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and Patrick Degryse

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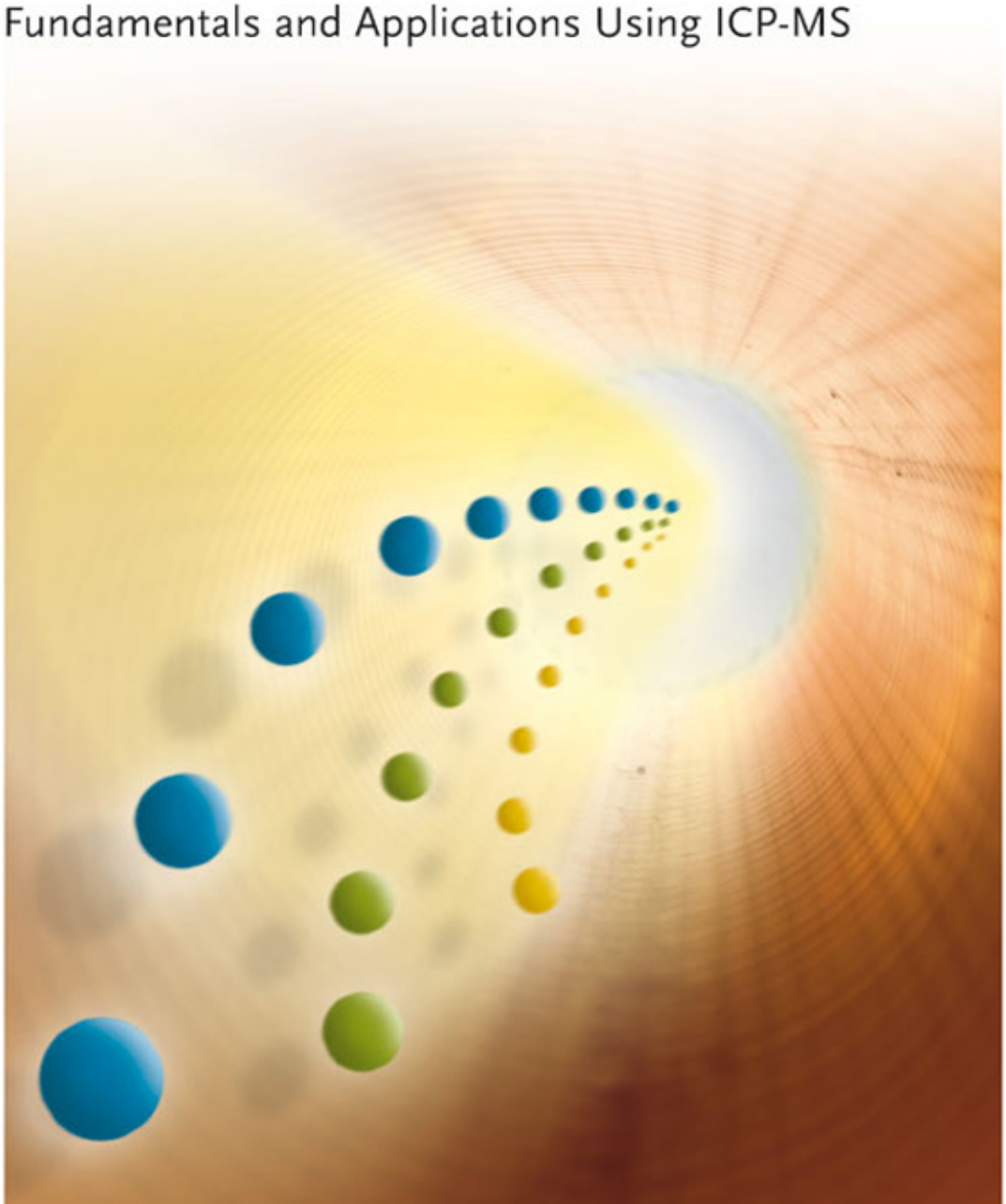
Isotopic Analysis

Fundamentals and Applications Using ICP-MS



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Preface

Although several instrumental techniques allow information on the isotopic composition of target elements to be obtained, mass spectrometry is without doubt the most versatile and most powerful.

