotopic ratios that have been measured in natural samples for these elements, from 10's to 100's of per mil (‰). As reviewed in Chapter 5 (Tomascak 2004), of the elements discussed in this volume, Li shows the greatest range in isotopic composition, commensurate with its low mass, high relative mass difference, and bonding environment (Fig. 3). Despite relatively small mass differences on the order of $\sim 1\%$, however, significant isotopic variations are seen up through Mo (Chapter 12), and, in fact, are seen for heavier elements such as Hg ($Z = 80$; Jackson 2001) and Tl ($Z = 81$; Rehkämper et al. 2002), indicating that new isotopic systems are likely to be developed across the Periodic Table as analytical precision improves, even for

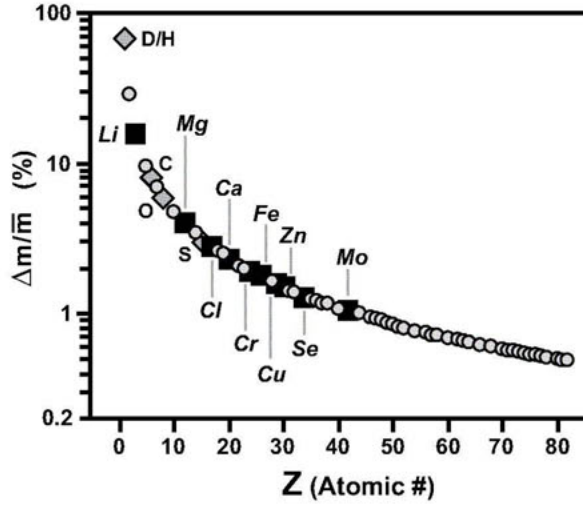


Figure 3. Relative mass differences for elements that have two or more isotopes, cast as $\Delta m/\bar{m}$, where Δm is the unit mass difference ($\Delta m = 1$), and $\bar{m}$ is the average mass of the isotopes of that element, as a function of atomic number (Z). Note that $\Delta m/\bar{m}$ is reported in percent, and is plotted on a log scale. Elements that are discussed in this volume shown in large black squares. Other elements that have been the major focus of isotopic studies shown in gray diamonds, and include H, C, O, and S. The relatively large mass differences for the light elements generally produce the largest isotopic fractionations, whereas the magnitude of isotopic fractionation is expected to markedly decrease with increasing mass.

heavy elements where the relative mass differences are only a few tenths of a percent.

The relatively small mass differences for most of the elements discussed in this volume requires very high-precision analytical methods, and these are reviewed in Chapter 4 by Albarède and Beard (2004), where it is shown that precisions of 0.05 to 0.2 per mil (‰) are attainable for many isotopic systems. Isotopic analysis may be done using a variety of mass spectrometers, including so-called *gas source* and *solid source* mass spectrometers (also referred to as *isotope ratio* and *thermal ionization* mass spectrometers, respectively), and, importantly, MC-ICP-MS. Future advancements in instrumentation will include improvement in *in situ* isotopic analyses using ion microprobes (secondary ion mass spectrometry). Even a small increase in precision is likely to be critical for isotopic analysis of the intermediate- to high-mass elements where, for example, an increase in precision from 0.2 to 0.05‰ could result in an increase in signal to noise ratio from 10 to 40.

The isotope fractionation factor and mass-dependency of fractionation

Following standard practice (e.g., O'Neil 1986a), the isotopic fractionation factor between two substances A and B is defined as:

$$\alpha_{A-B} = \frac{R_A^{i/j}}{R_B^{i/j}} \quad (4)$$

which may be cast in terms of $\delta^i E$ values as:

$$\alpha_{A-B} = \frac{1000 + \delta^i E_A}{1000 + \delta^i E_B} \quad (5)$$

Note that α_{A-B} simply reflects the contrast in isotopic compositions between two substances and, in terms of physical processes, could reflect equilibrium or non-equilibrium partitioning of isotopes. For an isotope exchange reaction in which one atom is exchanged, α_{A-B} is equal to the equilibrium constant. Because α_{A-B} is very close to unity, generally on the order of 1.00X, we may take advantage of the relation that $10^3 \ln(1.00X) \approx X$, which provides the useful relation:

$$10^3 \ln \alpha_{A-B} \approx \delta^i E_A - \delta^i E_B \equiv \Delta_{A-B} \quad (6)$$

This allows us to describe isotopic fractionations by simply subtracting the $\delta^i E$ values of substances A and B (carefully keeping the order of subtraction consistent). Assuming a fractionation of 10‰ ($\alpha_{A-B} = 1.010$), an error of only 0.05‰ is introduced if the fractionation is described using Δ_{A-B} as compared to α_{A-B} , which will be immaterial for most of the elements discussed in this volume, unless the fractionations are very large (several tens of per mil or greater).

Isotopic fractionations are sometimes discussed using the ϵ notation, and this has been most commonly used to describe kinetic isotope effects. This usage is common in the S isotope literature (e.g., Canfield 2001), and is also used in Chapter 9 (Johnson and Bullen 2004). The fractionation between reactant A and product B is defined as:

$$\epsilon_{A-B} = (\alpha_{A-B} - 1) 10^3 \quad (7)$$

ϵ_{A-B} therefore has units of per mil.

For elements that have three or more isotopes, isotopic fractionations may be defined using two or more isotopic ratios. Assuming that isotopic fractionation occurs through a mass-dependent process, the extent of fractionation will be a function of the relative mass differences of the two isotope ratios. For example, assuming a simple harmonic oscillator for molecular motion, the isotopic fractionation of R^{ij} may be related to R^{kj} as:

$$\alpha_{k/j} = (\alpha_{i/j})^Z \quad (8)$$

where $Z = (m_i/m_k)\{(m_k - m_j)/(m_i - m_j)\}$, and m refers to the masses of the individual isotopes i , j , and k (e.g., Criss 1999). We illustrate this mass-dependent relation for Mg in Figure 4, where Equation (8) becomes:

$$\alpha_{25/24} = (\alpha_{26/24})^{0.521} \quad (9)$$

Over small ranges in isotopic composition, Equation (8) may be approximated by the linear form:

$$\delta^k E \approx \left(\frac{k-j}{i-j} \right) \delta^i E \quad (10)$$

where i , j , and k are integer masses. In the case of Mg, this relation would be:

$$\delta^{25}\text{Mg} \approx 0.5 \delta^{26}\text{Mg} \quad (11)$$

Equations (8) and (10) are applicable to stable isotope systems where isotopic fractionation occurs through mass-dependent processes which comprise the majority of cases described in this volume. These relations may also be used to identify mass-independent fractionation processes, as discussed in Chapter 2 (Birck 2004). Mass-dependent fractionation laws other than those given above distinguish equilibrium from kinetic fractionation effects, and these are discussed in detail in Chapters 3 and 6 (Schauble 2004; Young and Galy 2004). Note that distinction between different mass-dependent fractionation laws will generally require very

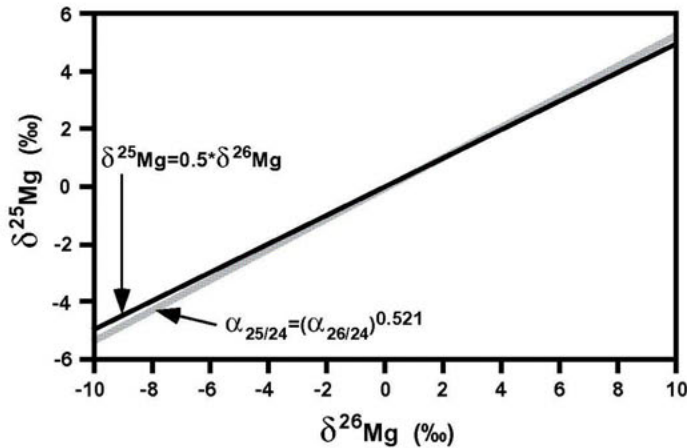


Figure 4. Illustration of mass-dependent fractionation of Mg isotopes, cast in terms of δ values. $\delta^{26}\text{Mg}$ and $\delta^{25}\text{Mg}$ values based on $^{26}\text{Mg}/^{24}\text{Mg}$ and $^{25}\text{Mg}/^{24}\text{Mg}$ ratios, respectively. A common equilibrium fractionation model, as defined by exponential relations between α values (fractionation factors) for different isotope ratios, is shown in the gray line. A simple linear relation, where the slope is proportional to the mass difference of the isotope pair, is shown in the black line. Additional mass-dependent fractionation laws may be defined, and all are closely convergent over small ranges (a few per mil) in isotope compositions at δ values that are close to zero.

high-precision isotopic analyses, depending on the range in isotopic compositions that are produced (Chapters 4 and 6).

The choices for defining δE values for new isotope systems that contain multiple isotopes will be largely determined by consideration of the analytical precision. For example, Ca isotope ratios might be reported using the extreme end members ^{40}Ca and ^{48}Ca , representing an 8 mass-unit spread. But, as discussed in Chapter 8, the very low abundance of ^{48}Ca (0.19%) makes this a poor choice. Although $^{44}\text{Ca}/^{40}\text{Ca}$ fractionations are one-half those of $^{48}\text{Ca}/^{40}\text{Ca}$ fractionations, the much higher precision with which the $^{44}\text{Ca}/^{40}\text{Ca}$ ratio may be determined makes this ratio a superior choice. In the case of Mg, where the two minor isotopes ^{25}Mg and ^{26}Mg have nearly equal abundances of 10.00% and 11.01%, respectively, $^{25}\text{Mg}/^{24}\text{Mg}$ and $^{26}\text{Mg}/^{24}\text{Mg}$ ratios should be determined with equal precision, making the $^{26}\text{Mg}/^{24}\text{Mg}$ ratio the clear choice for providing the largest signal to noise ratio because $^{26}\text{Mg}/^{24}\text{Mg}$ fractionations will be approximately twice those of $^{25}\text{Mg}/^{24}\text{Mg}$ fractionations for mass-dependent processes. In practice, however, both ratios are commonly measured to provide insight into different mass-dependent processes, as well as monitor possible anomalies in ^{26}Mg abundances due to decay of ^{26}Al , which may be an issue for extraterrestrial samples; these issues are discussed in detail in Chapters 2 and 6 (Birck 2004; Young and Galy 2004).

