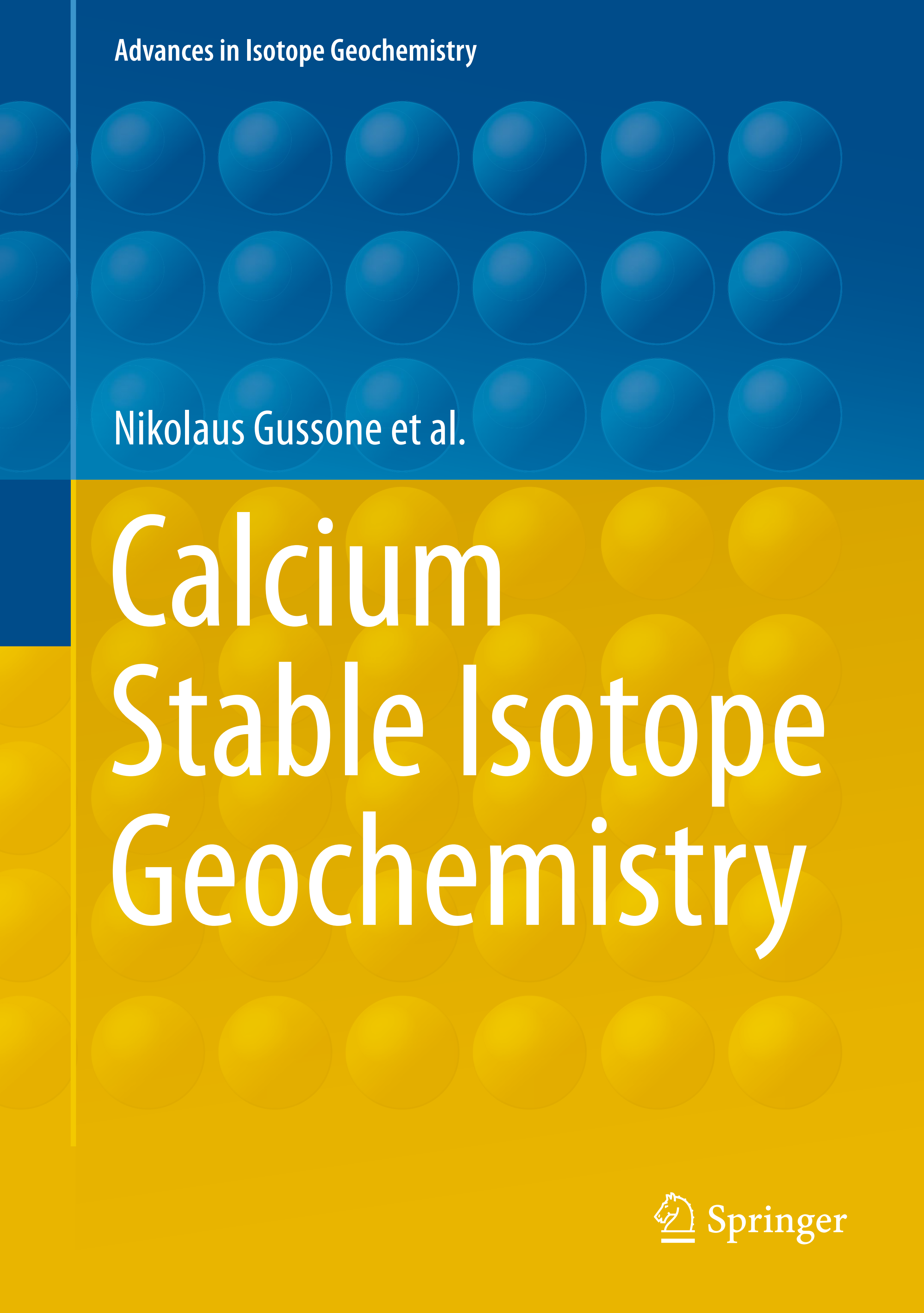

Advances in Isotope Geochemistry

Nikolaus Gussone et al.

Calcium Stable Isotope Geochemistry

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Calcium Stable Isotope Geochemistry

Springer

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Preface

First studies on variations in Ca stable isotope compositions were carried out early on (Backus et al. 1964; Hirt and Epstein 1964; Artemov et al. 1966; Miller et al. 1966; Mesheryakov and Stolbov 1967). However, reliable results were not obtained before Russel et al. (1978) published their seminal paper entitled "Ca isotope fractionation on the Earth and other solar system materials". This work facilitates the reliable and accurate determination of Ca stable isotope compositions using double spike—thermal ionisation mass spectrometry. Albeit further improvements were made, their method is still the method of choice for most Ca stable isotope analysis. Only few studies focused on Ca stable isotopes until the late 1990s, since then the number of studies dealing with Ca stable isotope fractionation is steadily increasing. This reflects both analytical advances and promising results obtained in a large variety of applications in Earth and Life sciences, including medicine.

The aim of this book is to provide an overview of fundamentals and reference values for Ca stable isotope research ("Introduction"), current analytical methodologies including detailed protocols for sample preparation and isotope analysis ("Analytical Methods") and different fields of applications including low-temperature mineral precipitation and biomineralisation ("Calcium Isotope Fractionation During Mineral Precipitation from Aqueous Solution" and "Biominerals and Biomaterial"), Earth surface processes and global Ca cycling ("Earth-surface Ca Isotopic Fractionations" and "Global Ca Cycles: Coupling of Continental and Oceanic Processes"), high-temperature processes and cosmochemistry ("High Temperature Geochemistry and Cosmochemistry") and finally human studies and biomedical applications ("Biomedical Application of Ca Stable Isotopes"). These major areas of research are introduced and their current state of the art is discussed and open questions and possible future directions are identified.

We gratefully acknowledge Florian Böhm, Vasileios Mavromatis, Jianwu Tang, Peter Stille, François Chabaux, and Barbara Teichert for discussions and their constructive comments on pre-versions of selected chapters that helped to improve the present version. AH would like to thank Petra Frings-Meuthen, Jörn Rittweger, Steve Galer, Toni Eisenhauer, Katharina Scholz-Ahrens and Jürgen Schrezenmeir for numerous discussions regarding biomedical application of Ca isotopes. FW thanks Jan Fietzke, Michael Wieser and Victoria Kremser for data and figures. Finally, we are grateful to

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Introduction

Frank Wombacher, Anne-Desirée Schmitt,
Nikolaus Gussone and Alexander Heuser

Abstract

The first part of this chapter briefly introduces the application of Ca stable isotopes in Earth sciences and other branches of natural sciences and summarizes the early history of Ca isotope research. Furthermore, tables with fundamental reference data are provided. The second part introduces the principles of equilibrium and kinetic isotope fractionation theory and discusses isotope fractionation in open and closed systems. It briefly touches on the mass-dependence of equilibrium and kinetic isotope fractionation and approaches to obtain equilibrium isotope fractionation factors experimentally. The reference at the end of this chapter provides a list of general introductions to stable isotope geochemistry and to previous reviews that focused on Ca stable isotopes.

Keywords

Calcium stable isotope geochemistry · Equilibrium isotope fractionation · Kinetic isotope fractionation · Rayleigh fractionation · Mass fractionation laws · Calcium isotope fractionation factors

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1 Introduction to Calcium Stable Isotope Geochemistry

Until the beginning of the 21th century, stable isotope effects for elements others than the traditional light elements C, O, H, N and S where little investigated mainly due to the restrictions of suitable mass spectrometers. In step with analytical advances, the application of Ca isotopes increased steadily (Fig. 1) and Ca isotopes are now applied in different areas as diverse as (bio-) mineralogy, Earth-surface processes, ecosystem science, global geochemical cycles, paleoceanography, cosmochemistry, archeology and biomedical applications. The present book is mainly focused on mass-dependent stable isotope fractionation of Ca within these subjects.

