



SELENIUM

**GLOBAL PERSPECTIVES OF IMPACTS ON
HUMANS, ANIMALS AND THE ENVIRONMENT**

硒：对人、动物和环境影响的全球展望

Gary S. Bañuelos

Z.-Q. Lin

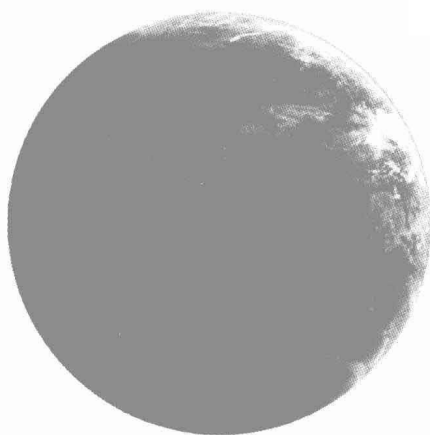
尹雪斌

段 宁

主编

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Edited by Gary S. Bañuelos, Z.-Q. Lin, Xuebin Yin and Ning Duan

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Published by University of Science and Technology of China Press

96 Jinzhai Road, Hefei 230026, P.R. China

图书在版编目 (CIP) 数据

硒: 对人、动物和环境影响的全球展望 = Selenium: Global Perspectives of Impacts on Humans, Animals and the Environment: 英文/(美)巴纽艾洛斯(G. S. Bañuelos), (美)林治庆(Z.-Q. Lin), 尹雪斌, 段宁主编. —合肥: 中国科学技术大学出版社, 2011.10

ISBN 978-7-312-02929-5

I. 硒… II. ①巴… ②林… ③尹… ④段… III. 硒—国际学术会议—文集—英文
IV. O613.52-53

中国版本图书馆 CIP 数据核字 (2011) 第 200519 号

出版 中国科学技术大学出版社
安徽省合肥市金寨路 96 号, 邮编: 230026
<http://www.press.ustc.edu.cn>
印刷 安徽省瑞隆印务有限公司
发行 中国科学技术大学出版社
经销 全国新华书店
开本 880mm×1230mm 1/16
印张 8.5
字数 230 千
版次 2011 年 10 月第 1 版
印次 2011 年 10 月第 1 次印刷
定价 28.00 元

Preface

Health problems associated with soil selenium (Se) deficiency and its low efficient uptake by plants have become major human and animal nutritional issues in many countries. In particular, the urgent need to improve the bioavailability of Se in soil and recognize the importance of increasing plant Se accumulation are conjunctly influential in preserving and improving food and feed quality, and ultimately human nutrition. The connection between the environment, agriculture and human health must be established if we are to develop sustainable solutions to Se deficiency and associated diet-related chronic diseases that affect the health of large numbers of people in both Se-deficient and Se-sufficient regions of the world.

Based upon the tremendous success of the First International Conference on Selenium in the Environment and Human Health in 2009 in Suzhou, China, it was overwhelmingly decided that the Second International Conference on Selenium in the Environment and Human Health should take place on 23-28 October 2011 in Suzhou, China. The need to continue sharing and evaluating recent Se research findings obtained worldwide provided the impetus for the continuation of this conference series, as well as for the completion of this book containing peer-reviewed extended abstracts. At this Conference, authors from 20 countries addressed some key research topics that included: natural sources of Se in the soil environment, State-of-the-Art analytical technology for identification of different species of Se, environmental pollution and remediation concerns, benefits associated with Se, role of Se in human and animal health, biochemical and Se metabolism, and the development of Se-biofortified agricultural products. A total of 61 extended abstracts from eminent scientists attending the Second International Conference on Selenium in the Environment and Human Health have presented a multitude of research endeavors on their new insights into environmental, analytical, biological, and biochemical health issues related to significance and impact of Se in today's modern life worldwide.

We would like to acknowledge the gracious financial support provided by the Chinese Academy of Sciences, the Chinese Research Academy of Environmental Sciences, National Science Foundation of China, Suzhou Industrial Park, and University of Science and Technology of China. The contributions made by the international advisory committee members, including Elias Arner (Sweden), Martin Broadley (UK), Raymond Burk (USA), Joel Caton (USA), Karaj S. Dhillon (India), Graham Lyons (Australia), Steve McGrath (UK), Milton Moraes (Brazil), and Yongguan Zhu (China), are greatly appreciated.