Predicted and measured isotopic variations

The general “rules of thumb” for isotopic fractionations discussed in Chapter 3 (Schauble 2004), including bonding, redox state, and relative mass differences, lay out broad expectations for the extent of isotopic fractionations that may be observed in new isotopic systems. Several examples of isotopic fractionations for various elements are illustrated in Figure 5. Commensurate with its large relative mass difference, $^{18}\text{O}/^{16}\text{O}$ fractionations may be quite large at low temperatures, exceeding, for example 20‰ for $\text{CaCO}_3\text{--H}_2\text{O}$ fractionations at 50°C (Fig. 5). Although isotopic fractionations are relatively large at low temperatures

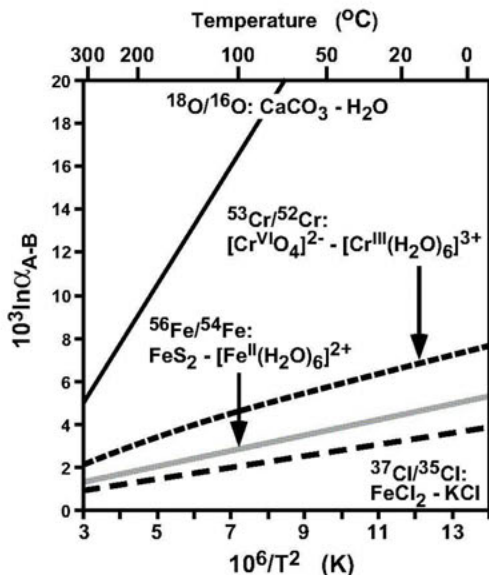


Figure 5. Examples of predicted and measured isotopic fractionations for O, Cr, Fe, and Cl, as cast in the traditional $10^3 \ln \alpha_{A,B} - 10^6/T^2$ diagram. The quantity $10^3 \ln \alpha_{A,B}$ places the isotope fractionation factor $\alpha_{A,B}$ in units of per mil (‰). Isotopic fractionations for relatively light elements, such as O, are generally higher than those of higher-mass elements, as expected based on changes in their relative mass differences (Fig. 3). $\text{CaCO}_3 - \text{H}_2\text{O}$ curve for $^{18}\text{O}/^{16}\text{O}$ fractionations based on experiments from O'Neil et al. (1969). $[\text{Cr}^{\text{VI}}\text{O}_4]^{2-} - [\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$ curve for $^{53}\text{Cr}/^{52}\text{Cr}$ fractionations based on calculations from Schauble et al. (2004). $\text{FeS}_2 - [\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$ curve for $^{56}\text{Fe}/^{54}\text{Fe}$ fractionations based on calculations from Polyakov and Mineev (2000) and Schauble et al. (2001). $\text{FeCl}_2 - \text{KCl}$ curve for $^{37}\text{Cl}/^{35}\text{Cl}$ fractionations based on calculations by Schauble et al. (2003).

they are generally much smaller for higher-mass elements, where they are rarely expected to exceed 10‰ at temperatures of 100°C or less. For example, calculations of $^{37}\text{Cl}/^{35}\text{Cl}$, $^{53}\text{Cr}/^{52}\text{Cr}$, and $^{56}\text{Fe}/^{54}\text{Fe}$ fractionations for the systems $\text{FeCl}_2\text{--KCl}$, $\text{Cr(VI)}_{\text{aq}}\text{--Cr(III)}_{\text{aq}}$, and $\text{FeS}_2\text{--Fe(II)}_{\text{aq}}$, respectively, range from 1 to 5‰ at 100°C (Fig. 5; Schauble 2004). Although these isotopic fractionations are significantly smaller than those found for H, C, O, and S, they are still significant relative to current state-of-the-art analytical precisions (Chapter 4; Albarède and Beard 2004).

In Figure 6 we summarize the range in isotopic compositions measured for natural terrestrial samples for the elements discussed in this volume (Li, Cl, Ca, Cr, Fe, Cu, Zn, Se, and Mo). As discussed in Chapter 2, as well as in several subsequent chapters, the range in isotopic compositions for many of these elements is extended considerably if extraterrestrial samples are included. The very large relative mass difference of 15% for ^6Li and ^7Li has produced a very large range in isotopic compositions in nature of ~75‰ (Fig. 6). As reviewed in Chapter 6 (Tomascak 2004) the largest Li isotope fractionation is produced in relatively low-temperature environments, including seafloor weathering and marine hydrothermal systems. Most igneous rocks have relatively homogenous $\delta^7\text{Li}$ values, unlike other light isotopes such as those of oxygen, suggesting that larger fractionations are associated with covalently bonded O in silicates as compared to the ionic bonds that characterize Li. The isotopes of Mg have one-third of the relative mass difference of Li, but, so far, the range in $\delta^{26}\text{Mg}$ values are proportionally much smaller than suggested by the contrast in relative mass differences of the two elements (Fig. 6). $\delta^{26}\text{Mg}$ values for Mg-bearing carbonates appear to vary by ~2‰, but little is yet known about Mg isotope fractionations at low temperatures. Because Mg is a light element which has two of its three isotopes that are similar in abundance, it is ideally suited to investigation of different mass-dependent fractionation mechanisms that may operate in nature, and Young and Galy (2004) discuss this in detail in Chapter 6.

Chlorine isotope compositions vary by up to 15‰ (Chapter 7; Stewart and Spivack 2004). These large variations in Cl isotope compositions are found in marine environments, including mid-ocean ridge basalts, seafloor and hydrothermal alteration products, and sedimentary pore

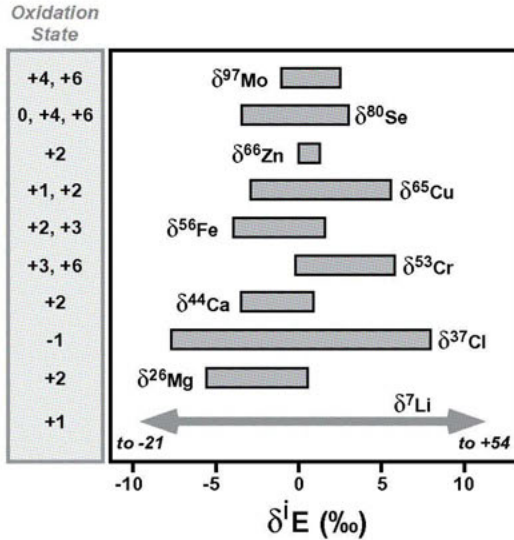


Figure 6. Summary of ranges in isotopic compositions for natural terrestrial samples as discussed in this volume. Isotopic variability in extraterrestrial samples is often greater. Isotopic compositions reported as δ values in units of per mil (‰), based on isotopic ratios and reference standards as used in this volume (Table 1). Note that the range of isotopic compositions for Li is much greater than the scale used in the diagram, where $\delta^7\text{Li}$ values vary from -21 to +54. In many cases, relatively large isotopic fractionations occur during redox reactions (see Chapter 3), and the common oxidation states in near-surface natural environments are listed on the left.

fluids. $\delta^{37}\text{Cl}$ values of fumarolic gases are also quite variable, suggesting a potential genetic tracer. Stewart and Spivack (2004) also note that significant Cl isotope variations are found in chlorinated organic compounds produced by industrial processing, similar to those found for industrially processed Li. These observations highlight the potential environmental applications of Li and Cl isotope variations.

Mantle-derived igneous rocks appear to be homogenous with respect to mass-dependent Ca isotope variations, although some K-rich rocks may have anomalously low $\delta^{44}\text{Ca}$ values reflecting ^{40}Ca enrichments from ^{40}K decay (Chapter 8; DePaolo 2004). One of the more important contrasts in Ca isotope compositions in the Earth is that measured between seawater Ca and igneous Ca, which appears to reflect Ca isotope fractionation during weathering and transport to the oceans. In contrast to the relatively high $\delta^{44}\text{Ca}$ values for seawater, biologically-processed Ca has relatively low $^{44}\text{Ca}/^{40}\text{Ca}$ ratios, and this appears to systematically decrease up the food chain. These observations highlight the potential for using Ca isotopes to trace biological processing of Ca in higher-order animals.

The isotope geochemistry of two redox-sensitive elements, Cr and Se, are compared in Chapter 9 by Johnson and Bullen (2004). Because Cr(VI) is quite soluble in natural waters, and is highly toxic, the significant fractionation in $^{53}\text{Cr}/^{52}\text{Cr}$ ratios that occurs during redox cycling of Cr is likely to find wide application in environmental geochemistry. Production of high $\delta^{53}\text{Cr}$ values for aqueous Cr seems likely to be a fingerprint for chromium reduction in natural systems. Selenium commonly occurs in three oxidation states in near-surface natural environments, Se(0), Se(IV), and Se(VI), and thus it is not surprising that significant isotopic fractionations are observed during redox cycling. The largest Se isotope fractionations appear to occur during reduction of Se(VI) and Se(IV) oxyanions, and this may occur through microbial activity, or through abiotic reduction.

