Preface

Advances in experimental and theoretical isotope geochemistry

1. Introduction

This special issue is partly built on and around the special session V09: ‘Frontiers in isotope fractionation in geomaterials: theory and experiments’ organized at the AGU Fall Meeting 2007. Since then, similar sessions are commonly organized at EUG and AGU meetings illustrating the increasing interest of the different scientific communities involved in this domain.

This special issue and the related conference sessions arrive as recent advances in mass spectrometry allow the study of a wider range of isotopic systems on ever smaller samples with increasing accuracy. These technical improvements lead to new isotopic insights into the Earth and the Solar system. But they also rely on physico-chemical processes, the effect of which was not considered to affect isotopes ratios at a discernable level until recently. In this respect, contributions of high temperature processes, diffusion, ionic speciation, and mass-independent isotope fractionation cannot be neglected any longer. Because smaller samples can be analyzed with remarkable accuracy, it is also now possible to experimentally study isotopic fractionation at extreme conditions, such as at high pressure or in mineral nanocrystals or in biological and aqueous systems. In addition, improvements in empirical and ab initio atomistic modeling allow us to decipher subtle effects of mass differences on the dynamic and thermodynamic properties of solid and fluid materials.

This special issue aims to illustrate the renewal of theoretical and experimental approaches of isotope geochemistry induced by the tremendous analytical advances seen recently. This issue as summarized below gathers a wide range of contributions related to the study of isotopes in geomaterials from an experimental, analytical and theoretical viewpoint.

2. Summary of this special issue

In the first contribution of this issue, Watson and Müller (2009-this issue) explore the diffusion-driven isotopes fractionation produced during the fast growth of crystals in different geological settings (igneous and metamorphic). Their model demonstrates that during fast growth, a significant fractionation can be observed between crystals and the growth medium and that this fractionation can be recorded by the radial concentration profiles. They finally suggest that compositional core to rim profiles of a crystal may be a proxy for the near surface composition of the growth medium during crystal growth.

Moynier et al. (2009-this issue) investigate the isotopic fractionation and transport mechanisms of Zn in plants. By investigating different plant components, they found significant Zn isotopic fractionation during both diffusive processes and cross-cell membrane transport. This study also shows a clear interspecies variability for Zn isotopic fractionation and prompts for further study to elucidate biological controls on metal stable isotope fractionation.

The vivid field of iron isotopes geochemistry is then explored experimentally by Kavner et al. (2009-this issue). They focus here on electron-transfer related Fe isotopes fractionation and more specifically, they examine the effect of mass transport on isotope fractionation during electroplating of iron. They show that mass transport to the electrode tends to attenuate the fractionations associated with processes at the electrode.

Mass-independent isotope fractionations are addressed from an experimental point of view by Fujii et al. (2009-this issue). In their comprehensive review they discuss origins of mass-independent isotope effects from both theoretical and experimental point of view. This contribution will certainly help non-specialist to understand the so-called nuclear field shift effect introduced by Bigeleisen (1996).

In a companion paper, Fuji et al. (2009b-this issue) present new Cd-isotope data showing nuclear field shift effect in the isotope exchange reaction of cadmium using a liquid–liquid extraction technique with a crown ether, dicyclohexano-18-crown-6. When the isotope enrichment factors were calculated, the odd atomic mass isotopes \((^{111}\text{Cd} \text{ and } ^{113}\text{Cd})\) showed excesses of enrichment comparing to the even atomic mass isotopes \((^{110}\text{Cd}, ^{112}\text{Cd}, ^{114}\text{Cd} \text{ and } ^{116}\text{Cd})\). This odd–even staggering property has been interpreted as originating from the nuclear field shift effect, which may present an alternative origin of certain Cd isotopic anomalies observed in nature.

The discovery of sulfur mass-independent fractionation (S-MIF) in Archean sediments (Farquhar et al., 2000) has up to now motivated new work on atmospheric sulfur chemistry. Here, Lyons (2009-this issue) presents a critical review of the evidence of the SO\(_2\) photolysis origin for S-MIF and claims that SO\(_2\) photoexcitation, near-UV CS\(_2\) photolysis, OCS photolysis, non-statistical sulfur allotrope reactions, and surface reactions during thermochemical sulfate reduction (Lasaga et al., 2007) are unlikely sources of Archean S-MIF. Finally, he presents a schematic illustration of how S-MIF-containing elemental sulfur aerosol is incorporated into sulfides and sulfates in marine sediments, and demonstrates how a mixture of pyrite derived from photochemically produced elemental sulfur and bacterial sulfate reduction derived pyrite can explain the reduced range of \(\delta^{34}\text{S}\) values compared to that of SO\(_2\)-self-shielding.

Early iron isotope studies concluded that all igneous rocks had homogeneous iron isotopic composition. However, improvements in precision have revealed significant fractionation that could be used to understand the conditions of melting and differentiation in terrestrial planets. Very high precisions have recently been claimed for iron isotopic analyses by HR-MC-ICPMS but these uncertainties may not encompass all sources of error. Dauphas et al. (2009-this issue) present a detailed protocol, from sample digestion to data reduction, to measure the isotopic composition of iron with precisions of \(\pm 0.03\perthousand\) for \(\delta^{56}\text{Fe}\). They provide ample evidence to demonstrate that the measurements are accurate within the quoted error bars. These analytical developments have found a recent application at Kilauea Iki lava lake, where measurable iron isotopic variations have been
documented in this textbook example of magmatic differentiation (Teng et al., 2008).

Finally, we also would like to mention two other companion contributions published in other issues of Chemical Geology. In the first one, Reynard and Caracas (2009) evaluate the hydrogen/deuterium isotope fractionation between brucite and water from both vibrational spectroscopy and ab initio modeling. They show that progress in the modeling of anharmonic effects, especially at geologically-relevant temperatures, is required in order to be able to predict isotopes fractionation by a purely ab initio method. The authors show that the level of accuracy of these calculations for low frequency is enough to predict the partition functions in minerals having a complexity of lattice vibrations that obscures isotopic effects such as serpentines. In the second one, Asael et al. (2009) report the controls of low temperature copper isotopes fractionation by fluid speciations. They show that copper isotopes can be used as tracers of redox conditions in various hydrothermal ore deposits.

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References


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