1.1 Alkaline Earth Elements

The alkaline earth metals (Table 1), group 2 in the periodic table, comprise the elements beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). In nature, they do not occur in their elemental state as soft metals. Instead, they easily lose or share their two s-valence electrons forming divalent cations in minerals and in solution. Calcium is the most abundant alkaline earth metal in the Earth's crust, while Mg is almost ten times more abundant than Ca in the bulk Earth (Table 2). Due to their high abundance and the relative large mass-difference between their isotopes, many studies focused on Ca and Mg stable isotopes. In contrast, mass dependent Sr and Ba isotope fractionations are less intensively studied, but resolvable variations were revealed (Fietzke and Eisenhauer 2006; Halicz et al. 2008; Rüggeberg et al. 2008; von Allmen et al. 2010; Krabbenhöft et al. 2010; Shalev et al. 2013; Pearce et al. 2015; Widanagamage et al. 2015). Beryllium has only one stable isotope and all Ra isotopes are radioactive, thus stable isotope fractionation cannot be readily investigated. In Earth sciences, however, cosmic ray induced ^{10}Be provides an important tracer and ^{226}Ra is of relevance in uranium-series dating.

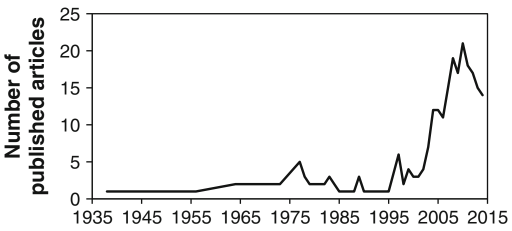

Fig. 1 Number of published articles on Ca isotopes

1.2 Calcium and Its Isotopes

Calcium has one major isotope, ^{40}Ca, with an abundance of about 97 %. Calcium-40 is a primary product of O and Si burning in massive stars. Due to its efficient production, Ca is an abundant element in the universe and the Solar System. The interest into Ca isotope studies stems in part to its high abundance in the Earth's crust and to the ubiquitous presence of minerals, in which Ca is the major cation or one of the major cations. In this regard, Ca is of particular relevance to the biomineralization of tests, shells, bones and teeth. Calcium is also one of the major dissolved components of seawater (presently ~400 ppm) and the most abundant cation in rivers (~20 ppm) (Gibbs 1972). The concentrations of Ca and other alkaline-earth elements in important terrestrial reservoirs are summarized in Table 2.

The relatively high abundance of Ca is also related to the stability of its nucleus, which contains 20 protons. The number of neutrons ranges for all stable and radioactive Ca nuclides between 15 and 38 (i.e. ^{35}Ca–^{58}Ca) (Pfennig et al. 1998), thus Ca has a total of 24 isotopes (Amos et al. 2011). The "magic number" of protons also accounts for the large number of six stable (or extremely long-lived) naturally occurring Ca isotopes (Table 3) that span a large mass range of eight atomic mass units u (or Da for Dalton) corresponding to a relative mass difference of 20 % between the heaviest and the lightest stable Ca isotope (^{48}Ca and ^{40}Ca). With the nuclides $^{40}_{20}Ca$ and $^{48}_{20}Ca$, Ca is the only element having 2

Table 1 Chemical, physical, and geochemical properties of alkaline earth metals (Lide 1995; Dean 1999)

	Be	Mg	Ca	Sr	Ba	Ra
Atomic number (Z)	4	12	20	38	56	88
Standard atomic weight (g/mol)	9.012182	24.305	40.078	87.62	137.327	226.03
Stable isotopes (nominal mass)	9, (10[a])	24, 25, 26	40[b], (41[a]), 42, 43, 44, 46, 48[a]	84, 86, 87[b], 88	130, 132, 134, 135, 136, 137, 138	(226)[a]
Maximum mass difference for stable isotopes in %	(11.1)	8.3	20	4.8	6.2	–
Electron configuration	[He]$2s^2$	[Ne]$3s^2$	[Ar]$4s^2$	[Kr]$5s^2$	[Xe]$6s^2$	[Rn]$7s^2$
Melting point (°C)	1287	650	842	777	727	700
Boiling point (°C)	2471	1090	1484	1382	1897	1737
Density of solid at 25 °C (g/cm^3)	1.848	1.736	1.55	2.63	3.51	5
Oxidation states	2+					
Electronegativity (Pauling units)	1.57	1.31	1	0.95	0.89	0.9
First ionization energy (kJ/mol)	899.5	737.7	589.8	549.5	502.9	509.3
Second ionization energy (kJ/mol)	1757.1	1450.7	1145.4	1064.2	965.2	979
Atomic radius (pm)	111	160	197	215	217	220
Ionic radius (pm):						
[4] coordination	27	57				
[6] coordination	45	72	100	118	136	
[8] coordination		89	112	126	142	148
[12] coordination			135	144	160	170
Atomic volume (cm^3/mol)	4.9	13.97	29.9	33.7	39.24	45.20
Specific heat capacity (J/mol·1/K)	16.443	24.869	25.929	26.4	28.07	27.12
Discovery date	1798	1775	1808	1790	1774	1898
Discovered by	N.L. Vauquelin	J. Black	H. Davy	A. Crawford	C. Scheele	P. & M. Curie
Date of first isolation	1828	1808	1808	1808	1808	1911
Isolated by	F. Wöhler/ A. Bussy	H. Davy	H. Davy	H. Davy	H. Davy	M. Curie

[a] Radioactive isotopes half-lifes (^{226}Ra :1601 years; ^{41}Ca: 103 kyears; ^{48}Ca: 43 × 10^{18} years; ^{10}Be: 1.387 × 10^{6} years),
[b] radiogenic isotopes (^{40}K → ^{40}Ca, see Chapter Analytical Methods; ^{87}Rb → ^{87}Sr, 48.8 Gyears)

Table 2 Abundance of Mg, Ca, Sr and Ba in different reservoirs (McDonough and Sun 1995; Lide 1995; McDonough 2001; Rudnick and Gao 2003; Palme and O'Neill 2007)

Reservoir	Mg (wt%)	Ca (wt%)	Sr (ppm)	Ba (ppm)
C I Meteorite	22.17	0.932	7.26	2.41
Bulk silicate Earth	22.8	2.53	20	6.6
Bulk Earth	15.4	1.71	13	4.5
Mantle	22.17	2.6	20	6.7
Continental crust	2.8	4.6	320	456
Average conc. in seawater	0.129	0.041	7.9	0.013
Average conc. in humans	0.027	1.4	4.6	0.3

Table 3 Abundances, masses and nuclear properties of naturally occurring calcium isotopes (Meija et al. 2016; Lide 1995)

Isotope	Atomic mass (u)	Natural abundance (atom %)	Nuclear spin (I)	Magnetic moment (μ/μ_N)	Electric quadrupole moment (b)
^{40}Ca	39.9625909 (2)	96.941 (156)	0	0	0
^{42}Ca	41.958618 (1)	0.647 (23)	0	0	0
^{43}Ca	42.958766 (2)	0.135 (10)	7/2	−1.3173	−0.05
^{44}Ca	43.955482 (2)	2.086 (110)	0	0	0
^{46}Ca	45.95369 (2)	0.004 (3)	0	0	0
^{48}Ca	47.9525228 (8)	0.187 (21)	0	0	0

doubly magic isotopes, i.e. isotopes which have a magic number of protons (20) as well as neutrons (20 and 28). Of all elements, $^{40}_{20}Ca$ is the heaviest stable isotope which has equal numbers of protons and neutrons and ^{40}Ca is also by far the most abundant Ca isotope (Table 3). The heaviest Ca isotope considered as stable (^{48}Ca) is in fact a radioisotope but with a very long half-life (43×10^{18} year). Besides the stable isotopes, Ca has a cosmogenic isotope, ^{41}Ca, which is formed by neutron capture of ^{40}Ca, mainly in the upper few meters of soils. It decays with a half-life of 103 ka to ^{41}K. Radioactive Ca isotopes that are used for medical and research purposes include the aforementioned ^{41}Ca as well as ^{45}Ca and ^{47}Ca, with half-lifes of 163 and 4.54 days, respectively (Pfennig et al. 1998).