G.S. Bañuelos

Z.-Q. Lin

Xuebin Yin

Ning Duan

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Section I

Selenium in the Environment

Selenium in Soils and the Need for Biofortification of Crops

McGrath S P* and Zhao F J
Rothamsted Research, Harpenden, Herts, AL5 2JQ, UK
(*E-mail: steve.mcgrath@rothamsted.ac.uk)

Introduction

Selenium (Se) is thought to exist in many soils mainly in the inorganic species selenite (SeIV) or selenate (SeVI), and as various organic reduced Se compounds. The latter are not well characterized, but may include organic molecules that contain the selenium-substituted amino acids and selenomethionine, selenocysteine and selenocystine. At soil pHs ranging from 3-10 selenate is the predominant form when the soils are highly oxic and the redox potential (Eh) is high, but selenite can also predominate in soils of only slightly lower Eh, because reduction of selenate to selenite occurs at Eh values above 0 to +200 mV (Neal et al., 1987). Also, soils may also have microsites with slightly less oxic conditions, which may help reduction to occur. Further reduction to elemental Se or selenide metal complexes is possible, but this is likely only in highly reducing soils, in systems with prolonged flooding such as rice paddy.

Plants take up selenate and selenite species from soil solution around the roots and because selenium is not thought to be essential for plants, the uptake is not regulated across of wide range of concentrations. In most plant species, the uptake of selenate is thought to be through sulfate transporters, and its uptake depends on the sulfate concentration in the soil and sulfur status in the plant. When sulfur status is low, plants up-regulate the production of sulfate transporters in the plasma membrane in roots, which also increases the uptake of selenate. Less is known about the mechanism of selenite uptake, but this may be related to the phosphate transport transporters in the plasma membrane. The finding that selenate and selenite uptake are enhanced in sulfur-starved and phosphorus-starved plants respectively, confirms the ideas about the sulphate and phosphate systems, being involved in the uptake of the two main species of Se present in soils (Li et al., 2010).

Selenate is not strongly bound by most soils and, like sulfate, is readily taken up by plants, but is also easily leached out of the rooting zone. On the other hand, selenite is more strongly bound to Al- and Fe-oxides in soils and is therefore less available to plants and less likely to be leached.

Both the total amount of Se in soil and its speciation are important in determining whether the concentrations of Se in food crops are sufficient to satisfy animal and human requirements.

Soils

In England and Wales, the National Soil Inventory sampled topsoils (0-15 cm depth) at 5 km grid points, yielding almost 6000 samples. These have recently been analyzed for total Se by wavelength-dispersive XRF (Rawlins et al., 2011) and the results are summarized in Table 1.

Table 1. Selenium concentrations in topsoils of England and Wales (Rawlins et al., 2011).

	Se (mg kg ⁻¹)
Mean	0.71
Median	0.48
10th percentile	0.21
25th percentile	0.32
75th percentile	0.80
90th percentile	1.50

These data show that more than 50% of soils were below the threshold value of 0.6 mg kg⁻¹ associated with low Se status in crops (Lyons et al., 2003). Furthermore, geographical analysis showed that nearly all the wheat growing areas were at the low end of the distribution. Unsurprisingly, the majority of UK wheat produced is low in Se (Adams et al., 2002).

Biofortification of Wheat

Four field trials were used to test the responses to selenate (Na_2SeO_4), with two trials in each of two years at different sites in England (Broadley et al., 2010). No effect was detected on grain yield of the wheat varieties in any year. However, there was a strong response in Se concentrations in wheat grain, which was approximately linear at all sites and in two wheat varieties. Concentrations of Se in grain increased by 16–26 $\mu\text{g Se kg}^{-1}$ per gram of Se applied. For example, an application of 20 g Se ha^{-1} increased the Se concentration in grain to approximately 400 $\mu\text{g kg}^{-1}$, which constitutes around 16-fold increase compared to untreated UK wheat (Adams et al., 2002).

The fate of the applied Se in the soil-crop system was investigated. Recoveries in the harvested biomass were 21%, 23%, 20% and 23% of the applied Se in the 5, 10, 15 and 20 g Se ha^{-1} treatments, respectively (i.e., application rates that are likely to be utilized in practice). This means that a large proportion of the Se applied either remained in the soil or was lost, mostly likely by leaching.