For isotopic analysis of metals and metalloids, thermal ionization mass spectrometry (TIMS) has been the "gold standard" for a long time. Although also serving other purposes, such as accurate and precise determination of element concentrations in the context of the production of reference materials and characterization of materials from the nuclear industry, TIMS was predominantly deployed in the domain of geo- and cosmochemistry. The introduction of single-collector inductively coupled plasma mass spectrometry (ICP-MS) in 1983 and, especially, of multi-collector (MC) ICP-MS about a decade later, however, had a tremendous impact on the field of "isotopic analysis." The much higher ionization efficiency of the inductively coupled plasma (ICP) ion source, the enhanced sample throughput, and the flexibility in terms of sample introduction are the reasons most quoted to explain the current success of MC-ICP-MS. In effect, MC-ICP-MS is gradually replacing/has gradually replaced TIMS as the "gold standard" for isotopic analysis by now.

ICP-MS was not immediately introduced as a tool for isotopic analysis, but as a very powerful technique for (ultra-)trace element determination, combining the multi-element capabilities of inductively coupled plasma optical emission spectrometry (ICP-OES) with an even higher detection power than atomic absorption spectrometry (AAS). As a result, the user community of ICP-MS was different from that of TIMS, although also here the geochemical community has often been working at the forefront of development, especially in the domains of isotopic analysis and of direct bulk and spatially resolved analysis by using laser ablation (LA) as a means of sample introduction. However, by using ICP-MS instead of spectrometric techniques such as AAS or ICP-OES that have only marginal capabilities for isotopic analysis, also scientists from other fields learned to appreciate the additional capabilities offered by the isotope-specific information that a mass spectrometric technique provides. In fact, all ICP-MS users rely on isotopic information, for example, for identifying element patterns in the mass spectrum and for revealing and correcting for spectral interferences via mathematical equations. A new community of users discovered the merits of isotope dilution as

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a calibration approach, not only as a means for obtaining the highest accuracy and precision, but also for compensating for analyte losses during sample pretreatment and element speciation procedures, and more "adventurous" uses of isotope dilution were explored. Given the diversity of the ICP-MS community, it came as no surprise that the technique was also increasingly used for tracer experiments with stable isotopes aiming at obtaining a more profound insight into various physical processes and (bio)chemical reactions in the context of both fundamental physicochemical studies, for example, concerning reaction rates, and applied research, for example, in environmental and biomedical studies. The user community also started to use ICP-MS for determining isotope ratios that show variation in Nature as a result of the presence of one (e.g., Sr) or more (e.g., Pb) radiogenic isotopes although, as a result of the rather modest precision of single-collector ICP-MS, only the less demanding cases could be tackled in this way.

The gap in isotope ratio precision existing between TIMS and single-collector ICP-MS was bridged by the introduction of MC-ICP-MS, in which the noisy character of the ICP ion source is counteracted by simultaneous monitoring of the ion beams involved, a practice that was already established earlier in TIMS. The user community of MC-ICP-MS nowadays seems to consist of two groups: researchers from the geo- and cosmochemical domain have added MC-ICP-MS to their instrumentation and/or replaced (part of their) TIMS instruments by MC-ICP-MS devices, while single-collector ICP-MS users looking for an improved isotope ratio precision are also keen MC-ICP-MS users.

The introduction of MC-ICP-MS has not only facilitated the work otherwise done using TIMS, it also allows the study of elements that were previously not or barely accessible using TIMS. The most prominent example is Hg, the volatility of which precludes the use of TIMS. Furthermore, the introduction of MC-ICP-MS has revolutionized the field as its use contributed strongly to the current awareness that the isotopic composition not only shows variations as a result of isotope fractionation for the lighter elements, but actually varies for all of them, even for U, the heaviest naturally occurring element.