In the solid Earth, Ca is a major element in magmatic, metamorphic and sedimentary rocks and a major constituent in minerals from very different mineral groups including carbonates, silicates, sulfates, halogenides and phosphates as well as organo-minerals (e.g. oxalates) (Table 4). Thus, Ca bearing minerals are involved in reactions that take place during weathering, ocean floor alteration, diagenesis, biomineralization, metamorphism, melting and crystallization of rocks. The weathering of Ca bearing rocks, transport of the dissolved Ca into the ocean and precipitation as $CaCO_3$ links tectonic processes to the carbon cycle and hence global climate on geological timescales (Berner et al. 1983).

Calcium plays also an important role in biology, where it is an essential part of biological tissues of animals and plants, and the most abundant cation in products of biomineralization, e.g. as calcite (e.g. foraminifera, coccolithophores, brachiopods), aragonite (e.g. corals), apatite (bones and teeth) and in leaves (Marschner 1995; Weiner and Dove 2004). Due to climate change, modern biomineralization of $CaCO_3$ is affected by ocean acidification.

Calcium is also involved in metabolic processes, like cell signaling and blood coagulation. It is an essential nutrient for plants that plays multiple roles in plant functioning, both at cellular and intracellular scales. For instance, it is important for the formation and stability of the cell walls and the functioning of the cell membranes (Marschner 1995; Taiz and Zeiger 2010).

Some of the chemical reactions involved in biological and geological processes slightly discriminate Ca isotopes depending on their masses. These fractionation patterns can be utilized to study Ca cycling on different temporal and spatial scales or may be used as proxy for different paleo-environmental parameters.

1.3 Notations in Ca Stable Isotope Geochemistry

Before we delve into Ca stable isotope geochemistry, some definitions and notations, for

Table 4 Selected Ca-bearing minerals (Rösler 1988)

Mineral class	Mineral group	Mineral	Chemical composition
Carbonates		Calcite/aragonite/vaterite	$CaCO_3$
		Dolomite	$CaMg(CO_3)_2$
		Ikaite	$CaCO_3 \cdot 6H_2O$
		Monohydrocalcite	$CaCO_3 \cdot H_2O$
		Amorphous calcium carbonate	$CaCO_3 \cdot nH_2O$
Sulphates		Gypsum	$CaSO_4 \cdot 2H_2O$
		Anhydrite	$CaSO_4$
Halogenates		Fluorite	CaF_2
Phosphates		Apatite	$Ca_5(PO_4)_3(OH, F, CO_3)$
Oxides		Perovskite	$CaTiO_3$
Silicates			
Tectosilicates	Feldspars	Anorthite	$CaAl_2Si_2O_8$
	Zeolithes	Heulandite	$(Ca,Na_2,K_2)\ [Al_2\ Si_7\ O_{18}] \cdot 6\ H_2O$
		Chabasite	$Ca\ [Al_2\ Si_4\ O_{12}] \cdot 6\ H_2O$
	Feldspathoids	Lazurite	$(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2$
Inosilicates	Pyroxenoid	Wollastonite	$Ca_2Si_2O_6$
	Pyroxenes	Augite	$(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$
		Diopsite	$MgCaSi_2O_6$
		Hedenbergite	$FeCaSi_2O_6$
		Augite	$(Ca,Na)(Fe^{3+},Mg,Fe^{2+})Si_2O_6$
	Amphibole	Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)$
		Hornblende	$Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH)_2$
		Richterite	$Na_2Ca(Mg,Fe)_5Si_8O_{22}(OH)_2$
		Pargasite	$NaCa_2Mg_3Fe^{2+}Si_6Al_3O_{22}(OH)_2$
Nesosilicates	Garnets	Andradite	$Ca_3Fe_2Si_3O_{12}$
		Grossular	$Ca_3Al_2Si_3O_{12}$
		Uvarovite	$Ca_3Cr_2Si_3O_{12}$
Nesosubsilicates		Titanite	$CaTi[SiO_5]$
Sorosilicates	Epidote	Zoisite/clinozoisite	$Ca_2Al_3(SiO_4)(Si_2O_7)O(OH)$
		Epidote	$Ca_2(Fe^{3+},Al)Al_2(SiO_4)(Si_2O_7)O(OH)$
	Vesuvianite	Vesuvianite	$Ca_{10}Mg_2Al_4(SiO_4)_5(Si_2O_7)_2(OH)_4$
Organo-minerals		Ca oxalate	CaC_2O_4
		Whewellite	$Ca(C_2O_4) \cdot H_2O$
		Weddellite	$Ca(C_2O_4)_2 \cdot 2H_2O$
		Earlandite	$Ca_3(C_6H_5O_2)_2 \cdot 4H_2O$
		Ca tartrate	$C_4H_4CaO_6$
		Ca malate	$C_4H_4CaO_5$

mass-dependent isotope fractionation effects are required. A more detailed discussion of notations for Ca stable isotope geochemistry is given in Chapter Analytical Methods.

Mass-dependent variations of Ca stable isotope ratios in samples are commonly expressed *relative* to a reference standard using the well-known δ-notation (Coplen 2011). Frequently, the ^{44}Ca/^{40}Ca isotope ratio is chosen for the calculation of δ-values:

$$\delta^{44/40}Ca = \left(\frac{(^{44}Ca/^{40}Ca)_{sample}}{(^{44}Ca/^{40}Ca)_{standard}} - 1\right) \quad (1)$$

As the variations of the Ca isotope compositions are small, δ-values are typically reported as per mill (‰), i.e. the δ-value obtained by Eq. 1 is then multiplied by 1000. Ratios of heavy over light isotopes are always chosen for the calculation of δ-values; positive δ-values thus refer to samples being enriched in the heavy isotopes relative to the reference standard, negative values denote light isotope enrichments in the sample relative to the standard. Since, Ca has six naturally occurring stable isotopes; many different δ-values can be defined. To avoid ambiguity, Hippler et al. (2003) and Eisenhauer et al. (2004) suggested to denote both, numerator and denominator isotope in the δ-notation, e.g. $\delta^{44/40}$Ca or $\delta^{44/42}$Ca rather than e.g. δ^{44}Ca.

The isotope fractionation factor (α) is defined as the ratio of two isotopes in the substance *A* divided by the same isotope ratio in substance *B*:

$$\alpha_{A-B} = \frac{R_A}{R_B} \quad (2)$$

Isotope fractionation effects are temperature dependent in most cases, therefore temperatures need to be reported along with fractionation factors. Knowledge of fractionation factors is central to the discussion of stable isotope data and much effort focusses on the accurate determination of fractionation factors. Fractionation factors can be obtained by calculations based on either spectroscopic data or ab initio modelling, from laboratory experiments and from natural samples. All three approaches have shortcomings, for example modelling may suffer from incomplete or inaccurate spectroscopic data, force field models and assumptions. Laboratory experiments allow for well-constrained run conditions such as temperature and composition, but may not achieve natural or equilibrium conditions. Fractionation factors determined from natural systems may suffer from conditions that may be less well constrained as in experiments.

