

Contents

Introduction	1
Frank Wombacher, Anne-Desirée Schmitt, Nikolaus Gussone and Alexander Heuser	
1 Introduction to Calcium Stable Isotope Geochemistry	2
1.1 Alkaline Earth Elements	2
1.2 Calcium and Its Isotopes	2
1.3 Notations in Ca Stable Isotope Geochemistry	4
1.4 History of Ca Stable Isotope Research	6
1.5 Applications of Ca Stable Isotope Geochemistry	7
1.6 Other Applications of Ca Isotopes: Cosmogenic ⁴¹ Ca and Tracer Studies	8
2 Principles of Mass-Dependent Stable Isotope Fractionation	8
2.1 Equilibrium Isotope Partitioning	8
2.2 Kinetic Stable Isotope Fractionation	12
2.3 Open System Rayleigh Fractionation and Closed System Equilibrium Fractionation	15
2.4 The Mass-Dependence of Equilibrium and Kinetic Stable Isotope Fractionations	16
2.5 Experimental Determination of Equilibrium Isotope Fractionation Factors	17
References	18
Analytical Methods	23
Alexander Heuser, Anne-Désirée Schmitt, Nikolaus Gussone and Frank Wombacher	
1 Introduction	24
2 Notations and Data Presentation	24
2.1 δ -Notation	24
2.2 Fractionation Factor (α)	26
2.3 Δ -Notation	26
2.4 ϵ_{Ca} -Notation for Radiogenic ⁴⁰ Ca Ingrowth	26
2.5 ϵ - and μ -Notations in Cosmochemistry	27
3 Reference Materials	27
3.1 Used Reference Materials	27
3.2 Conversion of δ -Values Based on Different Reference Materials	29

4	Sample Preparation	31
4.1	Digestion and Cleaning Techniques	31
4.2	Chemical Separation	35
5	Mass Spectrometry	37
5.1	Introduction to Mass Spectrometry for Ca Isotope Analysis	37
5.2	Thermal Ionization Mass Spectrometry (TIMS)	39
5.3	Multiple Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS)	43
5.4	Double Spike Approach for Stable Isotope Analysis	54
5.5	Other Instrumentation	57
5.6	Error Representation	58
	References	66
	Calcium Isotope Fractionation During Mineral Precipitation from Aqueous Solution	75
	Nikolaus Gussone and Martin Dietzel	
1	Inorganic Precipitation Experiments	75
1.1	Carbonates	76
1.2	Sulfates	83
1.3	Other (Hydrous) Phases	86
1.4	EASI Fractionation During Mineral Precipitation from Aqueous Fluids	88
2	Calcium Isotope Fractionation Models for Calcium Carbonate Formation	89
2.1	Principles and Conceptions of Isotope Fractionation Models	89
2.2	Comparison of Ca Isotope Fractionation Models and Concluding Remarks	93
3	Inorganic Mineral Precipitation in Natural Environments	95
3.1	Carbonates	95
3.2	Phosphates	102
3.3	Sulfates	102
4	Diffusion, Exchange and Adsorption of Cations in Aqueous Systems	104
	References	106
	Biominerals and Biomaterial	111
	Nikolaus Gussone and Alexander Heuser	
1	Procaryota—Microbial Induced Biomineralisation	112
2	Protista	113
2.1	Foraminifera	113
2.2	Coccolithophores	120
2.3	Calcareous Dinoflagellates	123
2.4	Coralline Algae	124