As the community of MC-ICP-MS users is more diverse than that of TIMS was/is for the reasons outlined above, there seemed to be a demand for a book on isotopic analysis via single- and multi-collector ICP-MS with a wider scope, one that addresses not only applications from the domains of geo- and cosmochemistry (but certainly also without denying the pioneering role that researchers in this research field have played and are still playing), but also from other areas, such as archeometry, forensics, and biomedical studies. The Editors were invited to realize such a book, a task that could only be completed with contributions from prominent scientists from diverse fields. It was the intention to provide a book that is accessible to the interested newcomer to the field, while also supplying the more experienced user with some new insights. To achieve this goal, both the very basics and also advanced topics are addressed, as detailed below.

Chapter 1 especially aims at providing newcomers to the field with general information on the origin of natural variations in the isotopic composition of metals and metalloids.

Chapters 2 and 3 present an overview of single- and multi-collector ICP-MS instrumentation and their respective capabilities. Also appropriate ways to overcome spectral overlap are addressed. As the ICP is a robust ion source operated at atmospheric pressure, there are various means of sample introduction. Although pneumatic nebulization of sample solution is the standard approach, LA of solid material avoids the need for digestion in bulk analysis, and also allows spatially resolved information to be obtained. Recent advances in LA are discussed in Chapter 4, in which the fundamental technical challenges associated with the handling of transient signals are also considered.

Although MC-ICP-MS permits isotope ratios to be measured with very high precision (down to 0.002% RSD), it needs to be realized that the raw data show a substantially larger bias (1% per mass unit order of magnitude at mid-mass) with respect to the corresponding true value. This bias is caused by preferential transmission of the heavier isotope during the extraction process, and obviously this instrumental mass discrimination needs to be corrected for. The methods used for this purpose are discussed into detail in Chapter 5.

Chapters 6 and 7 focus on the "quality" of isotope ratio measurement data by concentrating on isotopic reference materials (and the current shortage thereof) and on the total uncertainty accompanying all measurement data.

Chapter 8 provides the reader with the basic principles of isotope dilution mass spectrometry used for elemental analysis and also discusses more advanced features of this calibration approach, such as its use in direct solid sample analysis and in elemental speciation work, wherein not the total amount but that of various chemical species of a target element need to be determined.

Chapter 9 presents an accessible overview of methods for geochronological dating and illustrates the capabilities and limitations of MC-ICP-MS in this context with real-life applications reported in the literature.

Chapters 10–12 put geo- and cosmochemical applications in the spotlight. Chapter 10 clarifies the origin of cosmochemical isotopic variations and explains how these variations can be exploited for advancing insight into the universe and our solar system with its planetary bodies. Chapters 11 and 12 bring the reader back to Earth. Chapter 11 addresses paleoproxies in more detail, but instead of providing an overview of all the contexts in which it is attempted to reconstruct paleoconditions (e.g., pH, temperature, redox potential, salinity) prevailing during a physicochemical process in the past by investigating an isotopic signature systematically affected by the above-mentioned conditions, this chapter focuses on paleoredox proxies only and discusses into detail all factors that jeopardize a correct interpretation in this context. Chapter 12 then provides a more general description of how isotopes can be used as tracers of elements across the geosphere–biosphere interface.

Chapters 13 and 14 illustrate how the isotopic composition of selected target elements may be interpreted as a fingerprint, providing information on the provenance of materials and objects of relevance in an archeometric or forensic context.

In Chapter 15, nuclear applications are described and it is clarified in which contexts ICP-MS is superior to radiometric techniques that have to rely on the actual decay of the radionuclides present in the sample for data collection.