The fractionation factor α is related to the δ-values of substances A and B:

$$\alpha_{A-B} = \frac{\delta_A + 1000}{\delta_B + 1000} \quad (3)$$

Note that Eq. 3 applies for δ-values given in ‰. The capital delta notation (Δ) is usually also given in ‰. It describes the offset in the isotope composition between two substances *A* and *B* as the difference between their δ-values:

$$\Delta_{A-B} = \delta_A - \delta_B \quad (4)$$

The Δ-values in ‰ can also be obtained from the fractionation factor α according to:

$$\Delta_{A-B} \approx 1000 \ln \alpha_{A-B} \approx 1000\,(\alpha_{A-B} - 1) \quad (5)$$

Note, δ-values (usually in ‰) relate the isotope composition of a sample to a (measured) reference material, while the fractionation factor α and Δ (usually in ‰) define the fractionation between two substances or compartments, for example between a calcite shell and seawater.

1.4 History of Ca Stable Isotope Research

During the 1920s and 1930s all stable Ca isotopes have been discovered. First, Dempster (1922) reported the discovery and abundances of ^{40}Ca and ^{44}Ca. Aston (1934) reported the discovery of

^{42}Ca and ^{43}Ca followed by the discovery of ^{46}Ca and ^{48}Ca by Nier (1938). A more detailed overview on the discovery of Ca isotopes (^{35}Ca–^{58}Ca) is given by Amos et al. (2011).

The first studies of Ca isotopes attributed the measured variations (with up to 40 ‰ between ^{48}Ca and ^{40}Ca) to analytical artefacts and suggested an absence of fractionation or smaller than the analytical resolution (Backus et al. 1964; Hirt and Epstein 1964; Artemov et al. 1966; Miller et al. 1966; Meshcheryakov and Stolbov 1967; Corless 1968; Letolle 1968; Stahl 1968; Stahl and Wendt 1968; Möller and Papendorff 1971; Heumann and Luecke 1973). Russell et al. (1978) where the first who published a reliable measurement protocol for calcium isotopes using a thermal ionization mass spectrometer (TIMS) and a double spike technique. The main result of their study is that the natural mass-dependent variation of Ca isotopes on Earth is minor (<1.3 ‰ per u) and that high analytical precision and accuracy is necessary to resolve natural differences in Ca isotope ratios. Since then, double-spike thermal ionization mass spectrometry remains the principle method for Ca stable isotope analysis but many improvements were made, resulting in an increasing number of publications from about 2000 onwards (Fig. 1). In addition, precise Ca stable isotope data has also been obtained by MC-ICP-MS (multi collector inductively coupled plasma mass spectrometry) instruments (Halicz et al. 1999) and ion probes (Rollion-Bard et al. 2007). A detailed discussion of these methods is provided in Chapter Analytical Methods.

1.5 Applications of Ca Stable Isotope Geochemistry

The applications of Ca isotopes are ubiquitous and steadily increasing (see Fig. 1). In this book we present the current state of knowledge about this isotope system.

This chapter introduces the fundamental concepts needed for the application of stable isotopes and reports reference data for Ca stable isotope research. Current analytical methodologies are reviewed in Chapter Analytical Methods, including a detailed discussion of sample preparation and isotope analysis.

The two introductory chapters are followed by chapters that identify and discuss six major areas of research and their current state of the art. Open questions and possible future directions are then identified.

Chapter Calcium Isotope Fractionation During Mineral Precipitation from Aqueous Solution focusses on Ca isotope fractionation related to mineral precipitation and diffusion in aqueous solutions in natural and experimental conditions from an inorganic perspective, which sets the stage for the subsequent Chapter Biominerals and Biomaterial, which is devoted to Ca stable isotope studies that comprise a range of products from biomineralization to studies of ecosystems, paleoclimate and archeology. Both chapters include a discussion on stable isotope fractionation of alkaline earth elements other than Ca for comparison.

Topics in Chapters Earth-surface Ca Isotopic Fractionations and Global Ca Cycles: Coupling of Continental and Oceanic Processes comprise Earth surface processes and global cycling. Chapter Earth-surface Ca Isotopic Fractionations focusses on biotic and abiotic processes that lead to Ca isotopic fractionations in the weathering environment. Chapter Global Ca Cycles: Coupling of Continental and Oceanic Processes describes present-day continental and oceanic budgets as well as past oceanic budget and the causes of its variation through the Phanerozoic.

Chapter High Temperature Geochemistry and Cosmochemistry focusses at stable isotope fractionations related to high-temperature processes in the Earth and on cosmochemical applications of stable Ca isotopes including nucleosynthetic effects. Furthermore, radiogenic ^{40}Ca excesses from ^{40}K decay are briefly summarized. This is also relevant for the interpretation of mass dependent Ca isotope effects as potential complications could arise from the use of isotope ratios involving ^{40}Ca.

Finally in Chapter Biomedical Application of Ca Stable Isotopes, this new and emerging field of application for (Ca) stable isotopes, are presented and discussed.

1.6 Other Applications of Ca Isotopes: Cosmogenic ^{41}Ca and Tracer Studies

Other applications of Ca isotopes exist, they are however not further considered in the present book. These aspects include tracer techniques in medical, earth and life sciences using long and short lived radio-isotopes.

For instance, in medicine, "dual-tracer experiments" have been developed in order to estimate the Ca absorption rate in human gastro-intestinal tract (e.g. Beck et al. 2003; Barger-Lux et al. 1989; López-Huertas et al. 2006). A ^{48}Ca was used to study biomineralization in foraminifers (Lea et al. 1995). In forest studies a ^{42}Ca tracer has been injected under pressure in trees or spread over the ground in order to follow its uptake, its storage in the tree, its return to the soil (litter, leaves) and its fate and behavior after decomposition (Zeller et al. 1998, 2000; Caner et al. 2004; Augusto et al. 2011; van der Heijden et al. 2013).

Short-lived radionuclides of Ca (e.g. ^{45}Ca, ^{47}Ca) were used for instance to study biomineralization of corals and foraminifers (Anderson and Faber 1984), while long-lived radionuclides (^{41}Ca) were used as tracer for medical applications (e.g. Denk et al. 2007; Walczyk et al. 2010; Sharma et al. 2011) and as a proxy for nuclear bomb fallouts (Zerle et al. 1997).

2 Principles of Mass-Dependent Stable Isotope Fractionation

Mass-dependent stable isotope fractionation typically results from isotope exchange reactions under thermodynamic equilibrium or from kinetic processes. Mass-independent isotope fractionation effects as observed for O, S and Hg isotopes were so far not observed for Ca isotopes and are rather unlikely to be of relevance. Nucleosynthetic Ca isotope anomalies, however, are present in some early solar system materials (Chapter High Temperature Geochemistry and Cosmochemistry).

Equilibrium isotope partitioning arises from the change of vibrational frequencies in molecules and condensed phases upon substitution by isotopes of different mass. Equilibrium isotope fractionation is temperature sensitive and becomes negligible at high temperature, which may be at several hundred or larger than 1000 K depending on the magnitude of fractionation and analytical precision.

Kinetic isotope fractionation refers to chemical or physical processes with no or only partial back reaction, i.e. bond breaking chemical reactions or physical transport processes like diffusion or evaporation. Kinetic isotope fractionation due to bond breaking reactions is temperature sensitive too. It results from the effect of isotopic substitution on activation energies required to reach a transition state. Kinetic isotope fractionations accompanying diffusion and evaporation/condensation are due to the differential translational velocities of isotopes or isotopically substituted molecules (isotopologues) of different mass. This class of kinetic transport phenomena can lead to large isotope fractionations even at high temperatures.

The role of kinetic and equilibrium processes in driving Ca stable isotope fractionation is often debated and therefore demands consideration in this introductory text. However, isotope fractionation theory will be simplified and only briefly touched and the reader is referred to other sources (see reference section).