Iron isotope geochemistry is reviewed in Chapter 10A (Beard and Johnson 2004) where summaries are given of the variations in $^{56}\text{Fe}/^{54}\text{Fe}$ ratios in inorganic experimental systems and natural igneous, metamorphic, and sedimentary rocks. Large fractionations of $^{56}\text{Fe}/^{54}\text{Fe}$ ratios occur during redox cycling of Fe, where low $\delta^{56}\text{Fe}$ values appear to be characteristic of reducing near-surface environments. In contrast, terrestrial surface weathering does not

appear to fractionate Fe isotopes for bulk sedimentary materials, although isotopic variations during hydrothermal alteration of oceanic crust is well documented. Significant Fe isotope variations are also found in some high-temperature samples. In Chapter 10B, Johnson et al. (2004) discuss experimental evidence for biological fractionation of Fe isotopes, during microbial reduction and oxidation, as well as supporting studies in mineral dissolution and sorption. Microbial reduction of ferric oxides produces aqueous Fe(II) that has low $\delta^{56}\text{Fe}$ values whose origin lies in a number of pathways, whereas microbial oxidation produces ferric Fe precipitates that have relatively high $\delta^{56}\text{Fe}$ values.

Review of the isotope geochemistry of the transition metals is continued by Albarède (2004) in Chapter 11, where isotopic variations in Cu and Zn are discussed. The significant changes in bonding environments of Cu(I) and Cu(II) produce significant differences in $\delta^{65}\text{Cu}$ values for oxidized and reduced Cu compounds, and isotopic variations of up to 9‰ are observed in nature. Isotopic variations of Zn are significantly more restricted, where $\delta^{66}\text{Zn}$ values vary by less than 2‰, but systematic variations are recorded in Fe–Mn nodules from the ocean floor. Measurable isotopic variations are found for Cu and Zn in sedimentary rocks, as well as ore deposits, and this remains a promising aspect of future Cu and Zn isotope studies.

Molybdenum isotope variations appear to be on the order of 3.5‰ in $^{97}\text{Mo}/^{95}\text{Mo}$ ratios, where the largest fractionation is seen between aqueous Mo in seawater and that incorporated in Fe–Mn crusts and nodules on the seafloor (Chapter 12; Anbar 2004). This isotopic contrast is interpreted to reflect fractionation by Mo sorption to Mn oxide-rich sediments relative to aqueous Mo. The $\delta^{97}\text{Mo}$ values for euxinic sediments in turn are distinct from those of Fe–Mn crusts, highlighting the isotopic contrasts between major repositories of Mo in surface and near-surface environments. As discussed by Anbar (2004) in Chapter 12, a major focus of research on Mo isotopes has been the potential use as a paleoredox indicator in marine systems.

Processes that may produce isotopically distinct reservoirs

We briefly review processes in which isotopic fractionations may be recorded in isotopically distinct reservoirs that are preserved in nature. These concepts have been extensively covered in the H, C, O, and S isotope literature, and we illustrate several examples for the *non-traditional* stable isotope systems discussed in this volume. One of the simplest processes that produces isotopically distinct reservoirs would be slow reaction of substance A to B, where A and B remain open to complete isotopic exchange during the process. This is commonly referred to as *closed system equilibrium*, and the changes in isotopic compositions that occur may be defined by the exact relation:

$$\delta^i E_B = \frac{\alpha_{B-A} \delta^i E_{\text{SYS}} + 1000f(\alpha_{B-A} - 1)}{\alpha_{B-A} - \alpha_{B-A}f + f} \quad (12)$$

where α_{B-A} is the *B-A* fractionation factor, $\delta^i E_{\text{SYS}}$ is the $\delta^i E$ value for the total system, and f is the fraction of A remaining ($f = 1$ when the system is entirely A) (Eqn. 3.19, p. 105, Criss 1999). Note that Equation (12) is simpler if cast in terms of α_{A-B} rather than α_{B-A} , as was defined in Equation (4) above. If α_{B-A} is close to unity, Equation (12) may be simplified to:

$$\delta^i E_B \approx \delta^i E_{\text{SYS}} + f(\alpha_{B-A} - 1) 10^3 \quad (13)$$

(Criss 1999), which may be further simplified to:

$$\delta^i E_B \approx \delta^i E_{\text{SYS}} + f\Delta_{B-A} \quad (14)$$

using the approximation $\Delta_{B-A} \approx (\alpha_{B-A} - 1) \times 10^3$ (note that this is equivalent to ε_{B-A} , following Eqn. 7 above). Following these simplifications, the corresponding $\delta^i E_A$ value, at a given f , is:

$$\delta^i E_A \approx \delta^i E_B - \Delta_{B-A} \quad (15)$$

(Criss 1999). Equations (14) and (15) describe a straight line in terms of $\delta^i E_A$ or $\delta^i E_B$ as a function of f or the fraction of B produced (Fig. 7). For example, in a system that is initially composed only of A and has an initial $\delta^i E$ value of zero, where $10^3 \ln \alpha_{B-A} \approx \Delta_{B-A} = -1.5\text{‰}$, the first fraction of B to form will have $\delta^i E_B = -1.5\text{‰}$ (Fig. 7). As the reaction proceeds, the shifting mass balance of phases A and B will require shifts in their $\delta^i E$ values while maintaining a constant isotopic fractionation between A and B (Fig. 7). When the reaction is

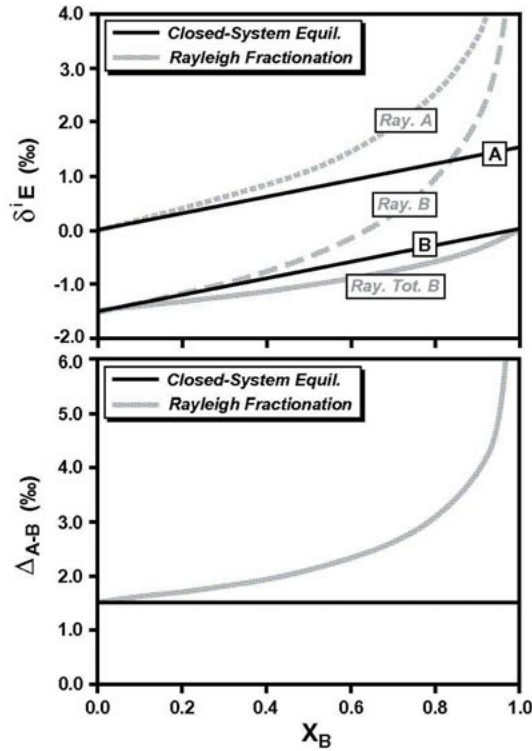


Figure 7. Comparison of isotopic fractionations produced by closed-system equilibrium and Rayleigh fractionation processes where phase A is reacted to phase B , as a function of the proportion of B (X_B) that is produced. Isotopic compositions are reported as $\delta^i E$, in units of per mil, and the fractionation factor α_{B-A} is 0.9985 ($\alpha_{A-B}=1.0015$). In the upper diagram, solid black lines mark the $\delta^i E$ values of reactant A and product B that reflect the isotopic mass-balance constraints imposed by a closed system where A and B continuously maintain isotopic equilibrium. During Rayleigh fractionation (gray lines), the product B is isolated from isotopic exchange with A immediately after formation, producing more extreme isotopic variations than in closed-system equilibrium fractionation. The $\delta^i E$ values of remaining phase A are shown in the short-dashed line in the upper diagram, and the $\delta^i E$ values of the instantaneous product B is shown in the long-dashed lines in the upper diagram. Variations in the $\delta^i E$ values for the *total* product B shown in solid gray line. In the lower diagram, the measured isotopic contrast between A and B , which may be conveniently defined as Δ_{A-B} (see text), is constant for closed-system equilibrium fractionation (solid horizontal line), but changes during Rayleigh fractionation (curved gray line), even for a constant fractionation factor α_{A-B} that may reflect equilibrium conditions.

complete and the system is entirely B , mass balance requires that $\delta^i E_B$ is the same as the initial $\delta^i E_A$ value (Fig. 7). The importance of this illustration is that in cases where reactions go to completion, if there is no addition or loss of element E from the system, there will be no net change in isotopic composition, even if α_{B-A} is significantly different than unity. Although data that fall along linear $\delta^i E - f$ trends are likely to be indicative of isotopic equilibrium, there are cases where incremental (Rayleigh) fractionation may occur under kinetic conditions that may be mistaken for closed-system equilibrium (e.g., p. 154-157, Criss 1999), requiring other approaches to establishing isotopic equilibrium such as use of enriched isotope tracers.

In the case of reactions where the products do not continue to exchange with other phases in the system, as might be the case during precipitation of a mineral from solution, Rayleigh fractionation may best describe the changes in $\delta^i E$ values for the individual components. The well-known Rayleigh equation (Rayleigh 1902) is:

$$\frac{[R^{i/j}]}{[R^{i/j}]_i} = f^{(\alpha_{B-A}-1)} \quad (16)$$

where $[R^{i/j}]_i$ is the initial ratio $R^{i/j}$ (which may be defined for either A or B), and f is the fraction of A remaining. Cast in terms of $\delta^i E$ values, Equation (16) becomes:

$$(1000 + \delta^i E)/(1000 + \delta^i E_i) = f^{(\alpha_{B-A}-1)} \quad (17)$$

where $\delta^i E$ may be defined for either A or B , and the subscript i refers to the initial $\delta^i E$ value.

The products of Rayleigh fractionation are effectively isolated from isotopic exchange with the rest of the system immediately upon formation. If the process occurs slowly, such that each increment of product B forms in isotopic equilibrium with the reactant A prior to isolation of B from the system, then α_{B-A} would be an equilibrium isotope fractionation factor. However, if the process of formation of B is rapid, incremental formation of B may be out of isotopic equilibrium with A . In this case, α_{B-A} would be a kinetic isotope fractionation factor, which may be a function of reaction rates or other system-specific conditions.