Isotopic analysis using ICP-MS can also advance our insight into the human metabolism, as illustrated extensively in Chapter 16. Various concepts in tracer studies with stable isotopes are delineated and case studies are reviewed on an element-by-element basis. Also, emerging applications based on natural variations in the isotopic composition of mineral elements are considered.

Finally, in Chapter 17, the relatively recent use of MC-ICP-MS in elemental speciation work – realized by coupling a chromatographic separation technique to an MC-ICP-MS device as an isotope-specific detector – is discussed. Also, the consequences of the transient nature of the signals thus obtained on the data collection are considered.

Considerable work both from the Editors and from the other contributors went into the making of this volume. We hope that these efforts have resulted in a book that is considered "useful" by our colleagues working in or interested in working in the still rapidly evolving and fascinating field of isotopic analysis using single- and multi-collector ICP-MS.

Ghent and Leuven, March 2012

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1
The Isotopic Composition of the Elements

Frank Vanhaecke and Kurt Kyser

1.1
Atomic Structure

Early in the twentieth century, Rutherford realized that Thomson's late nineteenth century plain cake model for the atom, describing the atom as consisting of electrons floating around in a positive sphere, had to be replaced by a "Saturnian" model, describing the atom as consisting of a small central nucleus surrounded by electrons, rotating on rings [1]. This view was supported by a study of the behavior of a beam of α particles (see below, particles resembling the nucleus of an He atom, thus consisting of two protons and two neutrons) directed on to a very thin Au metal foil, known as the Geiger–Marsden experiment [2]. Since only a minor fraction of the α-particles were recoiled or deflected, and for the majority the path was not affected, it had to be concluded that for the largest part, an atom consists of empty space. According to Bohr's later model [3], the atom contains a nucleus composed of positively charged protons and neutral neutrons, having approximately the same mass. This nucleus is a factor of $\sim 10^4$ smaller than the size of the atom (although the concept of size itself is not self-evident in this context) and holds practically all of its mass. As they both reside in the nucleus, protons and neutrons are also referred to by the common term nucleon. The negatively charged electrons are substantially lighter (almost 2000 times) and rotate around the central nucleus in different orbits (also termed shells), corresponding to different energy levels. Subsequently, insight into the atomic structure has evolved tremendously and a multitude of other particles have been discovered, but for many chemical considerations – including a discussion of isotopes – the Bohr model still largely suffices.

As all protons carry the positive unit charge (1.602×10^{-19} C), they mutually repel one another. This electrostatic repulsion is overcome by the so-called nuclear force [4]. This is a very strong force, but effective only within a very short range. In fact, the very short range over which this force is effective even causes the largest nuclei (e.g., those of U) to be unstable (see below). Further clarification of the nature of this nuclear force requires a more thorough discussion of the atomic

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structure, including a discussion on quarks, but this is beyond the scope of this chapter. Electrostatic attraction between the positive nucleus and the orbiting negative electrons provides the centripetal force required to keep the electrons from drifting away from the nucleus.

1.2 Isotopes

The chemical behavior of an atom is governed by its valence electrons (electron cloud) and, therefore, atoms that differ from one another only in their number of neutrons in the nucleus display the same chemical behavior (although this statement will be refined later). Such atoms are called isotopes and are denoted by the same chemical symbol. The term isotopes refers to the fact that different nuclides occupy the same position in the periodic table of the elements and was introduced by Todd and Soddy in the early twentieth century [5].

To distinguish between the isotopes of an element, the mass number A – corresponding to the sum of the number of protons and the number of neutrons (the number of nucleons) in the nucleus – is noted as a superscript preceding the element symbol: ${}^{A}\mathrm{X}$. The atomic number Z, corresponding to the number of protons in the nucleus, may be added as a subscript preceding the element symbol $-{}^{A}_{Z}\mathrm{X}$ – but is often omitted as this information is already inherent in the element symbol.