2.1 Equilibrium Isotope Partitioning

2.1.1 Isotope Exchange Reactions

Equilibrium isotope fractionation refers to the partial separation of isotopes between two or more substances in chemical or more precisely in isotopic equilibrium (Urey 1947; Bigeleisen and

Mayer 1947). It is a quantum-mechanical phenomenon driven mainly by differences in the vibrational energies of molecules and crystals containing isotopes of different masses. These differences lead to higher concentrations of the heavy isotopes in substances, in which the vibrational energy is most sensitive to isotope substitution, i.e. those with higher bond force constants (see discussion further below).

For an isotope exchange reaction between two components A and B, where * denotes the component enriched in the heavy isotope and a and b refer to the coefficients to balance the reaction, the general expression is:

$$\mathrm{aA+bB^{*}\Leftrightarrow aA^{*}+bB} \tag{6}$$

Note that both sides of the isotope exchange equation give the same chemical species and differ only in the distribution of isotopes. The following equation provides an example where all coefficients (a and b) are unity:

$$^{40}\mathrm{CaCO_3} + {}^{44}\mathrm{Ca^{2+}} \Leftrightarrow {}^{44}\mathrm{CaCO_3} + {}^{40}\mathrm{Ca^{2+}} \tag{7}$$

For the general case, the isotope exchange constant K is equal to:

$$K_{eq} = \frac{(A^{*})^{a}(B)^{b}}{(A)^{a}(B^{*})^{b}} = \frac{(A^{*}/A)^{a}}{(B^{*}/B)^{b}} \tag{8}$$

Concentrations rather than activities are commonly used in Eq. 8, as the difference between activities and concentrations is commonly negligible for isotopically substituted substances. If the isotopes are randomly distributed among all possible sites of the molecule at equilibrium, the fractionation factor α is connected to the equilibrium constant K_{eq} for the isotope exchange (Bigeleisen 1965):

$$\alpha_{\mathrm{A-B}} = K_{eq}^{\frac{1}{ab}} \tag{9}$$

where the product of the stoichiometry coefficients a and b gives the number of atoms exchanged during the reaction. Thus, if isotope exchange reactions are written such that only one atom is exchanged (ab = 1), the equilibrium constant K_{eq} is identical to the fractionation factor α_{A-B} as is the case for the above example (Eq. 7):

$$K_{eq} = \frac{\left(\frac{^{44}Ca}{^{40}Ca}\right)_{CaCO_3}}{\left(\frac{^{44}Ca}{^{40}Ca}\right)_{Ca^{2+}}} = \alpha_{CaCO_3-Ca^{2+}} \tag{10}$$

2.1.2 Equilibrium Isotope Fractionation Theory

In the following, we will briefly examine the basics of isotope fractionation theory. For more in-depth treatments, the readers are referred to Criss (1999), Schauble (2004) and citations therein including the classical papers by Urey (1947) and Bigeleisen and Mayer (1947). For isotope exchange reactions, an equilibrium constant can be determined from the free energy difference between reactants and products according to:

$$\Delta \mathrm{G}^{0} = -\mathrm{RT}\ \ln\left(\mathrm{K_{eq}}\right) \tag{11}$$

where ΔG^0 is the Gibbs free energy of the reaction, R is the molar gas constant ($\sim 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$) and T the absolute temperature in K. The Gibbs free energy is several orders of magnitude smaller for isotope exchange reactions than for chemical reactions. Pressure volume work is commonly neglected, since isotopic substitution has a negligible effect on volume and because the number of molecules on both sides of the isotope exchange reactions is the same. Thus the Gibbs free energy ΔG^0 can be replaced by the Helmholtz free energy ΔF. Then rearranging Eq. 11 yields:

$$\ln\left(\mathrm{K_{eq}}\right) = -\left(\frac{\Delta F_{motion}}{RT}\right) \tag{12}$$

The bond structure and thus potential energy of each molecule is not changed by the isotopic substitution. Only the dynamic energy associated with atomic motions changed (therefore $\Delta F_{\mathrm{motion}}$). The dynamic energy includes translational, rotational and vibrational energies (Schauble 2004). Among these, only vibrational energies are significantly large (at about ≥100 K) relative to ambient thermal temperatures to drive chemical reactions (Schauble 2004). It is instructive to first consider the simple case of harmonic oscillations of a diatomic molecule like H_2 or O_2, where the vibrational energy is given by:

$$E_{vib} = (n + 1/2)h\nu \tag{13}$$

with h being Planck's constant (6.626×10^{-34} Js), ν the vibrational frequency and n the vibrational energy level (with n = 0, 1, 2, etc.). With increasing temperature, higher energy levels are more frequently populated. However, with n = 0, atoms vibrate even at absolute zero with $E_{vib,0} = ½\ h\nu$. This property is known as the zero point energy. Since the vibrational frequencies are a function of the atomic masses in motion, vibrational frequencies are affected by isotopic substitution. In the example for the harmonic oscillation of a diatomic molecule, vibrational frequencies relate to the atomic masses m_i and m_j according to:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k_s}{\mu}} = \frac{1}{2\pi}\sqrt{k_s\left(\frac{1}{m_i} + \frac{1}{m_j}\right)} \tag{14}$$

where k_s is the spring or force constant in N/m, which is a measure of bond stiffness, and

$$\mu = m_i * m_j/(m_i + m_j) \tag{15}$$

is the reduced mass of the molecule. The harmonic oscillation of a diatomic molecule is often envisioned as two spheres (atoms) that are connected by a spring and move towards and away from each other with the frequency ν. Isotopic substitution changes the mass of the bond partner, but not the force constant k_s. Thus, substitution with a heavier isotope leads to slightly lower frequencies (Eq. 14) and hence lower vibrational energies. Therefore, substances with high force constants k_s and thus stiffer bonds will have larger zero-point energy shifts upon heavy isotopic substitution and will therefore tend to be enriched in the heavy isotopes. (Vibrational) frequencies are commonly measured and tabulated as wavenumbers (ω in cm^{-1}), where ν = c*ω and c refers to the speed of light. Vibrational frequencies range from ca. 100 up to about 4000 cm^{-1}, which corresponds to force constants of ∼50–2000 N/m (Schauble 2004).

While zero point energy shifts are regarded as the principle driver of equilibrium isotope fractionations, an accurate treatment of molecular motions requires the higher energy states to be included. The probability of a molecule to have a distinct energy state follows the Boltzmann distribution law and this is expressed in the partition function ratio Q, which gives the sum of all possible quantum states i:

$$Q = \sum g_i e^{-E_i/kT} \tag{16}$$

where e refers to the exponential function, k is Boltzmann's constant (1.381×10^{23} J/K), T is the temperature (in K) and g is the degeneracy factor that is sometimes given to refer to quantum states with the same energy level.

For the case of harmonic vibrations, Eq. 13 is inserted into Eq. 16. Doing so and following the approach of Urey (1947), Schauble (2004) derived an expression where the fractionation factor $\beta_{XR\text{-}X}$ between a diatomic or larger molecule and a monatomic gas can be estimated from data for vibrational frequencies of heavy and light isotopologues only:

$$\beta_{XR-X} = \left[\prod_i \frac{\nu^*}{\nu} \times \left(\frac{exp\left[-\frac{h\nu^*}{2kT}\right]}{1 - exp\left[-\frac{h\nu^*}{kT}\right]}\right) \times \left(\frac{1 - exp\left[-\frac{h\nu}{kT}\right]}{exp\left[-\frac{h\nu}{2kT}\right]}\right)\right]^{\frac{1}{n}} \tag{17}$$

Molecule XR contains n atoms of the element of interest X, and N total atoms. The frequencies ν and ν* refer to molecule XR containing the light and heavy isotopes, respectively. Diatomic molecules have one vibration, but for polyatomic linear or nonlinear molecules the product is over 3N-5 or 3N-6 vibrational frequencies, respectively. While isotope fractionation relative to a monatomic gas is not of practical significance, the fractionation factor α between two different molecules A and B is simply $\alpha_{A-B} = \beta_A/\beta_B$. Because the rotational and translational terms cancel, β is often referred to as the reduced partition function ratio. Schauble (2004) points out, that, in order to simplify the calculations, this approach assumes harmonic vibrations, rigid-body rotation, a simplified treatment of rotational energies and averaged intra-molecular isotope fractionations. Nevertheless, he concludes that these assumptions are reasonable for elements other than H, C, N, O, and S and temperatures above about 100 K.