No increase in total Se was detectable at any of the soil depths sampled to 90 cm (Stroud et al., 2010). In addition, no significant increase in KH_2PO_4 extractable Se was found (data not shown). No selenate was detected in any of the KH_2PO_4 extracts of soil samples. However, in all samples (including control), selenite was detected at 3.5–4.3 $\mu\text{g kg}^{-1}$ soil.

Biofortification of Rice

We investigated the effects of water management on the Se speciation dynamics in the soil solution and Se uptake and speciation in rice in a controlled pot experiment (Li et al., 2010). Either no Se or 0.5 mg kg^{-1} of soil of selenite or selenate was added to the soil, and plants were grown either under aerobic or flooded conditions. Flooding soil increased the soluble Se concentration when no Se or selenite was added to the soil, but decreased it markedly when selenate was added. Selenate was the main Se species in the selenate treatment, whereas selenite and selenomethionine, Se oxide were detected in the flooded soil solutions of the control and selenite treatments. Grain Se concentration was 49% higher in the flooded than in the aerobic treatments without Se addition. In contrast, when selenate and selenite were added, flooding decreased Se in grain by 96% and 51% respectively, compared to aerobically

grown rice.

Conclusions

We showed that it is possible to increase the Se concentrations in two widely grown UK bread-making wheats from a low level (that is inadequate for human nutrition) to concentrations that supplement the diet in such a way that consumption of a few slices of bread per day would bring the intake to recommended levels. None of the selenate added was detectable in the soils, which indicates that losses of selenate and transformation to selenite or organic forms may have occurred. For rice, selenate addition to aerobic soil was the most effective way of increasing the Se concentration in rice grain.

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Sources and Transformations of Selenium in the Soil-plant System

Dhillon K S

Department of Soil Science, Punjab Agricultural University, Ludhiana 141 004, Punjab, India
 (E-mail: dhillon_karaj@yahoo.com)

Introduction

Selenium (Se) is a naturally occurring metalloid element which occurs nearly in all materials of the earth's crust. Most of the Se in earth's crust (average $0.09 \mu\text{g g}^{-1}$) occurs in association with sulfide minerals as metal selenide. It is rarely seen in elemental form (Se^0). As a consequence of different geological conditions, Se status of crops, animals and humans vary markedly around the world. Since diet is the most important source of Se, understanding the biogeochemical controls on the distribution and mobility of environmental Se is the key to the assessment of Se related health risks.

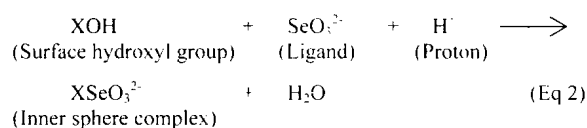
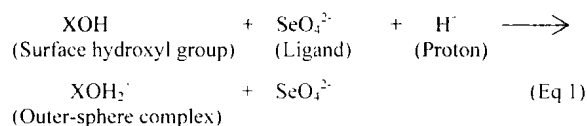
Selenium Sources

Concentration of Se in igneous rocks is usually low ($< 0.05 \mu\text{g g}^{-1}$) followed by almost similar levels in metamorphic rocks. Selenium concentrations are higher in sedimentary rocks where it is associated with clay fraction. Shales are generally rich in Se than sandstone or limestone, but seldom contain $> 500 \mu\text{g Se g}^{-1}$. Shales constitute the principle sources of Se in seleniferous soils developed in Ireland, Australia, Israel, USA and Canada (Rosenfeld and Beath, 1964). Selenium content of a soil reflects, to a great extent, Se content of the parent material. Soils developed from Cretaceous shales in western United States have Se content ranging from 2 to $> 10 \text{ mg kg}^{-1}$, whereas those developed from igneous, old metamorphic and sedimentary rocks that predate the major Cretaceous period contain $< 0.5 \text{ mg Se kg}^{-1}$. Although natural weathering of rocks and minerals is a major source of Se in aquatic and terrestrial ecosystems, human activities contribute substantially to the redistribution and cycling of Se on a global scale (Nriagu, 1989). Two principle anthropogenic sources of Se in soils are the disposal of fly ash (77%) and dumping of agricultural and

municipal wastes (20%) on land. The man-induced mobilization of Se into the biosphere and its inevitable transfer to the human food chain has become an important environmental issue, which entails significant health risks for future generations. Selenium content of most soils is very low (0.01 to $2 \mu\text{g g}^{-1}$, mean $0.4 \mu\text{g g}^{-1}$) but high concentrations of up to $1200 \mu\text{g g}^{-1}$ have also been reported in seleniferous areas (Fordyce, 2005).