3	Metazoa	125
3.1	Sclerosponges	125
3.2	Corals	125
3.3	Molluscs	129
3.4	Brachiopods	133
3.5	Other Taxa	134
4	Applications, Ecosystems and Climate Change	135
4.1	Monitor of Trophic Levels	135
4.2	Archaeology	137
4.3	Paleoclimate	138
	References	140
	Earth-Surface Ca Isotopic Fractionations	145
	Anne-Désirée Schmitt	
1	Introduction	145
2	$\delta^{44/40}\text{Ca}$ Fractionations Related to Continental Weathering Processes	146
2.1	Range of $\delta^{44/40}\text{Ca}$ Variations in Earth-Surface Processes	146
2.2	Forested Ecosystems	149
2.3	Non-forested Ecosystems	157
3	Change in $\delta^{44/40}\text{Ca}$ Signature During Downstream Transportation into the Ocean	159
3.1	Importance of the $\delta^{44/40}\text{Ca}$ Weathering Flux to the Oceans	159
3.2	Small Scale Catchments	159
3.3	Global Scale Catchments	161
4	Potential of Ca Isotopes Applied to Earth-Surface Processes	163
4.1	Internal Ca Cycling Processes Within the Tree	163
4.2	Ca Uptake Mechanisms Within the Rhizosphere	164
4.3	Ca Recycling by the Vegetation	164
4.4	Time Integrated Vegetal Turnover Marker	165
4.5	Hydrological Tracer	165
5	Conclusion	166
	References	166
	Global Ca Cycles: Coupling of Continental and Oceanic Processes	173
	Edward T. Tipper, Anne-Désirée Schmitt and Nikolaus Gussone	
1	Introduction	173
2	Principal Ca Reservoirs at the Earth's Surface: Estimates of $\delta^{44/40}\text{Ca}$	176
2.1	Rocks	176
2.2	Hydrosphere	178
2.3	Biospheric Cycling of Ca	188
2.4	Soils	189
2.5	Atmospheric Ca in Dust and Rain Waters	196
3	Modern Global Budgets of Ca	199
3.1	The Continental Cycle of Ca	199
3.2	The Oceanic Cycle of Ca	200

4	Global Ca Cycling in Earth's History	203
4.1	Archives of $\delta^{44/40}\text{Ca}_{\text{sw}}$	204
4.2	Past Changes in $\delta^{44/40}\text{Ca}_{\text{sw}}$	208
5	Conclusions	211
	References	211
	High Temperature Geochemistry and Cosmochemistry	223
	Martin Schiller, Nikolaus Gussone and Frank Wombacher	
1	High Temperature Ca Isotope Geochemistry of Terrestrial Silicate Rocks, Minerals and Melts	223
1.1	Calcium Isotope Fractionation Between Minerals Formed at High Temperatures	223
1.2	Igneous Rocks	225
1.3	The Earth's Silicate Reservoirs and Global Tectonics	226
1.4	Diffusion in Silicate Melts	229
2	Extraterrestrial Materials	231
2.1	Scope and Framework of Ca Isotope Cosmochemistry . . .	231
2.2	Nucleosynthesis of Ca Isotopes	232
2.3	Nucleosynthetic Ca Isotope Signatures in Presolar Grains	233
2.4	Nucleosynthetic Anomalies in Meteorites and Calcium-Aluminum-Rich Inclusions (CAIs)	234
2.5	Mass-Dependent Variations in CAIs and Related Experiments	237
2.6	Mass-Dependent Variations in Meteorites	238
2.7	Lunar Samples	239
3	The ^{40}K – ^{40}Ca Decay System	239
3.1	Evolution of Earth's Reservoirs	239
3.2	Dating	241
	References	243
	Biomedical Application of Ca Stable Isotopes	247
	Alexander Heuser	
1	Introduction	247
2	Ca Isotope Transport Model	248
2.1	Ca Isotopic Composition of the Diet	248
2.2	From Food to Blood	249
2.3	Fractionation Between Soft Tissue and Mineralized Tissue	251
2.4	Fractionation in the Kidneys	253
2.5	Calcium Isotope Fractionation During Milk Lactation . . .	255
2.6	Calcium Use Index (CUI)	255
3	The Individuality of the Ca Metabolism	255
4	Current Biomedical Application of Ca Isotopes	256
4.1	Bone Loss	256
4.2	Bone Cancer	258
5	Summary and Outlook	258
	References	259