Calcium isotope geochemistry rarely deals with gas-phase molecules, but is commonly concerned with condensed phases such as aqueous solutions or crystals. Crystals however contain far more vibrational frequencies that cannot be explicitly treated and dissolved ions or molecules interact with the surrounding water molecules.

Since vibrational frequencies in crystals appear like a continuous spectrum, Kieffer (1982) calculated reduced partition function ratios using an integral:

$$\beta_{crystal-X} = \left(\frac{m}{m^*}\right)^{\frac{3}{2}} \times \exp\left[\frac{1}{n}\frac{\int_0^{v_{max}} ln\left(\frac{\exp\left[-\frac{h\omega}{2kT}\right]}{1-\exp\left[-\frac{h\omega}{kT}\right]}\right) g^*(\omega)d\omega}{\int_0^{v_{max}} ln\left(\frac{\exp\left[-\frac{h\omega}{2kT}\right]}{1-\exp\left[-\frac{h\omega}{kT}\right]}\right) g(\omega)d\omega}\right] \tag{18}$$

The above equation, taken from Schauble (2004), gives the fractionation factor β for element X in a crystal relative to that of the monatomic gas, where g and g* are the continuous vibrational densities of state for crystals containing the light and the heavy isotope of the element of interest. The highest vibrational frequency of the crystal is represented by v_{max}.

Equilibrium stable isotope fractionation factors can thus be calculated from vibrational frequencies. The necessary input data may be obtained from spectroscopic measurements. However, spectroscopic data, where available, are commonly incomplete and only available for phases of natural isotope composition. This requires additional estimates to be made to obtain vibrational frequencies for isotopically substituted phases (except for diatomic molecules with $\nu^* = \nu(\mu/\mu^*)^{-0.5}$; cf. Eq. 14). If no, imprecise or incomplete vibrational data are available, missing vibrational frequencies need to be modelled, either by force field modelling or by ab initio quantum mechanical calculations (Schauble 2004, 2009).

2.1.3 Summary of General Characteristics of Equilibrium Isotope Fractionation

Following O'Neil (1986) and Schauble (2004) some general rules regarding equilibrium stable isotope fractionation are summarized:

Temperature-dependence

Equilibrium isotope fractionations decrease with temperature (Urey 1947; Bigeleisen and Mayer 1947), usually as $1/T^2$. Over a small temperature interval, the decrease in the isotope fractionation in per mill per K can be estimated as $-2000(\alpha - 1)/T$ (Schauble 2009). At low temperature or for high frequency vibrations where almost all molecules are in the vibrational ground-state, temperature dependence more closely approaches 1/T (Criss 1999; Schauble 2004). At higher temperatures, high energy vibrational levels are more frequently populated. Since the energy difference upon isotopic substitution becomes smaller at higher vibrational energy levels, equilibrium isotope fractionation decreases with increasing temperature.

Mass-dependence

Equilibrium isotope fractionation increases with the mass-difference between the heavy and light isotope, but decreases with the absolute mass according to $(m_{heavy} - m_{light})/m_{heavy}*m_{light}$. This mass term decreases e.g. from 0.0238 for $^{7/6}$Li, 0.0069 for $^{18/16}$O, 0.0032 for $^{26/24}$Mg, 0.0023 for $^{44/40}$Ca to 0.0003 for $^{88/86}$Sr. This indicates that in terms of *mass only*, the isotope fractionation between ^{44}Ca and ^{40}Ca should be about a third of that observed for oxygen and significantly larger than for heavier elements like Sr.

Dependence on bond-stiffness

As shown in Eq. 14, heavy isotopes will tend to be enriched in the phase with the highest force constants, i.e. the stiffest bonds. Bond stiffness is generally larger for short strong bonds, i.e. at high oxidation states, high covalent character of the bond and low coordination numbers. Schauble (2004) cautions that it is presently not clear which chemical properties are most important in regard to bond stiffness especially in regard to "new" isotope systems.

The extent of isotope fractionations will increase if large differences in bond stiffness exist between the phases involved. Calcium isotopes generally do not display fractionations in excess of one or at best a few per mill. This is in accord with the restricted variation in bond environments compared to e.g. O or S, the ubiquitous presence of Ca in the 2+ oxidation state and with the ionic character of bonds involving Ca. This leaves coordination as one of the main driver of equilibrium Ca stable isotope fractionations (Schauble 2004; Gussone 2005).

2.2 Kinetic Stable Isotope Fractionation

Kinetic stable isotope fractionations arise either from (i) chemical bond-breaking dissociation reactions, including most biochemical transformations or (ii) physical transport phenomena, i.e. evaporation, condensation and diffusion though solid, liquid or gaseous media (e.g. Schauble 2004; Richter et al. 2009; Eiler et al. 2014).

If equilibrium between two (or more) components is attained, forward and back reaction rates are equal. In kinetics, the reaction products become isolated from the reactants. Often, kinetic reactions are defined as unidirectional. However, kinetic effects are involved in *disequilibrium* or *non-equilibrium* isotope fractionations where the forward reaction overrides the back reaction:

$$\text{reactant(s)} \underset{R_b}{\overset{R_f}{\rightleftharpoons}} \text{product(s)} \tag{19}$$

Here, R_f, R_b and R_{net} denote the forward, back and net reaction rates with $R_{net} = R_f - R_b$.

Effective disequilibrium fractionation factors α_{eff} will be intermediate between those describing equilibrium isotope fractionation (α_{eq}) or unidirectional kinetic forward reaction (α_f). This is illustrated in Eq. 20 (DePaolo 2011) and Fig. 2:

$$\alpha_{eff} = \frac{\alpha_f}{1 + \frac{R_b}{R_f}\left(\frac{\alpha_f}{\alpha_{eq}} - 1\right)} = \frac{\alpha_f}{1 + \frac{R_b}{R_{net} + R_b}\left(\frac{\alpha_f}{\alpha_{eq}} - 1\right)} = \frac{\alpha_f}{1 + \left(\frac{\alpha_f}{\alpha_{eq}} - 1\right)\Big/\left(\frac{R_{net}}{R_b} + 1\right)} \tag{20}$$

Equilibrium isotope fractionation dominates were R_b/R_f approaches 1 and R_{net}/R_b is very small. If R_b is only a minor fraction of R_f such that the $R_{net} \gg R_b$, kinetic isotope fractionation dominates α_{eff}. For R_{net}/R_b increasing from ~0.01 to ~100, α_{eff} changes from values near α_{eq} towards α_f (Fig. 2).