Selenium Transformations

Identification of the chemical forms of Se is difficult because of the small amounts of element present and the complex composition of soils. In the soil Se exists in a number of inorganic species such as selenate (SeO_4^{2-}), selenite (SeO_3^{2-}), selenide (Se^{2-}), elemental selenium (Se^0) and organic compounds like amino acids or methylated compounds. The specific chemical form of Se present in soils depends upon the pH, oxidation-reduction potential, complexing ability of soluble and solid ligands and biological interactions. The selenate species is very weakly adsorbed on available solid surfaces compared to selenite by forming outer and inner sphere complexes (Neal, 1995):



Elemental selenium (Se^0) is insoluble and is stable in mildly reducing conditions. Selenide-Se is stable

in strongly reducing conditions and its solubility is limited by insoluble metal (e.g., iron) precipitates. There is very little evidence to show that it is actually formed as a reaction product following the reduction of more oxidized Se forms. Although the reduced forms of Se are thought to be less soluble, these are known to get oxidized under favorable conditions and become water-soluble.

Selenium is taken up by plant roots from the soil solution predominantly as selenate followed by selenite. Organic Se is less readily available for plant uptake than both selenate and selenite species. Therefore, the presence of even small amounts of organic Se in the soil extraction solution (like water extraction, weak electrolyte extraction) may interfere with the validity of using these extractions to predict Se availability in soils. Because of the chemical similarity between Se and S, selenate is probably metabolized via the S-assimilation pathway thereby producing Se analogues of S compounds. Replacement of S by Se in methionine leads to disturbance in the process of protein synthesis, which may be partly responsible for Se toxicity.

The transformations between chemical forms of selenium can also be biologically mediated. Both plants as well as microorganisms are capable of volatilizing selenium through the process of methylation (Frankenberger and Benson, 1994). Biomethylation of toxic Se species including SeO_4^{2-} , SeO_3^{2-} , Se^0 and various organoselenium compounds into less toxic volatile forms (such as DMSe and DMDSe) is a widespread transformation taking place in seleniferous environments. Once Se is methylated into a volatile species, it is released into the atmosphere, diluted and dispersed by air currents away from the contaminated site.

An improved understanding of Se in the agroecosystem will allow us to constructively manage this element in areas where it exists at levels leading to deficiency, as well as toxicity in animals, humans and plants.

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Effect of Flood-Induced Redox Oscillations on Selenium Mobility in Soils

Charlet L*, Parsons C, Bardelli F, Fernandez-Martinez A and Rossetto L
Earth Science Institute (ISTerre), University of Grenoble and CNRS, F-38041 Grenoble, France
(*E-mail: charlet38@gmail.com)

Introduction

Selenium (Se) is usually known as the “double-edged sword element” for its dual toxic and beneficial character to health. Redox reactions, diffusion, adsorption and precipitation processes or interactions with organic matter and biota govern the speciation and mobility of Se in the environment. Recent advances on the mechanistic understanding of processes, which govern Se cycling and bioavailability, adsorption at the mineral/water interface, precipitation of elemental selenium, or bioavailability of nanoscaled precipitates have been reviewed (Fernandez-Martinez and Charlet, 2008).

In the present paper, these advances are applied to floodplain soils with extensive Se contamination that are present in areas with a legacy of mining activity or prone to geogenic Se input. Floodplain soils are used extensively and increasingly for agricultural purposes in Asia and Europe in part due to their high fertility, flat topography and limited utility for other forms of land use. These soils are subject to rapidly changing chemical conditions due to cycles of flooding and draining. Selenium associated with metal-oxides in soils can be either released under the reducing conditions experienced during flooding by desorption, mineral dissolution and competitive sorption, or reductively precipitated as Se^0 or iron selenide. We investigated the individual reduction mechanisms, as well as the cumulative effects of cyclic flooding on Se mobility and bioavailability, through a combination of batch experiments, spectroscopy and thermodynamic and kinetic modeling. Indeed, the advent of powerful spectroscopic techniques, like X-ray absorption spectroscopy, has allowed the structural description of Se adsorption and reduction processes that govern to a large extent Se bioavailability.