Because the product in Rayleigh fractionation is progressively isolated, large changes in $\delta^i E$ values in the remaining components may occur (Fig. 7). A common process by which this occurs would be condensation or precipitation. Assuming that α_{B-A} is constant, the differences in the instantaneous $\delta^i E$ values for A and incremental formation of B will be constant (Fig. 7). However, in practice, the isotopic composition of the *total* condensed or solid phase after a given extent of reaction is of interest, and the changes in $\delta^i E$ values for the total phase B are more modest than for the incremental portions of B (Fig. 7). Because the $\delta^i E$ values of the remaining reactant A change dramatically toward the end of the reaction, the apparent value of Δ_{B-A} between A and the *total* condensed or solid phase deviates strongly from the fractionation factor as the reaction proceeds, and this is a key feature of Rayleigh fractionation (Fig. 7). As can be seen in Figure 7, the difference in the measured $\delta^i E$ values for A and total B most closely match that of the true fractionation factor at the beginning of the reaction, where the measured isotopic contrast is insensitive to the specific mechanism (e.g., closed-system equilibrium or Rayleigh) by which A and B are physically separated (Fig. 7).

Adsorption of Mo to Mn oxyhydroxides produces an isotopic fractionation that appears to follow that of a closed-system equilibrium model as a function of the fraction of Mo adsorbed (Fig. 8). Barling and Anbar (2004) observed that the $\delta^{97}\text{Mo}$ values for aqueous Mo (largely the $[\text{MoO}_4]^{2-}$ species) were linearly correlated with the fraction (f) of Mo adsorbed (Fig. 8), following the form of Equation (14) above. The $\delta^{97}\text{Mo}-f$ relations are best explained by a $\text{Mo}_{\text{aq}}-\text{Mn}$ oxyhydroxide fractionation of +1.8‰ for $^{97}\text{Mo}/^{95}\text{Mo}$, and this was confirmed through isotopic analysis of three solution-solid pairs (Fig. 8). The data clearly do not lie

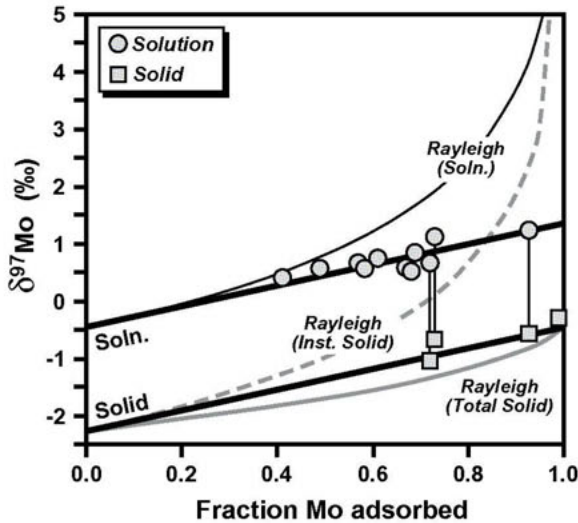


Figure 8. Example of apparent closed-system equilibrium fractionation, where Mo in solution is sorbed to Mn oxides (Barling and Anbar 2004). The $\delta^{97}\text{Mo}$ values of the Mo remaining in solution during sorption follow the linear trends that are consistent with closed-system equilibrium fractionation where isotopic equilibrium is continuously maintained between Mo in solution and that sorbed to the Mn oxides. Three aqueous-solid pairs (shown with tie lines) are consistent with this interpretation. The isotopic data cannot be explained through a Rayleigh process, where the product of the reaction (sorbed Mo) is isolated from isotopic exchange with aqueous Mo.

along a Rayleigh fractionation trend (Fig. 8), as would be expected if the adsorbed Mo did not remain in isotopic communication with Mo_{aq} at different degrees of total adsorption.

In contrast, reduction of Cr(VI) in solution, followed by precipitation of hydrated $\text{Cr}^{\text{III}}_2\text{O}_3$, produces fractionation in $^{53}\text{Cr}/^{52}\text{Cr}$ that follows a Rayleigh process (Fig. 9). When plotted as a function of the fraction of $\text{Cr(VI)}_{\text{aq}}$ reduced (f), the $\delta^{53}\text{Cr}$ values increase non-linearly, lying about a Rayleigh fractionation trend calculated for a $[\text{Cr}^{\text{VI}}\text{O}_4]^{2-}$ -hydrated $\text{Cr}^{\text{III}}_2\text{O}_3$ fractionation of +3.4‰ (Fig. 9). The $\delta^{53}\text{Cr}$ - f trends are not consistent with the linear trends expected for a closed-system equilibrium model. In the Cr(VI) reduction experiments of Ellis et al. (2002), the fractionation factor, $\alpha_{\text{Cr(VI)-Cr(III)}}$, derived from the data is interpreted to reflect kinetic isotope fractionation, although it is important to note that not all Rayleigh processes are associated with kinetic isotope fractionation.

DETERMINATION OF ISOTOPIC FRACTIONATION FACTORS

Isotopic fractionation factors may be calculated based on theory (e.g., Urey 1947; Bigeleisen and Mayer 1947), and the various approaches used for such calculations are discussed in detail in Chapter 3 (Schauble 2004). Calculated fractionation factors are extremely important for new isotope systems because they constrain the isotopic fractionations that may be anticipated in nature, and, in some cases, provide the only means for constraining fractionation factors for systems that are inaccessible to experiments. Isotopic fractionation factors may also be inferred from natural assemblages (e.g., Bottinga and Javoy 1975), although issues of attainment of isotopic equilibrium or differential exchange upon cooling remain in many cases (e.g., Gilotti 1986; Eiler et al. 1992; Kohn and Valley 1998). Ultimately, however, experimental verification of calculated fractionation factors is desirable. In their compilation of experimentally determined isotope fractionation factors for H, C, and O isotopes, Chacko et al. (2001) summarize measurements for 306 systems, many of which involved several independent studies. We are far from reaching this level of experimental calibration of isotope fractionation factors for the new isotopic systems discussed in this volume, and expanding the database of isotope fractionation factors remains a high priority for the isotope community.

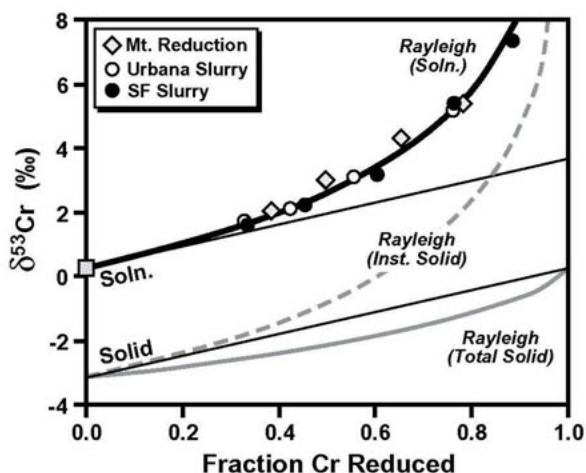


Figure 9. Example of Rayleigh fractionation produced during reduction of aqueous Cr(VI) to Cr(III), as reported in three reduction experiments by Ellis et al. (2002). Because the reduced product is a Cr(III)-hydroxide that does not continue to isotopically exchange with the aqueous Cr(VI), the $\delta^{53}\text{Cr}$ values of the remaining Cr(VI) increase along a Rayleigh trend. Although each of the three experiments of Ellis et al. (2002) produced slightly different Cr(III)-Cr(VI) fractionation factors, the curves illustrated are calculated for a single $\alpha_{\text{Cr(III)-Cr(VI)}} = 0.9966$. Ellis et al. (2002) interpret the inferred $\alpha_{\text{Cr(III)-Cr(VI)}}$ as reflecting kinetic isotope fractionation during reduction and precipitation.

The majority of experimental studies of isotope fractionation have involved fluid-mineral pairs, reflecting the common means by which minerals form, particularly in low-temperature environments. In fluid-mineral systems, isotopic exchange is limited by the exchange properties of the solid phase, where the mechanisms of exchange may include replacement, recrystallization, Oswald ripening, surface diffusion, volume diffusion, grain boundary diffusion, and dislocation/lattice diffusion (e.g., Cole and Chakraborty 2001). Attainment of isotopic equilibrium in fluid-mineral systems is often difficult in experimental systems, especially at low temperatures, where the rates of diffusion are very low. Determination of equilibrium isotopic partitioning is of particular interest because equilibrium fractionation factors provide insights into bonding environments and other physico-chemical properties of the species of interest and equilibrium isotope fractionation factors are independent of kinetic issues or pathways of formation.

Fluid-mineral fractionation factors

In addition to providing the means for calculating the isotopic compositions of ancient fluids based on analysis of minerals, mineral-fluid isotope fractionation factors provide an opportunity to combine fractionation factors when there is a common substance such as water. A fundamental strategy for compiling databases for isotopic fractionation factors is to reference such factors to a common substance (e.g., Friedman and O'Neil 1977). For example, the quartz-water fractionation factor may be combined with the calcite-water fractionation factor to obtain the quartz-calcite fractionation factor at some temperature. It is now recognized, however, that the isotopic activity ratio of water in a number of experimental determinations of $^{18}\text{O}/^{16}\text{O}$ mineral-fluid fractionation factors has been variable, in part due to dissolution of mineral components at elevated temperature and pressure. The influence of solute composition on mineral-fluid fractionation factors may be quite significant, and this effect has been termed the *isotope salt effect* (e.g., O'Neil and Truesdell 1991; Horita et al. 1993a,b; Hu and Clayton 2003). Using substances other than water as the exchange medium is one approach to

addressing this issue. Carbonate (Clayton et al. 1989), CO_2 (O'Neil and Epstein 1966; Matthey et al. 1990; Matthews et al. 1994; Fayek and Kyser 2002), and H_2 (Vennemann and O'Neil 1996) have been used successfully. In the case of $^{18}\text{O}/^{16}\text{O}$ fractionation factors for minerals of wide geologic interest, it is generally accepted that use of carbonate as the exchange medium offers a superior reference compared to water (e.g., Clayton et al. 1989; Chacko et al. 1996; Hu and Clayton 2003). Alternatively, mineral-mineral fractionation factors may be obtained in three-phase systems that contain two minerals and water, where the isotopic effect of dissolved components in the fluid cancels out (Hu and Clayton 2003). As new isotopic systems are developed, it seems likely that a variety of reference exchange media will be required, depending on the element, as databases of fractionation factors are developed.