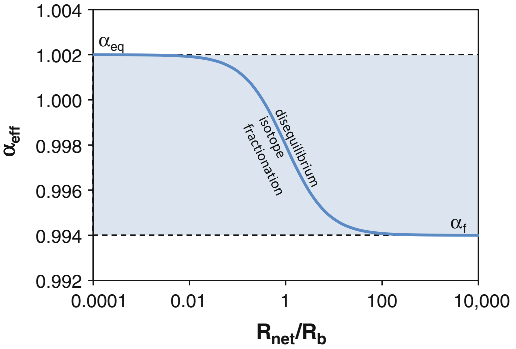

Fig. 2 Dependence of α_{eff} on the ratio of net reaction rate to the back reaction rate as given in Eq. 20. Arbitrary values have been assumed for α_{Eq} (1.002) and α_f (0.994) Redrawn after DePaolo (2011)

DePaolo (2011) derived Eq. 20 to describe Ca isotope fractionation associated with the precipitation of calcite from aqueous solutions at variable precipitation rates. The above description assumes steady state conditions, i.e. no change in the isotope composition of the crystal surface layer or liquid reservoirs with time and furthermore, the absence of transport effects (diffusion) within the crystal or the liquid. Diffusive transport could limit the delivery of ions to the growing crystals surface at high precipitation rates. Such a transport-control could also result in additional kinetic isotope effects. Isotope fractionation associated with transport phenomena and reservoir effects are discussed further below.

Dissociation

The theory of kinetic isotope fractionation associated with the dissociation of molecules has been discussed previously by Bigeleisen (1949), Bigeleisen and Wolfsberg (1958) and Melander (1960). This type of fractionation is due to differences in the reaction rates between isotopes or molecules of different masses (isotopologues). In by far most cases, the lighter isotopes or isotopologues react faster than the heavier ones and thus become concentrated in the product of the reaction. If the reaction pool is limited (e.g. a closed system), the reactant becomes correspondingly enriched in the heavier isotope. There are rare cases of inverse kinetic isotope effects with the reactant being enriched in the heavy isotope that most commonly occur when hydrogen atoms are involved (Bigeleisen and Wolfsberg 1958). Kinetic isotope fractionation can be described with first-order kinetics.

For two competing isotope reactions:

$$A_1 \rightarrow B_1(k_1) \text{ and } A_2 \rightarrow B_2(k_2) \qquad (21)$$

with k_i $(i = 1, 2)$ corresponding to the rate constants for the reaction and 1 and 2 referring to the light and heavy isotope, respectively. The fractionation factor α corresponds to the ratio of the rate constants:

$$\alpha_{A-B} = k_1/k_2 \qquad (22)$$

Physical transport processes: evaporation, condensation, diffusion

In gases, the average translational kinetic energy E_{kin} is the same for all molecules or atoms:

$$E_{kin} = \frac{3}{2}kT = \frac{1}{2}mv^2 \qquad (23)$$

where k is the Boltzmann constant, m the mass of the molecules or atoms in motion and v is the average velocity. If a gas consists of different isotopes or isotopologues of masses m_1 and m_2 with the same average kinetic energy, the velocity will be slower for heavier isotopes or isotopologues compared to lighter ones, as evident from:

$$E_{kin} = \frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2 \qquad (24)$$

this can be rearranged into:

$$\alpha_f = \frac{v_1}{v_2} = \left(\frac{m_2}{m_1}\right)^{0.5} \qquad (25)$$

where α_f is the corresponding kinetic fractionation factor. Equation 25 is often referred to as Graham's law; it shows that kinetic transport effects are not expected to be temperature sensitive. Graham's law is frequently used to predict the fractionation factor for free evaporation into vacuum. However, in experiments, free evaporation commonly yields fractionation factors smaller than those predicted by the square root of the mass dependence aka Grahams law (Richter et al. 2007, 2009). This observation can be accounted for by the introduction of evaporation coefficients γ (e.g. Richter et al. 2007; Zhang et al. 2014):

$$\alpha_{eff} = \frac{\gamma_1}{\gamma_2}\left(\frac{m_2}{m_1}\right)^{0.5}\alpha_{eq} \qquad (26)$$

the ratio of evaporation coefficients γ_1/γ_2 then accounts for different probabilities of two isotopes or isotopologues to leave the surface of the condensed phase. Equation 26 also contains the equilibrium isotope fractionation factor α_{eq}. At the high temperatures for evaporation or condensation of Ca $\alpha_{eq} = 1$ can be assumed.

Equation 26 is also expected to be valid for condensation. In this case γ refers to sticking (or condensation) coefficients that give the fraction of atoms or molecules that do not return to the vapor phase after impinging onto the surface of the condensed phase.

Evaporation provides probably the most classical example for kinetic isotope separation. Because Ca is a highly refractory element, Ca isotope fractionation due to evaporation (and condensation) is mostly restricted to calcium-aluminum-rich inclusions (CAIs) in meteorites (Chapter High Temperature Geochemistry and Cosmochemistry). A first thorough experimental investigation of Ca isotope fractionation during evaporation has been carried out recently (Zhang et al. 2014; see also Sect. 2.4 and Chapter High Temperature Geochemistry and Cosmochemistry).

For diffusion in gases or liquids, the isotope fractionation factor α_{diff} equals the ratio of diffusivities, which again is inversely related to mass M_i by a power law, with the exponent $\beta \le 0.5$ (e.g. Richter et al. 2006; Bourg et al. 2010; see also Eiler et al. (2014) and citations therein):

$$\alpha_{\text{diff}} = \frac{D_1}{D_2} = \left(\frac{M_2}{M_1}\right)^{\beta} \tag{27}$$

For diffusion of a trace gas through a carrier gas, β may be equal to 0.5 and M_i refers to the reduced mass (Eq. 15 with m_i = mass of trace isotope or isotopologue and m_j = average mass of carrier gas molecules) if both gases interact only by instantaneous binary collisions as suggested for Ca diffusion in H_2, considered relevant in cosmochemistry (Simon and DePaolo 2010).

The above power law (Eq. 27) is also consistent with data for diffusion in liquids, i.e. silicate melts and water (e.g. Bourg et al. 2010). Mass M_i may refer to reduced masses, but more commonly isotopic masses are used. For diffusion in liquids, the exponent β is much lower than 0.5, ranging from 0 to 0.22 (e.g. Richter et al. 2009; Bourg et al. 2010). This reflects chemical interactions with the solvent, but also the use of isotopic masses rather than molecular or reduced masses, as the latter is difficult to assign in the presence of chemical interactions. The mass-dependence of the ratio of diffusivities reflected in the empirical parameter β is thus intermediate between kinetic theory ($\beta = 0.5$) and predictions due to hydrodynamic transport ($\beta = 0$), where the solute is strongly coupled to solvent hydrodynamic modes (Bourg et al. 2010). This is in line with the observation that β-values are inversely related to the residence times of water molecules in the first solvation shells of the diffusing ions (Bourg and Sposito 2007).

Watkins et al. (2011) showed that isotope fractionation related to chemical diffusion in silicate melts, is related to the liquid structure. They observed that isotope separation increases with the ratio of mobility of the cation relative to that of the liquid matrix (e.g. D_{Ca}/D_{Si}), as the cation is not strongly bound to and hence diffusing through the alumosilicate framework.

Thermal gradients imposed on silicate melts lead to concentration gradients with enrichments of CaO, MgO and FeO on the cold end and SiO_2, K_2O and Na_2O on the hot end (Bowen 1921; Lesher and Walker 1986). This thermal (or Soret) diffusion is balanced by chemical diffusion such that a steady state is approached. Soret diffusion can lead to large stable isotope fractionations (Kyser et al. 1998) and experiments have shown that heavy Ca isotopes get enriched at the cold end (Richter et al. 2009; Huang et al. 2010). One fundamental difference for isotope and chemical fractionation due to Soret and chemical diffusion is that with time chemical diffusion homogenizes the melt, while Soret diffusion approaches a steady-state (e.g. Richter et al. 2009). Dominguez et al. (2011) explained Soret diffusion as a quantum mechanical effect, while Lacks et al. (2012) favor a classical mechanical collision effect. The analysis by Li and Liu (2015) support the classical approach for high temperatures.