Mechanisms of Se Reduction in Anoxic Environments

In an oxic and suboxic environment, inorganic Se is present as anionic species with little adsorbed on soil particles and mostly mobile. Therefore, leaching of desertic Se rich soils by irrigation leads to Se buildup in aquatic systems via strong evapotranspiration. The ecological disaster of Se has been previously observed in the San Joaquin Valley in the early 1980s and also recently in the Newport Beach, California (Fernandez-Martinez and Charlet, 2008). To limit the impact of Se on the environment, engineered treatment wetlands were set up, where biotic or abiotic (e.g., coupled to the reduction of Fe^{2+}) reduction of Se occurs. Under such suboxic environmental conditions, the reaction of Se(IV) with Fe^{2+} in presence of clay and calcite, or by Fe(II) -bearing minerals [siderite (FeCO_3), magnetite (Fe_3O_4), mackinawite (FeS) and nanopyrite (FeS_2)] was shown by a combination of XANES, XPS and Mössbauer spectroscopic studies to lead systematically to the precipitation of Se(0) (Charlet et al., 2007; Chakraborty et al., 2010). In contrast, no reaction was observed when Fe^{2+} was present as exchangeable species in the phyllosilicate interlayer or as a co-precipitated species within calcite. For calcite, a common soil mineral, combination of ab-initio simulations (VASP), neutron diffraction and EXAFS spectroscopy was also used to demonstrate that selenite ions can substitute for carbonate ions (Aurelio et al., 2009). In more reductive environments, we also observed a very fast reduction by nanoparticle mackinawite and magnetite. Depending on Fe(II) -bearing phase and pH, we observed four different reaction products, red and gray elemental Se, and two iron selenides with structures similar to Fe_7Se_8 and FeSe . The thermodynamically most stable form of Se, the iron

selenide ferroselite (FeSe_2), was only observed when Se(IV) reacted with pyrite-greigite nanocomposite.

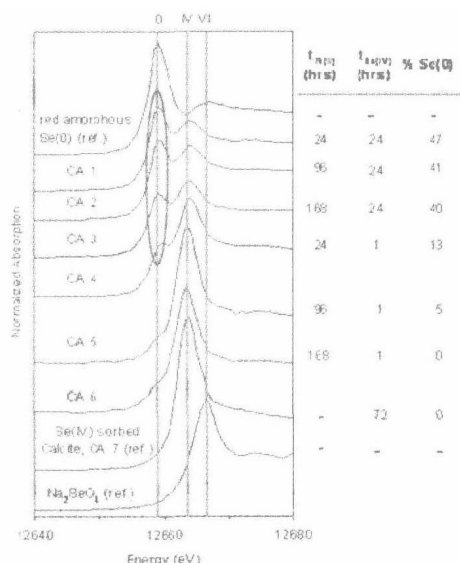


Figure 1. Selenium XANES spectra demonstrate that Se(IV) is reduced by Fe^{2+} freshly adsorbed onto calcite (with Se^0 peak circled with a red line), while no reduction occurs when Fe^{2+} was previously co-precipitated within calcite. (after Chakraborty et al., 2010)

Flood-Induced Soil Redox Oscillations

The recent research progress on the effect of soil redox oscillations on the mobility of Se in fluvisols has been discussed in this paper. The objective of these experiments was to use a redoxstat reactor (Thompson et al., 2006) to assess the influence of multiple Eh oscillations on the mobility of Se and its link to the dissolution-precipitation behavior of Fe in a complex natural flood plain soil system. We postulated that consecutive Feredox cycles would result in long-term behavior that differed from that observed in a single cycle, particularly with respect to the relative predominance of Fe-bearing solids. The approach was to force systematic redox oscillations on stirred soil suspensions, while applying a comprehensive geochemical sampling protocol. It is important to explore the Se concentration variation during redox cycles, and their description by fast (intra-cycle), slow (inter-cycle) immobilizing processes. Effective hydrological management in many redox-oscillating environments may be fundamental to reducing Se release and bioavailability.