The significant effects on $^{18}\text{O}/^{16}\text{O}$ fractionations due to dissolved components in mineral-water systems, up to 2‰ in high-temperature experiments, highlight the importance of speciation and activity in experimental systems in terms of their effects on isotopic fractionation factors. Thermodynamic data bases (e.g., Johnson et al. 1992; Shock et al. 1997; Sverjenski et al. 1997; Holland and Powell 1998) demonstrate that for all of the elements discussed in this volume, as well as many others, speciation in aqueous solutions may be highly variable, suggesting that the *isotope salt effects* that have been observed for oxygen in mineral-water systems are likely to be much greater for metals and halogens in mineral-fluid systems; indeed, calculated isotopic fractionation factors are, in general, highly variable among various aqueous species for metals and halogens, as reviewed in Chapter 3 (Schauble 2004). As the experimental databases for isotopic fractionation factors expand for the *non-traditional* stable isotope systems, the choices of exchange media for determining isotopic fractionation factors will be critical, as will consideration of the exact species involved.

Evaluating approach toward isotopic equilibrium in experiments

In this last section, we briefly review some of the methods that have been used to evaluate isotopic exchange in experiments, highlighting approaches used in well-studied systems such as oxygen, and note some new applications in the *non-traditional* stable isotopes. One classic method for determining equilibrium fractionation factors is to approach isotopic equilibrium from both sides (O'Neil 1986b). Alternatively, assessment of isotopic equilibrium may be done using the *three isotope method* (Matsuhisa et al. 1978, 1979; Matthews et al. 1983a,b). This approach involves starting materials that lie on two separate, but parallel, mass-dependent fractionation lines, where movement toward isotopic equilibrium will move the phases onto a new mass-dependent fractionation line at an intermediate position in a ratio-ratio diagram (Fig. 10). In its application to oxygen isotopes, the $^{18}\text{O}/^{16}\text{O}$ ratios of the starting materials have been chosen to lie close to those expected under equilibrium, whereas the $^{17}\text{O}/^{16}\text{O}$ ratios may be chosen to be far from equilibrium, providing a sensitive measure of the approach to isotopic equilibrium (Fig. 10). The *three isotope method* remains one of the most elegant and rigorous means for constraining the approach toward isotopic equilibrium, and is ideally suited for isotope systems where two isotope ratios may be determined independently.

In principle, the three isotope method may be widely applied to new isotope systems such as Mg, Ca, Cr, Fe, Zn, Se, and Mo. Unlike isotopic analysis of purified oxygen, however, isotopic analysis of metals that have been separated from complex matrices commonly involves measurement of several isotopic ratios to monitor potential isobars, evaluate the internal consistency of the data through comparison with mass-dependent fractionation relations (e.g., Eqn. 8 above), or use in double-spike corrections for instrumental mass bias (Chapter 4; Albarède and Beard 2004). For experimental data that reflect partial isotopic exchange, their isotopic compositions will not lie along a mass-dependent fractionation line, but will instead lie along a line at high angle to a mass-dependent relation (Fig. 10), which will limit the use of multiple isotopic ratios for isobar corrections, data quality checks, and double-spike corrections.

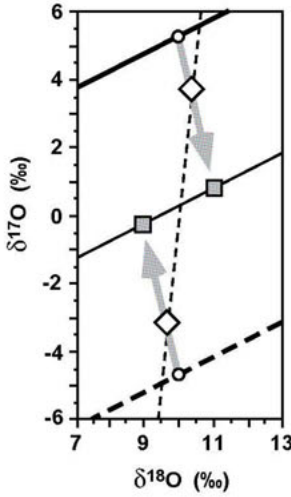


Figure 10. Three isotope method for assessing attainment of isotopic equilibrium for O isotope exchange experiments, based on the approach taken by Matthews et al. (1983a,b). Heavy solid black line (top line) reflects the terrestrial fractionation line for $^{17}\text{O}/^{16}\text{O}$ - $^{18}\text{O}/^{16}\text{O}$ variations, and the small open circle on this line represents a natural mineral sample. The lower heavy dashed line represents a fluid that lies below the terrestrial fractionation line that was obtained through mixing of two highly disparate isotope compositions (MEOW II water developed at the University of Chicago). Movement of the two phases toward isotopic equilibrium will be occur in the directions of the arrows; assuming equal proportions of oxygen in the fluid and mineral phases, isotopic equilibrium will be marked by data that lie in the middle (thin solid line), where the final isotopic compositions of fluid and mineral are separated by the equilibrium fractionation factor. Partial exchange will produce isotopic compositions (diamonds) that do not lie along a mass-dependent fractionation line, where mineral-fluid pairs will define a line (dashed thin line) that lies at a high angle to a mass-dependent line.

An alternative to the three isotope method is to use an enriched isotope tracer in experiments that are run in parallel to those involving “normal” isotope compositions under identical run conditions. Use of enriched isotope tracers to evaluate the kinetics of isotopic exchange has a long history (e.g., Mills and Urey 1940). The extent of exchange toward isotopic equilibrium may be defined as:

$$F = (\delta E - \delta E_i) / (\delta E_e - \delta E_i) \quad (18)$$

where δE_i and δE_e are the initial and equilibrium isotopic compositions, respectively, and δE is the isotopic composition observed at any time of interest (e.g., Criss et al. 1987). The fraction of isotopic exchange (F) varies from 0 to 1 as isotopic equilibrium is approached. Inspection of Equation (18) shows that F may be calculated with great sensitivity if enriched isotope tracers are used because the differences in the δ values will be large. Moreover, calculation of F using enriched isotope tracers will be relatively insensitive to the final equilibrium fractionation factor, which may be unknown at the start of an experiment. Calculation of F using Equation (18) is valid for ranges in δE values up to a few hundred per mil. For more extreme isotopic enrichments, F must be calculated using the atomic abundances and molecular weights of the two components:

$$F = \frac{W_N (X_S^i - R_{MEAS}^{i/j} X_S^j)}{W_S (R_{MEAS}^{i/j} X_N^j - X_N^i) + W_N (X_S^i - R_{MEAS}^{i/j} X_S^j)} \quad (19)$$

where W_N and W_S are the molecular weights of the normal and isotopically enriched element, respectively, X_S^i and X_S^j are the atomic abundances of isotopes i and j in the isotopically enriched “spike”, respectively, and X_N^i and X_N^j are the atomic abundances of isotopes i and j for the isotopically “normal” component, respectively. Equation (19) may be derived from standard two-component mixing relations (e.g., Albarède 1995).

Substituting F into a general rate equation produces:

$$\frac{-d(1-F)}{dt} = k_n(1-F)^n \quad (20)$$

where k is the rate constant, and n is the order of the reaction, generally an integer from 0 to 3. Although most isotope exchange reactions appear to follow a first-order rate law ($n = 1$) (e.g., Criss et al. 1987; Chacko et al. 2001), isotopic exchange may also follow a second-order rate law (e.g., Graham 1981; Johnson et al. 2002). Integration of equation 20 for first- and second-order rate laws ($n = 1$ and 2) yields the following linear forms:

$$\ln(1 - F) = -k_1 t \quad \text{for } n = 1 \quad (21)$$

$$\frac{F}{(1 - F)} = k_2 t \quad \text{for } n = 2 \quad (22)$$

An example using enriched isotope tracers to study the kinetics of isotopic exchange is shown in Figure 11, where an enriched ^{57}Fe tracer for the ferric Fe phase was used to determine the kinetics of isotopic exchange between aqueous ferric and ferrous Fe. In the system $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+} - [\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$, Fe isotope equilibrium is rapidly attained, where 95% isotopic equilibrium is established within ~60 seconds at 22°C (Fig. 11), or within ~5 minutes at 0°C, where isotopic exchange occurs via a second-order rate law. Despite the rapid exchange kinetics, the ferric Fe species was separated essentially instantaneously, effectively “freezing in” the isotopic composition of hexaquo Fe(III) and Fe(II), with minimal isotopic re-equilibration (~10–20%) during species separation (Johnson et al. 2002; Welch et al. 2003). If the timescale of species separation was on the order of that required for isotopic equilibrium between aqueous species, the measured isotopic compositions of the separated components would *not* preserve the instantaneous compositions in solution. For the range in isotopic compositions shown in Figure 11, calculation of F for the rate equations using Equation (18) produces an error of less than 0.005 relative to that calculated using Equation (19), which is insignificant.

