Calcium isotope fractionations from roots to shoots

SCHMITT A.-D.[1,2]*, STILLE P.[1], LABOLLE F.[3], COBERT F.[1,4], BOURGEADE P.[2], CHABAUX F.[1] AND GANGLOFF S.[1]

[1]Université de Strasbourg et CNRS-UMR 7517, LHyGeS/EOST ; 1 rue Blessig, F-67000 Strasbourg
[2]Université de Franche-Comté et CNRS-UMR 6249, Chrono-environnement ; 16, route de Gray, F-25000 Besançon
[3]Université de Strasbourg, Institut de Zoologie et de Biologie végétale, 12, rue de l'université, F-67000 Strasbourg
[4]Université de Liège, Faculté d'agronomie de Gembloux; 27 avenue du maréchal Juin, B-5030 Gembloux
* adschmitt@unistra.fr

Recent studies have shown that Ca isotope ratios have the potential to be important tracers of biological activities in forested ecosystems or more generally in plant physiology and in biogeochemistry.

Field studies performed in forested watersheds point to the importance of Ca isotope fractionations in soil solutions due to biological activity in the surficial soil horizons. Hydroponic experiments, performed on rapid growing bean plants, that allow to have a complete growth cycle, helped to identify the mecanisms responsible for these Ca isotope fractionations (Cobert *et al*., 2011; Schmitt *et al*., 2013). Indeed, the adsorption of Ca by lateral roots, that are enriched in ^{40}Ca compared to the nutritive medium, follows a closed-system equilibrium fractionation with a fractionation factor of 0.9988, suggesting that Ca forms exchangeable bonds with the $RCOO^-$ groups in the cell wall structure of the lateral roots. Two other fractionation levels have been identified within the plant during the Ca transfer from roots to shoots. When the xylem sap goes to the shoots, ^{40}Ca is preferentially bound to the polygalacturonic acids (pectins) of the middle lamella of the xylem cell wall. Finally, a third fractionation occurs in the reproductive organs also caused by cation-exchange processes with pectins. The fractionation mechanisms are the same whatever the Ca content and pH of the nutritive solution. Only the bean plants average signature as well as the amplitude of the Ca isotopic fractionation within plant organs are highly dependent on the composition of the nutritive solution. A comparative field study is installed to examine the Ca isotopic fractionation in trees of a forested watershed.

[1] Cobert *et al*. 2011, *GCA* **75**, 5467-5482; [2] Schmitt *et al*., 2013. *GCA* **110**, 70-83.

Atmospheric CF_4 trapped in polar ice – A new proxy for granite weathering

J. SCHMITT [1]*, B. SETH[1], P. KÖHLER[2], J. WILLENBRING[3] AND H. FISCHER[1]

[1]Climate and Environmental Physics & Oeschger Centre for Climate Change Research, University of Bern, CH, (*correspondence: schmitt@climate.unibe.ch)
[2]Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany
[3]University of Pennsylvania, Department of Earth & Environmental Sciences, Philadelphia, USA

The reconstruction of continental weathering rates using trace elements and their isotopes measured on marine sediments and crusts is a vigorously growing field. Here, we use a novel approach using the ppt-level trace gas CF_4, tetrafluoromethane, which can be analysed in air trapped in ice cores. CF_4 is a trace impurity in granites and other plutonic rocks, and during weathering this gas escapes into the atmosphere. In preindustrial times, this release from granitic rocks was the only natural source of CF_4. Because CF_4 is inert to destruction processes in the tropo- and stratospheres, its only sink is destruction by UV radiation and radicals in the mesosphere. This chemical inertness is responsible for an exceptionally long atmospheric lifetime which is expected to range between 50 kyr and 400 kyr. Althoug the globally integrated CF_4 emission flux from weathering is only a few tons per year, the exceptionally long lifetime allows to establish a long-term atmospheric concentration of about 33 ppt. We developed a vacuum melt-extraction system for ice core samples coupled to a mass spectrometry detector to precisely measure these trace amounts of CF_4 found in past atmosphere and applied this method to ice over the entire Dome C ice core. During the last 800 kyr, atmospheric CF_4 varied in a narrow band between 31 ppt and 35 ppt, i.e. only 10-15 % variability, providing a first estimate of the long-term weathering rate fluctuations. Our record shows that CF_4 increases during interglacials and falls during the coldest, glacial phases. However, our CF_4 record shows also a pronounced shift toward higher CF_4 levels after 430 kyr (the Mid-Brunhes Event). With the beginning of Marine Isotope stage 11, we find a steep rise in CF_4 that probably relates to intense weathering during the first full interglacial after a series of lukewarm interglacials.

www.minersoc.org
DOI:10.1180/minmag.2013.077.5.19