Conclusions

Different Se species in a soil or a model mineral suspension were investigated with wet chemistry and XAFS spectroscopy. In previous studies, iron selenide and ferroselite (FeSe_2) had never been observed to be formed at low temperature, either by biotic or abiotic pathways. Instead, clusters of Se^0 were usually found within bacteria or on mineral particles. In contrast, our on-going study demonstrates that pyrite-greigite nanocomposite, a common compound found in reductive environments, reacts with Se(IV) to form Fe selenide, and leads to the stabilization of Se in its most thermodynamically stable form, ferroselite. These findings will help us to better understand Se mobility in regularly flooded soils.

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Stable Isotope Ratios in Soils: A New Tool to Detect Processes Governing the Selenium Cycle

Schilling K^{1,*}, Johnson T M² and Wilcke W³

¹University of Utrecht, Faculty of Geoscience-Petrology, Budapestlaan 4, 3584 CE Utrecht, Netherlands

²Environmental Isotope Geochemistry Group, Department of Geology, University of Illinois at Urbana-Champaign, 245 Natural History Building, Urbana, IL 61801, USA

³Geographic Institute, University of Berne, Hallerstr. 12, 3012 Berne, Switzerland

(*E-mail: k.schilling@geo.uu.nl)

Introduction

Selenium (Se) is an essential trace element for animals and humans with a narrow margin between sufficiency and toxicity. Therefore, understanding the Se cycle is necessary, both to avoid deficiency as well as toxicity of Se. A novel tool to investigate the Se cycle is offered by the use of the natural abundance of stable Se isotopes. Environmental processes (e.g., biomethylation, plant uptake and recycling via litterfall) involving changes in redox conditions result in Se isotope fractionation. If the direction and size of the isotopic fractionation by individual processes is known, conclusions on the controls of the Se cycle can be drawn from observed Se isotope ratios in environmental media.

In Se-contaminated soils, biomethylation is an important detoxification process. The resulting volatilization of methylselenides is a widespread and important flux of Se in the environment. Biomethylation is a widely distributed metabolic process and offers a potential remediation strategy in Se-contaminated areas (Frankenberger and Karlson, 1989). Biomethylation tends to fractionate stable Se isotopes in response to biogeochemical formation conditions and type of Se source compound (Schilling et al., 2011a).

In Se-poor soils with Se concentrations up to 2 mg kg⁻¹, like those in central Europe, other processes than biomethylation such as local contamination, redox transformations and soil-plant cycling govern the Se cycling. Se isotope ratios in soil pools reflect these processes (Schilling et al., 2011b).

Our objectives were to determine (1) the Se isotope fractionation during biomethylation of different inorganic Se sources ([hydro]selenite and selenate)

in a controlled laboratory experiment using a microcosm approach (Schilling and Wilcke, 2011), and (2) the Se isotope ratios in urban soils of a selected central European city (Bayreuth, Germany) with insufficient Se concentrations.

Material and Methods

For our experiments, we used the fungus *Alternaria alternata* which is widespread in the environment, especially in soils. The fungus was cultured at 30°C and incubated with 5 mg Se L⁻¹ as (hydro)selenite or selenite in 100 mL glass serum bottles for 11-15 days. The methylated selenium compounds released by the fungi culture were collected in three alkaline-peroxide gas traps. Furthermore, nutrient medium and fungi were digested with concentrated nitric acid.

The soil samples were digested in 10 mL of concentrated nitric acid. The soil total digests were purified in two steps (hydride generation and anion exchange resin) before Se isotopic analysis.

Results and Discussion

Selenium isotope fractionation during biomethylation
Selenium isotopes were significantly fractionated both during the methylation of Se (VI) ($\delta^{82/76}\text{Se}$ of methylselenide = -3.97‰ to -3.25‰) and even more markedly of Se(VI) (-6‰). The pH between 3 and 7 did not have an influence on the size of Se isotope fractionation during biomethylation. The greater isotope fractionation in the Se(VI) compared to that in Se(VI) experiments may be explained by the transport of the different inorganic Se species into the cells (Schilling et al., 2011a).