Although closed-system isotopic equilibrium often may be attained among aqueous species at low temperatures on reasonable timescales (Fig. 11), it is much more difficult to reach isotopic equilibrium in fluid-mineral systems at low temperatures (a few hundred degrees or less). Solid-state diffusion rates at low temperatures are far too slow to allow isotopic equilibrium to be established through diffusion alone, and instead can only occur in low-temperature experiments through recrystallization (e.g., O’Neil 1986b; Chacko et al. 2001; Cole and Chakraborty 2001). Alternatively, estimates of mineral-fluid isotope fractionation factors via direct mineral synthesis through slow precipitation is an approach many workers have taken, particularly for carbonates and oxides (e.g., O’Neil et al. 1969; Tarutani et al. 1969; Yapp 1987, 1990; Carothers et al. 1988; Kim and O’Neil 1997; Bao and Koch 1999). It is, however, recognized that the high activation energies that are associated with

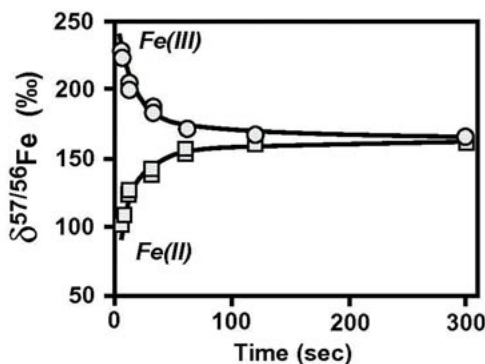


Figure 11. Determination of ferrous-ferric isotope exchange kinetics in dilute aqueous solutions using ^{57}Fe -enriched tracer solutions. Measured $\delta^{57/56}\text{Fe}$ values for ferrous (squares) and ferric (circles) Fe in solution versus time. Initial $\delta^{57/56}\text{Fe}$ values for $\text{Fe}(\text{II})_{\text{aq}} \sim 0\text{‰}$ and $\text{Fe}(\text{III})_{\text{aq}} \sim 331\text{‰}$. The rapid convergence in $\delta^{57/56}\text{Fe}$ ratios for the ferric and ferrous species indicates that isotopic equilibrium is attained within minutes. Adapted from Welch et al. (2003).

nucleation and crystal growth at low temperatures may be problematic in terms of estimating equilibrium isotope fractionation factors (Chacko et al. 2001), and these factors are a likely reason for the very wide range in isotope fractionation factors that have been measured in low-temperature experiments. For example, at room temperature, there is a 16‰ range in the experimentally determined $^{18}\text{O}/^{16}\text{O}$ fractionation factor for the magnetite-water pair (O'Neil and Clayton 1964; Becker and Clayton 1976; Blattner et al. 1983; Rowe et al. 1994; Zhang et al. 1997; Mandernack et al. 1999) and a 11‰ range for the hematite-water and goethite-water pairs (Clayton and Epstein 1961; Clayton 1963; Yapp 1987, 1990; Müller 1995; Bao and Koch 1999). The rate of precipitation of minerals from solution has long been known to influence isotopic fractionations for the light stable isotopes (e.g., Turner 1982; McConnaughey 1989; Romanek et al. 1992; Kim and O'Neil 1997), and point to the importance of kinetic effects during mineral synthesis or precipitation approaches to determining isotopic fractionation factors.

Recrystallization of minerals or precursor phases may promote isotopic exchange with a fluid (e.g., O'Neil and Taylor 1967; Matthews et al. 1983a,b; Bao and Koch 1999), and will often move minerals closer to isotopic equilibrium. Qualitative evidence for dissolution/re-precipitation in experimental runs is often found in SEM or TEM images, but such images do not quantify the amount of an element that has passed through the aqueous and solid phases during dissolution/re-precipitation. Ion-microprobe analysis may identify dissolution and re-precipitation and may allow determination of isotope fractionation factors for systems that have only partially exchanged (e.g., Fortier et al. 1995). Another approach to quantifying the extent of dissolution and re-precipitation is through use of enriched isotopic tracers that are added following initial mineral formation in synthesis experiments. An example of this approach is shown in Figure 12, where an ^{57}Fe -enriched tracer was used to calculate the degree of dissolution and re-precipitation in the system $[\text{Fe}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$ – Fe_2O_3 . This system was in approximate chemical equilibrium based on the observation that little change in aqueous Fe(III) contents occurred, demonstrating that the temporal changes in Fe isotope compositions reflect isotopic exchange during dissolution and re-precipitation where their relative rates were in balance; if such rates were slow, they should approach equilibrium conditions in terms of isotopic fractionation.

CONCLUSIONS

The principles of isotopic fractionation apply to all elements, and the methodologies that have been developed for the *traditional* isotopic systems such as H, C, O, and S are completely applicable to “new” isotopic systems, such as those discussed in this volume. Issues of nomenclature and standards will continue to be important as additional isotopic systems are explored, requiring the worker interested in these systems to be aware of differences among various studies that have yet to sort themselves out. Advances in theory and analytical methods promise to add many more isotopic systems to the field of *stable isotope geochemistry* than those reviewed in this volume. In addition to determining the ranges in isotopic compositions that may exist in natural systems, equal effort must be applied to experimental determination of isotope fractionation factors in carefully designed and implemented experimental studies, drawing upon the lessons that have been learned from several decades of study in the *traditional* stable isotope systems.

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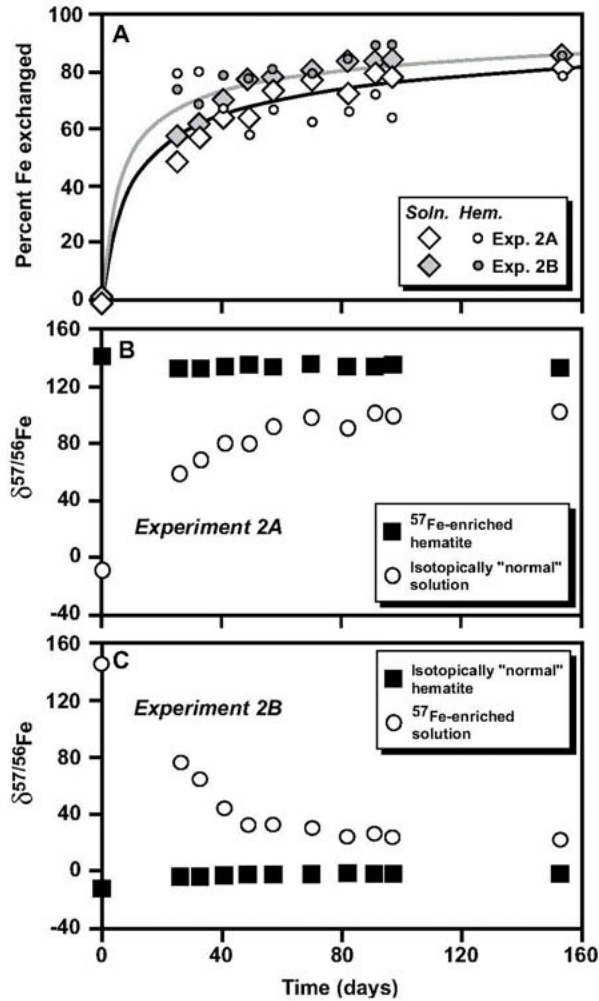


Figure 12. Extent of dissolution and re-precipitation between aqueous Fe(III) and hematite at 98°C calculated using ^{57}Fe -enriched tracers. **A.** Percent Fe exchanged (F values) as calculated for the two enriched- ^{57}Fe tracer experiments in parts B and C. Large diamonds reflect F values calculated from isotopic compositions of the solution. Small circles reflect F values calculated from isotopic compositions of hematite, which have larger errors due to the relatively small shifts in isotopic composition of the solid (see parts B and C). Curves show third-order rate laws that are fit to the data from the solutions. **B.** Tracer experiment using ^{57}Fe -enriched hematite, and “isotopically normal” Fe(III). **C.** Identical experiment as in part B, except that solution Fe(III) is enriched in ^{57}Fe , and initial hematite had “normal” isotope compositions. Data from Skulan et al. (2002).

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An Overview of Isotopic Anomalies in Extraterrestrial Materials and Their Nucleosynthetic Heritage

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INTRODUCTION

Isotopic anomalies are expected in primitive meteorites since astronomical observation and astrophysical modeling of stars predict a great variety of stellar processes. Protostellar clouds should partially preserve the memory of this diversity in solid grains. Since 1970, high precision mass spectrometry and high resolution ion probes have led to the discovery of numerous isotopic anomalies, which were rapidly associated with nucleosynthetic processes. A general rule is that small isotopic effects (parts in 10^3 – 10^4) are observed in centimeter size samples, whereas order of magnitude variations are observed at the micron scale in circumstellar grains.

Refractory materials in primitive meteorites were investigated first as they have the best chance of escaping homogenization in the early solar system. Inclusions in C3 carbonaceous chondrites exhibit widespread anomalies for oxygen and the iron group elements. Only a few members, dubbed “FUN” (for “Fractionated and Unknown Nuclear” effects), also display anomalous compositions for the heavy elements. Anomalies in inclusions have generally been connected with explosive or supernova nucleosynthesis.

Several types of presolar circumstellar grains have been separated from the matrix of chondrites: diamonds, silicon carbide, graphite, oxides. The isotopic ratios of the light elements (C-N-O) vary over several orders of magnitude in these grains. Only a few measurements have been performed for heavier elements with generally s-process signatures. AGB stars at different stages of their evolution are thought to be the sources of most circumstellar grains. Nevertheless grains with supernova signatures have also been found. For Cr and Mo in bulk primitive carbonaceous chondrites (C1, C2), large isotopic differences exist between the different major mineral phases of the bulk rock.

A number of now extinct radioactive isotopes have existed in the early solar system. This is shown by the variations that they induce in the abundances in their daughter nuclides. Their main use is in establishing a chronology between their parental presolar stellar sources, and the formation of the solar system and the planets. An active debate is presently going on whether some of these short-lived nuclides could have been made within the early solar system by an intense flux of energetic protons from the young sun.

This chapter presents an updated report of the data with necessarily some limitations, but I will try to keep the most striking features and highlight the clearest relation with nucleosynthesis in stars.