As a result of their difference in mass, isotopes of an element can be separated from one another using mass spectrometry (MS), provided that they are converted into ions. In fact, this is exactly how isotopes were discovered: Thomson separated the ion beams of two Ne isotopes using a magnetic field, while their detection was accomplished with a photographic plate [6]. With a similar setup, typically referred to as a mass spectrograph, Aston was subsequently able to demonstrate the existence of isotopes for a suite of elements [7].

Although several techniques provide a different response for the isotopes of an element, for example, infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and neutron activation analysis (NAA), MS is the technique of choice for the majority of isotope ratio applications. The isotopic composition of the light elements H, C, N, O, and S is typically studied via gas source MS, and for ${}^{14}\mathrm{C}$ dating, accelerator mass spectrometry (AMS) is replacing radiometric techniques to an increasing extent. For isotopic analysis of metals and metalloids, thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS) are the methods of choice. This book is devoted to the use of (single-collector and multi-collector) ICP-MS in this context and its basic operating principles, capabilities, and limitations are discussed in Chapters 2 and 3.

The relative abundance of one nuclide of the element M (${}^{1}\mathrm{M}$) is calculated as the amount (number of atoms N or number of moles n) of nuclide ${}^{1}\mathrm{M}$ divided by the total amount (number of atoms or number of moles) of the element M:

$$\theta(^1\mathrm{M}) = \frac{N(^1\mathrm{M})}{\sum_{i=1}^{i=m} N(^i\mathrm{M})} = \frac{n(^1\mathrm{M})}{\sum_{i=1}^{i=m} n(^i\mathrm{M})}$$

for an element with m isotopes.

1.3
Relation Between Atomic Structure and Natural Abundance of Elements and Isotopes

Except for the lightest atoms, the binding energy per nucleon is remarkably stable (varying only from 7.6 to 8.8 MeV) for the naturally occurring elements (Figure 1.1). On the basis of this curve, it is understood that fission of a heavy nucleus

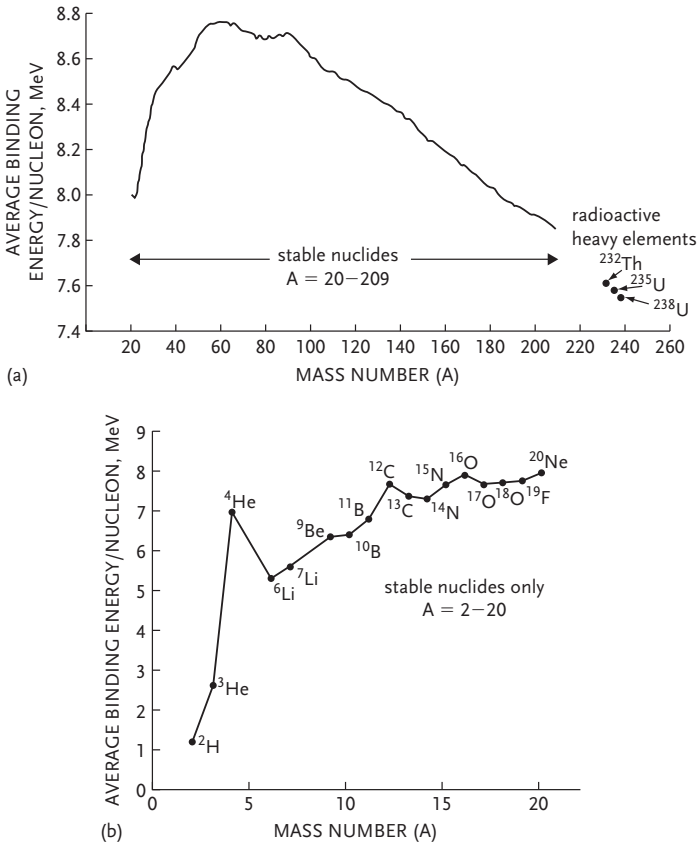

Figure 1.1 (a) Average binding energy per nucleon as a function of mass number for nuclides with a mass number from 20 to 238. (b) Average binding energy per nucleon as a function of mass number for nuclides with a mass number from 1 to 20. Reproduced with permission of John Wiley & Sons, Ltd., from [8].

