



## Experimental identification of mechanisms controlling calcium isotopic fractionations by the vegetation.

Florian Cobert (1), Anne-Désirée Schimtt (2), Pascale Bourgeade (2), Peter Stille (1), François Chabaux (1), Pierre-Marie Badot (2), and Thomas Jaegler (2)

(1) Université De Strasbourg et CNRS, Laboratoire d'Hydrologie et de Géochimie de Strasbourg, EOST, 1 rue Blessig, 67084 Strasbourg Cedex, France, (2) Université de Franche-Comté et CNRS (UMR 6249 chrono-environnement), 16 route de Gray, 25030 Besançon Cedex, France

This study aims to better understand the role of vegetation on the Ca cycle at the level of the critical zone of the Earth, in order to specify the mechanisms controlling the Ca absorption by plants at the rock/plant interface. To do this, we performed experiments using hydroponic plant cultures in a way that we could control the co-occurring geochemical and physiological process and determine the impact of the nutritive solution on the Ca cycle within plants. A dicotyledon and calcicole plant with rapid growth, the French bean (*Phaseolus vulgaris* L.), has been chosen to have access to one complete growth cycle. Several experiments have been conducted with two Ca concentrations, 6 (L) and 60 (H) ppm and two pH values (4 and 6) in the nutritive solution, for which the Ca concentration was maintained constant, so its Ca content is considered as infinite. A second experiment (non infinite L6) allowed Ca depletion in the solution through time; therefore, response effects on the Ca isotopic signatures in the plant organs and in the nutritive solution were observed. We determined Ca concentrations and isotopic ratios in the nutritive solution and in different organs (main roots, secondary roots, old and young stems, old and young leaves and fruits) at two different growth stages (10 days and 6 weeks).

Preliminary results show that: (1) the roots (main and secondary) were enriched in the light isotope ( $^{40}\text{Ca}$ ) compared to the nutritive solution, and leaves were enriched in the heavy isotope ( $^{44}\text{Ca}$ ) compared to stems. These results are in accord with previously published field studies (Wigand *et al.*, 2005; Page *et al.*, 2008; Cenki-Tok *et al.*, 2009; Holmden and Bélanger, 2010). Leaves and secondary roots were however enriched in the heavy isotope ( $^{44}\text{Ca}$ ) compared to bean pods, stems and main roots. These results could be related to kinetic fractionation processes occurring either during the Ca root uptake, or during the Ca transport within the plant, or physiological mechanisms occurring first at the level of secondary roots, and second at the level of leaves. (2) No Ca isotope difference was observed neither between old and young organs, (except for H6 leaves), nor between the two growth stages (except for H6 roots). This suggest that the mechanisms controlling isotopic fractionations of Ca within common beans do not vary during growth, and that the nutrients stored in the cotyledons have only a minor effect on the Ca isotope fractionations of plants harvested after 10 days. (3) Strongest Ca isotope fractionations were observed at the nutritive solution/root interface. This implies that the mechanisms of light isotope enrichments in the plant are mainly due to transport processes taking place at this interface. (4) The non infinite L6 nutritive solution became enriched in  $^{44}\text{Ca}$  during the experiment compared to the infinite L6 nutritive solution and all the other solutions (L4, H4, and H6). This enrichment can be explained by Rayleigh fractionation or isotopic equilibrium. (5) Bean organs, from L4 and non infinite L6 experiment conditions, were enriched in  $^{44}\text{Ca}$  compared to stems and roots cultivated under H4, H6 and infinite L6 conditions. This might be due to the limited Ca in the nutritive solutions that cause smallest Ca isotope fractionations in the bean organs.

All these results show that there is no simple correlation between Ca isotopic variations, Ca content and pH of the nutrient solution, and that physiological effects have also to be involved. They confirm the potential of the Ca isotopic system for tracing biological fractionations in natural ecosystems.