Historical background

In 1970 only three kinds of isotopic variations were known from measurements on solar system samples. Isotopic ratios involving the decay product of long-lived radioactive nuclei (^{40}K - ^{87}Rb - ^{147}Sm - ^{176}Lu - ^{187}Re -U-Th) constitute the first family. The second relates to physico-chemical fractionation of the light elements (H-C-N-O) which is mass dependent (hereafter referred to as “linear effects”). The third comprises the products of cosmic-ray spallation which produce very minor amounts of some nuclei (see Reedy et al. (1983) and Honda (1988) for an overview). A number of investigations for extinct radioactivities and isotopic heterogeneities had been carried out earlier but failed to demonstrate resolved isotopic variations (Wasserburg and Hayden 1955; Anders and Stevens 1960; Murthy and Sandoval 1965; Eugster et al. 1969; Schramm et al. 1970; Huey and Kohman 1972). The searches for isotopic variations due to irradiation by an early active Sun failed as well (Fowler et al. 1962; Burnett et al. 1966). Hence until the early 1970s, it was generally accepted that the solar system had undergone a high temperature stage volatilizing all, or almost all solids, and homogenizing at least the inner solar system where the samples were coming from (Cameron 1969). Nucleosynthetic theory in the same time was directed toward reproducing the solar system abundances (Burbidge et al. 1957).

One striking exception was the very early discovery of ^{129}I decay to ^{129}Xe (Jeffery and Reynolds 1961). This discovery reflects the particular properties of rare gases which are nearly absent in telluric planetary bodies. Because they are not diluted by high abundances of isotopically ‘normal’ noble gases, anomalies in rare noble gas components were the first to be detected. This is also the reason for the Xe record of the fission of ^{244}Pu (Rowe and Kuroda 1965). From the available data on short-lived nuclides at that time, it was concluded that the last nucleosynthetic input into the protosolar cloud predated the formation of the planets by 100-200 Ma.

The first evidence for non-mass dependent isotopic variations came from oxygen in the refractory inclusions of the carbonaceous chondrite Allende (Clayton et al. 1973). The large effects found for oxygen, a major constituent of rocks, acted as a trigger for numerous high precision isotopic studies for as many elements as were possible to measure, and creating a new field in planetology. The outcome of this profusion of successful studies has been summarized in several past reviews, with special emphasis on groups of elements or objects (Clayton et al. 1988; Lee 1988; Anders and Zinner 1993; Zinner 1997; Goswami and Vanhala 2000). The major advances in the field roughly correspond to two waves of new data: the high precision isotopic measurement in the cm size inclusions of the C3 chondrites and the discovery of presolar grains which thereafter were investigated with microprobe techniques. This is not fortuitous and connects to two significant instrumental evolutions. The lunar exploration program led to the development of a new generation of mass spectrometers, able to resolve 10^{-4} (100 ppm) relative isotopic differences (Papanastassiou and Wasserburg 1969; Wasserburg et al. 1969). The sample sizes of the inclusions is the same order of magnitude as some precious lunar samples. The development of high resolution SIMS/ion probe (Lepareur 1980) was also under way during the 1970s and was shown to be suitable for natural micro sample isotopic analysis (Hutcheon 1982).

The definition of isotopic anomalies

In a strict sense “isotopic anomalies” are defined here as isotopic variations that are not understood to have been generated from a once uniform reservoir by processes acting within the solar system. They may result from incomplete homogenization of isotopically very diverse nucleosynthetic components. They potentially possess two types of information: the nature of the nucleosynthetic sources of the material, and the processes acting during their transfer from within stars to their preservation in meteorites. The definition of the

“anomalous” composition reflect the status of knowledge around 1970 and by extension has been extended to all variations which were not identified in 1970. Effects related to extinct radioactivities, are also usually referred to as “Anomalies” as well as non-linear physico-chemical effects (Thiemens 1999; Clayton 2002) which will be briefly discussed at the end of this review. Extinct radioactivities can induce isotopic variations within the solar system starting with an isotopically homogeneous reservoir. They then do not strictly correspond to the first definition. Nevertheless they enter into the extended definition and are obviously related to nucleosynthesis occurring shortly before the formation of our planetary system; it is therefore useful to include them in this chapter.

THE MEASUREMENT OF ISOTOPIC ANOMALIES

Many of the isotopic anomalies would not be accessible without the ability to measure isotopic ratios with precisions down to 20-100 ppm. This is well below the level of instrumental fractionation for traditional thermal ionization mass spectrometers. From the experimental point of view, the data are often not interpretable in a straightforward manner and an isolated set of data may lead to ambiguities. These ambiguities will be greatly reduced or eliminated if more than one isotope ratio for the element under study can be measured, an appropriate normalization scheme is used to correct for instrumental fractionation, the presence of anomalous isotopic patterns in neighboring elements, and other astrophysical considerations are also taken into account. In addition, natural linear (or Rayleigh) mass fractionation is often present in primitive meteoritic samples as a result of partial evaporation or condensation. Nevertheless, the main observations, which will be presented in the following review, can be divided in four categories.

Large isotopic variations

Isotopic variations are large enough to exceed terrestrial variations by more than about an order of magnitude. As an example, this is the case for ion probe work on the CNO isotopes of circumstellar grains (see Section “Presolar stardust grains...”). These effects can be attributed unambiguously to nucleosynthetic reactions.

Two isotope elements and small effects

For some elements the variations are commensurate with, or smaller than the instrumental reproducibility or terrestrial variations, and it is difficult to distinguish between linear fractionation due to physico-chemical effects and nuclear effects. All the interpretation depends on the connections between the variation in the different elements and the phase they are in. This is also relevant to a number of radiochronometric systems in which the decay product belongs to an element having only two isotopes (e.g. ^{107}Pd - ^{107}Ag , ^{205}Pb - ^{205}Tl). Modern ICPMS instruments are able to resolve differences much smaller than the possible natural mass dependent effects (e.g., Carlson and Hauri 2001a, b). A correlation with the parent-daughter elemental ratio usually indicates that radioactive decay has occurred. Nevertheless, this interpretation must be used with caution when the overall isotopic ratio variations in the daughter element are small. It may be possible that in some cases processes such as volatilization, producing the spread in the parent-daughter ratio, could also produce mass dependent fractionation in the daughter element, resulting in a pseudo-isochron. Cross-checking with similar mineralogical situations without radioactive decay from the parent, alleviates this problem.

Three isotope elements and small effects

Non linear variations can be smaller (a few ϵ units) than instrumental fractionation in TIMS instruments (a few ‰ per mass unit). It is then the choice of the isotopic pair used for

normalization which determines that the third isotope displays non-linear effects. ICPMS is able to measure natural fractionation with a precision close to that obtained for non-linear effects (Carlson and Hauri 2001a; Kehm et al. 2003) but, if we take the instrumental fractionation observed in TIMS instruments as the possible extent of fractionation in natural processes, ICPMS does not lift this particular ambiguity. The choice of the normalizing pair is not unambiguous and has to be sustained by interelement comparison and theoretical considerations based on nucleosynthetic models. As an example when an extinct radioactivity is examined, the variations are expected on the daughter isotope in correlation with the elemental parent daughter ratio.

Elements having 4 and more isotopes

They are used as above, but in general they lead to more straightforward interpretations. The correction for instrumental fractionation involves an isotope pair for which the measurements are in agreement with the terrestrial ratio, whether this choice results from the measurement itself or from model considerations. In cases where all the ratios are different from the terrestrial ratios, model considerations are used to interpret the data. In the most common cases, one isotope displays wider variations than the others and constitutes a guideline for modeling the origin of the anomalies.

Double spike techniques have been used occasionally to quantify the fractionation produced in natural processes, but this does not change the magnitude of non-linear effects as the natural fractionation follows closely the same laws as the instrumental fractionation. For the following, the instrumental fractionation correction is not discussed as this is described in other chapters of this volume. I suggest that the reader consult the original papers reporting the data for the details. In general the exponential law is used (Russell et al. 1978). In its outcome, it is very close to the Rayleigh law which has a better grounding in the physics of evaporation, but is simpler to use in on line ratio calculations.

Units

Units which are used in isotopic work depend on the precision of the measurements. Generally δ units are used for stable isotopes and correspond to permil relative deviation. It is used occasionally also for non linear effects and then they are permil (‰) deviations without reference to mass differences between the isotopes. Since the beginning of the 70s (e.g., Papanastassiou and Wasserburg 1969) thermal ionization data are often given in ϵ units which are fractional deviation from the normal in 0.01%. With the new generation of more precise instruments, results are sometimes given in ppm (parts per million) relative to a terrestrial standard sample.

For the following text, isotopic “anomalies” always stands for non-linear or non-mass dependent variations; “linear” or “mass dependent” have the same meaning although mass dependent fractionation may not be strictly linear (Rayleigh). Usually, in the first approach the difference is not essential for description

STELLAR EVOLUTION AND NUCLEOSYNTHESIS

Almost all of the elements heavier than He are synthesized in the interiors of stars. The work of Burbidge et al. (1957) gives the theoretical framework for the synthesis of the elements. The experimental evidence of active nucleosynthesis came from the discovery of the unstable nuclei of technetium in the spectra of red giants (Merrill 1952). The solar elemental and isotopic abundances which are taken from the primitive carbonaceous chondrites constitute the guidelines for testing such models (Anders and Grevesse 1989). A minimum of eight basic processes are required to reproduce the observed compositions. Nucleosynthetic

theory has expanded since the initial work, but this frame is essentially still valid today. It was also realized that materials expelled into the interstellar medium by stellar winds or explosions contribute to the chemical evolution of the galaxy (Timmes et al. 1995) and become part of the raw material for the next generations of stars. As a result the materials constituting the solar system are a mixture of materials from a vast number of stellar sources (see Clayton 1988) for the primary nucleosynthetic sources of the elements up to Ni). The understanding of isotopic anomalies requires some basic concepts of stellar evolution and nucleosynthesis. The purpose here is only to give a broad outline. For further details, many textbooks (Clayton 1983; Rolfs and Rodney 1988; Bernatowicz and Zinner 1997) and review articles are available if the reader is interested in more details (e.g., Woosley 1986; Woosley and Weaver 1995; Arlandini et al. 1999; Busso et al. 1999; Rauscher et al. 2002 and references therein).