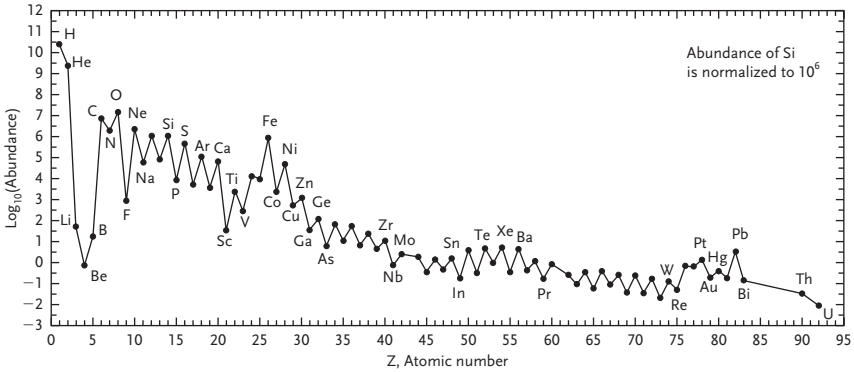

Figure 1.2 Natural relative abundance of the elements as a function of their atomic number. Reproduced with permission of John Wiley & Sons, Ltd., from [9]. The graph is based on the data published by Lodders [10].

into lighter nuclei (e.g., in a nuclear reactor) or fusion of two H atoms into He (the basis of solar energy) are exo-energetic because the process results in nuclei/a nucleus characterized by a substantially higher binding energy per nucleon.

With the lighter atoms (see Figure 1.1b), nuclei with an even number of protons and an even number of protons show a higher binding energy per nucleon and thus higher stability (compare, e.g., the binding energies for ^{4}He and ^{3}He, ^{12}C and ^{13}C, and ^{16}O and ^{17}O). In addition, elements with an even number of protons, reflected by an even atomic number Z, are more abundant in Nature than those with an uneven number (Figure 1.2).

This variation in binding energy per nucleon also exerts a pronounced effect on the isotopic composition of the elements, especially for the light elements. "Even–even isotopes" for elements such as C and O (^{12}C and ^{16}O) are much more abundant than their counterparts with an uneven number of neutrons (^{13}C and ^{17}O). Despite the *overall* limited variation in binding energy per nucleon as a function of the mass number for the heavier elements, its variation among isotopes of an element may vary substantially, leading to a preferred occurrence of even–even isotopes, as illustrated by the corresponding relative isotopic abundances for elements such as Cd and Sn (Table 1.1). In both the lower (^{106}Cd through ^{110}Cd) and the higher (^{114}Cd through ^{116}Cd) mass ranges, only Cd isotopes with an even mass number occur. In addition, the natural relative isotopic abundances for ^{113}Cd and, to a lesser extent, ^{111}Cd are low in comparison with those of the neighboring Cd isotopes with an even mass number. Similarly, Sn, for which 7 out of its 10 isotopes are characterized by an even mass number, the isotopes with an odd mass number have a lower natural relative abundance than their neighbors.

Table 1.1 Isotopic composition of Cd and Sn according to Böhlke *et al*. [11].