See other chapters, in particular Chapters Calcium Isotope Fractionation During Mineral Precipitation from Aqueous Solution and High Temperature Geochemistry and Cosmochemistry for further discussion of kinetic isotope fractionation related to dissociation, evaporation/condensation and diffusion.

2.3 Open System Rayleigh Fractionation and Closed System Equilibrium Fractionation

Rayleigh distillation (or fractionation) occurs when isotopically fractionated reaction products are continuously removed or isolated from the system. The Rayleigh equation (Eq. 28) describes the evolution of the isotope composition of the remaining reservoir R_A as a function of the fraction *f* of the reactant A that is remaining (Rayleigh 1902; Broecker and Oversby 1971):

$$R_A = R_{A,i} * f^{\alpha_{B-A}-1} \tag{28}$$

where $R_{A,i}$ refers to the initial isotope ratio and α_{B-A} to the fractionation factor between product B and reactant A. The isotope composition of the instantaneous forming product B_{inst} is simply offset from R_A according to the fractionation factor, thus

$$R_{B,inst} = \alpha_{B-A} * R_{A,i} * f^{\alpha_{B-A}-1} \tag{29}$$

The isotope composition of the accumulated product $R_{B,accum}$ is dictated by mass balance ($R_{A,i} = f * R_A + (1-f) * R_{B,accum}$). Rearranged and combined with Eq. 28 this gives:

$$R_{B,accum} = \frac{R_{A,i}(f^{\alpha_{B-A}} - 1)}{f - 1} \tag{30}$$

The evolution of R_A, $R_{B,inst}$ and $R_{B,accum}$ with progressive transformation of A to B is given in Fig. 3 in the Δ-notation (e.g. $\Delta_{B-A} = 1000 \times (R_B/R_{A,i} - 1)$) as a function of the fraction of the product $(1-f)$ and arbitrarily assuming $\alpha_{B-A} = 0.997$; i.e. that the product is 3 ‰ lighter than the instantaneous reservoir from which it becomes isolated. Figure 3 reflects the typical characteristics of Rayleigh fractionation: if the reaction proceeds to near completion, the isotope composition of the remaining reservoir becomes extremely fractionated (here enriched in the heavy isotopes). The same trend is observed for the instantaneously formed product as it is obviously only offset from the contemporaneous isotope composition of the reactant reservoir A (Eq. 29), with the offset defined by the fractionation factor. The accumulated product will eventually attain the initial isotope composition of the reactant as required by mass balance.

Rayleigh fractionation may describe equilibrium, disequilibrium and kinetic fractionations, but requires that the reaction product is continuously isolated and the fractionation factor does not change in the process. For example, Rayleigh evaporation of a water droplet into a dry atmosphere will enrich the remaining droplet progressively in heavy H and O isotopes as kinetic (or disequilibrium) evaporation proceeds. Equilibrium O and H Rayleigh fractionation may occur if water droplets condense in the atmosphere in equilibrium with the surrounding water

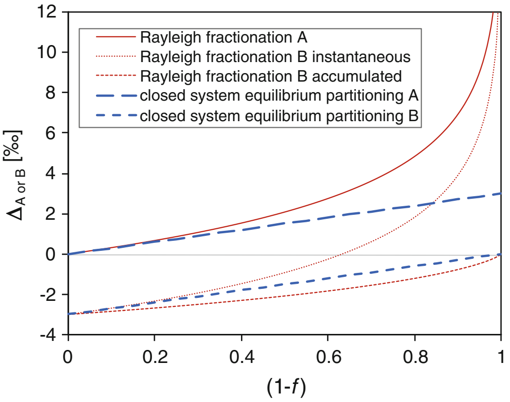

Fig. 3 Isotope ratio evolution for open system Rayleigh fractionation (*red curves*) and closed system equilibrium fractionation (*blue straight lines*) as a function of the elemental fraction in phase B. Given are deviations from $R_{A,i}$ or R_{SYS} as e.g. $\Delta_{B-A} = 1000 * (R_B/R_{A,i} - 1)$ in ‰, assuming $\alpha_{B-A} = 0.997$ in all calculations

vapor. Once big enough, the droplets will rain out, leaving the remaining atmospheric water vapor reservoir progressively enriched in the lighter isotopes. Calcium isotope fractionation during the precipitation of minerals from a restricted liquid reservoir may serve as another example for Rayleigh fractionation.

Figure 3 also shows the isotope evolution during closed-system equilibrium isotope fractionation which relies on mass balance equations. The two pools denoted A and B remain in equilibrium throughout and thus the reactant and product always differ by the same offset $\Delta_{B-A} = 1000 \times (\alpha - 1)$. As above, mass balance requires

$$R_{SYS} = f * R_{A,eq} + (1 - f) * R_{B,eq} \tag{31}$$

where R_{SYS} refers to the isotope ratio of the bulk system and $R_{A,eq}$ and $R_{B,eq}$ to the isotope composition of both pools, depending on the fraction f of the element in A. Because $\alpha_{B-A} = R_B/R_A$, R_B can be replaced by $\alpha_{B-A} * R_A$ and inserted into Eq. 31:

$$R_{A,eq} = \frac{R_{SYS}}{(f + \alpha(1 - f))} \tag{32}$$

See Schmitt et al. (2013) for an example for equilibrium Ca isotope fractionation during adsorption on bean roots.

2.4 The Mass-Dependence of Equilibrium and Kinetic Stable Isotope Fractionations

The mass-difference is double for ^{44}Ca/^{40}Ca compared to ^{42}Ca/^{40}Ca. Thus the mass-dependent stable isotope fractionation recorded in the former ratio is about twice as large as that of the latter one. However, the exact relationship between two isotope ratios depends on the fractionation mechanism (e.g. Young et al. 2002). The mass-dependence can be described by mass fractionation laws of the form

$$\alpha_{a/b} = \alpha_{c/d}^{\beta} \tag{33}$$

where a, b, c, and d refer to the mass numbers of isotopes of element E, $\alpha_{a/b}$ refers to the fractionation factor between two phases for isotope ratio ^{a}E/^{b}E, and $\alpha_{c/d}$ refers to the same fractionation factor for isotope ratio ^{c}E/^{d}E. In most cases b and d are identical as usually the same isotope is used as the denominator in both ratios. The exponent β defines the slope in linearized three isotope plots and is a function of the masses m_i of the isotopes involved (Young et al. 2002). For a heavy element like Ca (compared to oxygen; see Cao and Liu 2011), the slope β for equilibrium isotope exchange should be very close to:

$$\beta_{eq} = \frac{\left(\frac{1}{m_b} - \frac{1}{m_a}\right)}{\left(\frac{1}{m_d} - \frac{1}{m_c}\right)} \tag{34}$$

for kinetic isotope separation

$$\beta_{kin} = \frac{\ln\left(\frac{M_b}{M_a}\right)}{\ln\left(\frac{M_d}{M_c}\right)} \tag{35}$$

where mass M_i either refers to the mass of isotopes, isotopologues or reduced masses, depending on the kinetic process. In three isotope plots where the conventional δ-notation is used, fractionation lines according to β are slightly curved. This can be circumvented if the δ′-notation of Hulston and Thode (1965) is applied (Young et al. 2002), e.g.:

$$\delta' = 1000 * \ln\left(\frac{(^{44}Ca/^{40}Ca)_{sample}}{(^{44}Ca/^{40}Ca)_{standard}}\right) \tag{36}$$

Differences between kinetic and equilibrium fractionation lines are difficult to spot in three isotope plots (see Chapter Analytical Methods, Fig. 8) in particular if the stable isotope fractionation is small. The visual representation can be improved by using a format such as in Fig. 4 (cf. Young and Galy 2004), where the deviation of the data from the equilibrium