The energy powering stars results from nuclear fusion reactions transforming light nuclei into heavier ones. During their different evolutionary stages, a number of different nucleosynthetic process occur in different types of stars. Stars spend most of their lives in the core H-burning phase producing helium. When H is exhausted the star evolves into a red giant where part of the core material mixes convectively with the envelope and changes the surface composition. The next step is the onset of He combustion into ^{12}C , some of which gets converted into ^{16}O . When He is exhausted the future of the star depends on its mass. In the lighter stars ($M < 8 \text{ Mo}$, where $\text{Mo} = 1$ solar mass), the core pressure and temperature are too low to proceed with further fusion reactions and becomes inert. The outer layers expand into an Asymptotic Giant Branch star (AGB) while H and He fusion continues just outside the core in thin shells producing large amounts of ^{12}C and heavy elements by slow neutron capture (s-process). Periodic convection episodes bring freshly synthesized materials to the surface. Large stellar winds expel the outer layers of the stars into a planetary nebula leaving a white dwarf star.

Massive stars

Cores of stars heavier than about 8 Mo continue to produce heavier nuclei within their cores, first the silicon mass region and ultimately the iron group nuclei. The resulting structure is an onion shell structure in which each layer has experienced more extensive fusion history than the next overlaying layer. When the core is composed mostly of iron, nuclear fusion can produce no more energy, and the structure collapses and rebounds on the core in an energetic event called supernova. The shock wave expels most of the mass of the star e.g. more than 90% for a 25 Mo star in a type II supernova (Woosley and Weaver 1995). This shock wave also heats the material in the different layers that it crosses and causes extensive nuclear reactions known as explosive nucleosynthesis. Taking together the products of hydrostatic fusion combustion and explosive nucleosynthesis, type II Supernovae are considered to be major producers of elements heavier than H in the galaxy. They are also thought to be the major site of the r- and p- nucleosynthetic processes. In the last stages of the evolution of massive stars, the core reaches very high temperature, above about $4 \times 10^9 \text{ K}$, at which point the nuclear reaction network attains a thermal equilibrium called “nuclear statistical equilibrium” (NSE) or e-process. Variants having high neutron densities of this process have also been described to account for the production of neutron-rich isotopes (Hainebach et al. 1974; Cameron 1979; Hartmann et al. 1985).

Massive stars from 25 to 100 Mo already lose a substantial fraction of their mass in strong stellar winds ranging from $2 \times 10^{-6} \text{ Mo/y}$ during the H-Burning phase up to $5 \times 10^{-5} \text{ Mo/y}$ in the He-burning phase also known as Wolf-Rayet phase. As a large convective core develops in these stars, fresh nucleosynthetic product are soon exposed on the surface and ejected with the stellar winds (Prantzos et al. 1986). Wolf-Rayet stars may have been the principal source of ^{26}Al in meteorites (Arnould et al. 2000).

The fate of stars also depends on the presence of a companion. Other violent episodes known as Novae or type Ia supernovae result from the accretion of materials from a partner star. Supernovae of type I are thought to be responsible for most of the production of the neutron-rich isotopes of the iron group (Woosley et al. 1995; Höflich et al. 1998). One of the key parameters in stellar evolution, and consequently the nucleosynthetic outcome, is the “metallicity,” defined as the proportion of elements heavier than He.

p-r-s-processes

Elements heavier than iron are not produced by the stellar fusion reactions. They are endothermic products and, to reproduce observed isotopic abundances, three production mechanisms are required (Burbidge et al. 1957). Two of them are neutron addition reactions starting with nuclei from the iron group. They are divided according to their slow (s-process) or rapid (r-process) time scale, as compared with the β decay from unstable nuclei encountered along the neutron capture path. In the s-process, the orders of magnitude of the exposure to neutrons is: neutron densities of 3×10^8 n/cm³ at temperatures close to 3×10^8 K for pulses of a few years occurring at intervals in the scale of 10^4 y. The r-process is at the origin of the elements beyond bismuth, and especially U-Th. r-process nuclei are produced in a high temperature ($>10^9$ K) stellar environment having neutron densities in the range 10^{20} - 10^{25} n/cm³ as highly unstable precursors which then return to the stability valley by β -decay (Matthews and Cowan 1990; Meyer 1994). The neutron-rich isotopes of the elements from Zn to U result at least partially, if not totally, from this process. The neutron-deficient nuclei also called the p-nuclei cannot be produced by the two former processes. They represent no more than 1% of the bulk elemental abundances. It is generally considered that radiative proton capture and (γ , n) photodisintegration on preexisting neutron-rich nuclei are playing a key role in the p-process (Rayet et al. 1990; Lambert 1992; Meyer 1994).

In considering the mass balance of the solar system, the main production of s-process nuclei is attributed to the AGB phase. For the r- and p-process the relation with a particular astrophysical site is less straightforward but most models referred in the above reviews relate them to supernova events (Matthews and Cowan 1990; Rayet 1995).

As a concluding remark of this section, the theoretical models of nucleosynthesis within stars show that the isotopic compositions of the elements are highly variable depending on star size, metallicity, companion's presence. From the isotopic data obtained in diverse solar system materials it turns out that most of this material was highly homogenized in the interstellar medium or by the formation of the solar system. The presence of isotopic anomalies preserved in some primitive materials are the last witnesses of the initial diversity of the materials constituting our planetary system.

THE ISOTOPIC HETEROGENEITY IN THE REFRACTORY COMPONENTS OF THE EARLY SOLAR-SYSTEM

The contraction of the interstellar cloud at the origin of the solar system was a strongly exothermic process and the inner solar system went through a temperature peak which caused the loss of a number of volatile elements. This episode also promoted the isotopic homogenization of the elements. The completeness of the later process depends strongly on physical factors, such as the temperature and duration, but also on the mobility of the individual elements. In addition, parent body thermal metamorphism tends to erase isotopic heterogeneities and to reset radioactive chronometers (Göpel et al. 1994). Refractory mineral phases or phase assemblages are expected to better preserve any initial isotopic heterogeneity, and have therefore been the prime focus of isotopic measurements.

Carriers of anomalies were first investigated in carbonaceous chondrites, which are

the most primitive meteorites available. For reasons that are not well understood, there is considerable variation in the size, morphology and mineralogy of refractory components between primitive meteorite families. Millimeter to several cm sized inclusions are found in the CV3 carbonaceous chondrites (Christophe 1968). Their compositions are close to those predicted for early condensates in a high temperature gaseous nebula with solar composition (Grossman 1972; Grossman and Larimer 1974). They were first to be investigated for practical reasons, such as, ease of separation.

Other meteorite classes like C2, CO and ordinary chondrites contain much smaller inclusions less than 1mm (MacPherson et al. 1988) and require ion microprobe techniques to evaluate the isotopic compositions. On the least metamorphosed side, C1 have very few inclusions or oxide grains, but are the carrier of the greatest amounts of stellar nanodiamond and other carbides (Anders and Zinner 1993). As will be shown for Cr anomalies in carbonaceous chondrites, the survival of the mineral carriers of the anomalies also depends on the metamorphic grade of the meteorites. Nevertheless, isotopic anomalies have also been found in higher metamorphic grade from other classes, especially in the reduced enstatite chondrites.

Refractory inclusions of the CV3 carbonaceous chondrites (CAIs)

The initial data on isotopic anomalies resulted from the abundant Allende meteorite, of which about 3 tons were recovered in 1969. Inclusions often found in CV3 meteorites like Allende, are straightforward to separate from the surrounding matrix with traditional mineral separations. Their sizes were within the same order of magnitude as the small lunar samples, for which a large experimental development effort had just been made (Gast et al. 1970; Tera et al. 1970). Refractory inclusions are often easily identified in hand-specimen as whitish objects in the dark matrix. They make up about 5% of the bulk mass of the meteorite. Other CV3s contain similar inclusions with some petrographic differences, but their isotopic data fit within the range of observations of Allende inclusions and will not be discussed here. The isotopic compositions for inclusions clearly divide them into two groups.

The first group called “common” or “normal” inclusions, represents the overwhelming majority of the samples. These display isotopic anomalies up to 4% in O and in the iron group elements. For the other elements investigated to date, they have normal isotopic compositions within instrumental resolution. The second group is composed of a very few inclusions showing mass fractionated light elements, much larger and variable effects in the iron group elements, and anomalies in all other elements investigated so far, especially the heavy elements Sr, Ba, Nd, Sm. They have been dubbed “FUN” inclusions for “Fractionated and Unknown Nuclear” effects. “FUN” signatures are indistinguishable from the main group on petrographic or mineralogical grounds, except for an enhanced occurrence in purple spinel-rich inclusions (Papanastassiou and Brigham 1989). They clearly show that in some cases, specific nucleosynthetic products were able to escape complete rehomogenization between their ejection from stars and their incorporation into meteorites.

Common inclusions.

Oxygen. The first isotopic measurements were for oxygen (Clayton et al. 1973). In the 3 isotope diagram (Fig. 1) all terrestrial samples plot on a mass dependent fractionation line of slope 0.52. Refractory inclusions and their minerals plot on a slope 1 line, which deviates by up to 2% from the terrestrial line for the most anomalous samples. This indicates a mixing line between an ^{16}O enriched reservoir that is distinct from the Earth-Moon with a composition of $\delta^{17}\text{O} = -42\%$ and $\delta^{18}\text{O} = -40\%$, and a terrestrial-like reservoir (Young and Russell 1998). Detailed analysis of mineral separates from a number of inclusions indicate that the most refractory minerals, like spinel and pyroxene, possess the highest ^{16}O enrichments, whereas the smallest enrichments are found in melilite and feldspathoids. This suggests that the carrier of the anomaly is a solid that underwent exchange with a nebular gas close to terrestrial