Element	Atomic number *Z*	Isotopes and natural relative abundances (mol%)	
Cd	48	^{106}Cd	1.25
		^{108}Cd	0.89
		^{110}Cd	12.49
		^{111}Cd	12.80
		^{112}Cd	24.13
		^{113}Cd	12.22
		^{114}Cd	28.73
		^{116}Cd	7.49
Sn	50	^{112}Sn	0.97
		^{114}Sn	0.66
		^{115}Sn	0.34
		^{116}Sn	14.54
		^{117}Sn	7.68
		^{118}Sn	24.22
		^{119}Sn	8.59
		^{120}Sn	32.58
		^{122}Sn	4.63
		^{124}Sn	5.79

1.4 Natural Isotopic Composition of the Elements

As a first approximation, it can be stated that all elements have an isotopic composition that is invariant in Nature. This is the result of thorough mixing of most nuclides prior to the formation of the solar system some 4.6 billion years ago [12]. Addition of a stable isotopic tracer to a natural system induces a change in the isotopic composition of a target element. The use of isotope dilution for elemental assay (Chapter 8) and tracer experiments for monitoring a physical or a (bio)chemical process (Chapter 16) are based on measuring the induced changes in the isotopic composition of a target element thus obtained, as discussed in later chapters.

There are, however, various reasons why elements may show variations in their natural isotopic composition:

- **Radiogenic nuclides:** Some elements have one or several radiogenic nuclides, meaning that over time, such a nuclide is being produced as a result of the decay of a naturally occurring and long-lived radionuclide. The additional production of such a radiogenic nuclide has a pronounced effect on the temporal isotopic composition of the element with (the) radiogenic nuclide(s)

and – as a result of the way in which isotopic abundances are defined – also affects the relative isotopic abundances of the other isotopes.

- **Extraterrestrial materials:** In some extraterrestrial material such as meteorites, elements may show isotopic compositions that are distinct from all terrestrial material investigated. This is related to decay of radionuclides that may already be extinct, due to half-lives which are very short compared with the age of the solar system of 4.6×10^9 years. Such variations are rare for terrestrial materials, in large part due to preferential sampling of the crust, whereas some extraterrestrial material, such as iron meteorites, resemble the Earth's core, in which parent to daughter element ratios may be much higher than in the crust.
- **Interaction between cosmic rays and terrestrial matter:** The Earth's atmosphere and, to a lesser extent, its surface are constantly bombarded with cosmic radiation which interacts with terrestrial material, resulting in isotopic variations in some elements. The best known example is the production of ^{14}C from ^{14}N by (n,p) reaction in the atmosphere, with the neutron involved created by cosmic ray-induced spallation. ^{14}C, a radionuclide with a half-life of 5730 years, is oxidized to CO_2 and enters the food chain via photosynthesis, thus affecting the isotopic composition of C in all living organisms.
- **Mass-dependent isotope fractionation:** The original theory that isotopes of an element are chemically identical has to be refined. As a result of their slight difference in mass, the isotopes of an element tend to participate in physical processes and (bio)chemical reactions with slightly different efficiencies. These differences in efficiency are related to a slight difference in equilibrium for each different isotopic molecule (thermodynamic effect) or in the rate with which the isotopes participate in a process or reaction (kinetic effect). This phenomenon is referred to as isotope fractionation and is well characterized for the lighter elements H, C, N, O, and S, the isotopic composition of which is typically studied via gas source isotope ratio MS. Especially the light elements that are redox sensitive show substantial variations in their isotopic composition, because different oxidation states correspond to substantially different bonding environments. In general, the extent of isotope fractionation is governed by the extent to which an element takes part in physical processes, such as diffusion, or chemical reactions wherein there is a change in bonding environment, and the relative difference in mass between the isotopes. Among the metals and metalloids, Li and B show significant natural isotopic variations as a result of isotope fractionation because of the large relative difference in mass of their isotopes. For the heavier elements – for which the isotopes show a much smaller relative mass difference – conventional wisdom held that there was minimal isotope fractionation, but the enhanced capabilities offered by state-of-art MS have demonstrated that all elements are prone to isotope fractionation, even an element as heavy as U [13].
- **Mass-independent fractionation:** Most cases of isotope fractionation are characterized by a linear relationship between the magnitude of the effect established and the difference in mass between the isotopes considered. For an increasing number of elements, however, an apparently aberrant behavior is established for some of their isotopes. This is currently a hot topic of research