



Hydrology, environment

Processes controlling the stable isotope compositions of Li, B, Mg and Ca in plants, soils and waters: A review

Processus contrôlant les compositions des isotopes stables du Li, B, Mg et Ca des plantes, des sols et des eaux : une synthèse

Anne-Désirée Schmitt^{a,*,b}, Nathalie Vigier^c, Damien Lemarchand^a, Romain Millot^d, Peter Stille^a, François Chabaux^a

^a Laboratoire d'hydrologie et de géochimie de Strasbourg, université de Strasbourg/EOST, CNRS, 1, rue Blessig, 67000 Strasbourg, France

^b Université de Franche-Comté, CNRS-UMR 6249, Chrono-environnement, 16, route de Gray, 25030 Besançon cedex, France

^c CRPG-CNRS, université de Lorraine, 15, rue Notre-Dame-des-Pauvres, 54500 Vandœuvre-lès-Nancy, France

^d BRGM, Metrology, Monitoring, Analysis Department, 3, avenue C.-Guillemin, BP 36009, 45060 Orléans cedex 2, France

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ABSTRACT

Li, B, Mg and Ca isotopes became of increasing interest during the last decade due to their potential for better constraining the carbon cycle and nutrient cycling. At the soil-water-plant scale, Li and B isotopes are powerful tools for the understanding of processes leading to clay mineral formation in soils. Ca and Mg isotopes allow, for their part, to identify plant-mineral interactions and recycling by vegetation. At the scale of monolithological silicate watersheds, Li and B isotope fractionations are mainly controlled by the degree of mineral leaching and the amount of clay mineral formation. Ca and Mg isotope signatures in soil and waters vary seasonally, depending on the vegetation growth cycle and rain events. In mixed-lithology basins, B and Li isotopes are controlled by alteration rates of silicate minerals and the residence time of waters within the watershed. Ca and Mg isotope ratios of river waters appear to be also lithology-controlled.

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R É S U M É

Les isotopes du Li, B, Mg et Ca ont été de plus en plus étudiés au cours de la dernière décennie, en raison de leur potentiel pour mieux contraindre les cycles du carbone et des nutriments. À l'échelle locale eau-sol-plante, les isotopes du Li et du B sont des outils puissants permettant de comprendre la formation des minéraux argileux dans les sols. Pour leur part, les isotopes du Ca et du Mg permettent d'identifier les interactions entre les plantes et les minéraux ainsi que le recyclage par la végétation. À l'échelle des bassins versants monolithologiques, les fractionnements isotopiques du Li et du B sont principalement contrôlés par le degré de lessivage des minéraux et la quantité de minéraux argileux formés. Les signatures isotopiques en Ca et en Mg dans les sols et les eaux de rivière varient saisonnièrement, en fonction du cycle de croissance des végétaux et des épisodes pluvieux. Dans des bassins versants plurilithologiques, les isotopes du B et du

* Corresponding author.

E-mail address: adschmitt@unistra.fr (A.-D. Schmitt).

Li sont contrôlés par les taux d'altération des minéraux silicatés ainsi que par les temps de résidence des eaux au sein des bassins versants. Par ailleurs, les isotopes du Ca et du Mg des eaux de rivière semblent également contrôlés par la lithologie.

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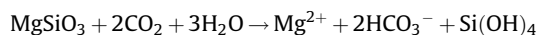
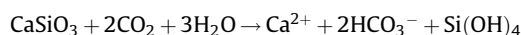
1. Introduction

Alteration of silicate minerals is a key process controlling not only the carbon cycle but also the (bio)geochemical cycles of elements, especially of plant nutrient elements (Berner and Berner, 1996; Goudie and Viles, 2012). Presently several major uncertainties remain unresolved that preclude precise quantification of present-day and past impact of silicate alteration on the oceanic budget and on climate variations. In particular, the role of plants, for example during rapid changes of the continental biomass and of vegetation species, on the chemical alteration intensity of silicate minerals is poorly constrained (Amundson et al., 2007; Berner et al., 2004; Lucas, 2001). The onset of vascular plants on the continent during the Late Ordovician and their diversification up to the Devonian (Steemans et al., 2009) is known to have accelerated weathering rates and thereby lowered atmospheric CO₂ content (Berner et al., 1983; Berner, 1998; Lovelock and Whitfield, 1982; Moulton et al., 2000). Rooted vascular plants excrete organic acids and chelates that enhance chemical weathering rates in soils (Griffiths et al., 1994). Plants are also known to accelerate chemical weathering processes by mobilizing metals from soils by a factor of two to five compared to the rates when plants are absent; they may also retard metal release to drainage waters by recycling (Berner et al., 2004). Finally, plants cause mechanical fractionation of rocks by increasing their specific surface area and, thus, influence indirectly chemical weathering rates. As a result, plants can control the biogeochemical cycle of nutrients and, therefore, affect their chemical availability in soils: they take up nutrients from the soil solution via their roots, store them in tissues, and finally return them to the soil system via litter fall and organic matter decomposition. While considerable work has been done to understand nutrient fluxes and exchanges between soil-water-plant compartments with classical geochemical tools (Marschner, 1995), developing new tools in this thematic could expand our understanding of these processes.

Instrumental improvements in mass-spectrometry made during the last decade allowed developing more precise isotope measurements of “non-traditional” stable isotopes like Li, B, Mg, Ca and Si in samples from the soil-water-plant interface. A review of Si isotopes is provided separately in this issue (see Opfergelt and Delmelle, this volume). Since Li, B, Mg and Ca have distinct and complementary implications in soil-forming reactions and in vegetation development, their coupled analyses should help gaining insights in mechanisms and rates governing the transfer of matter from bedrocks to surface waters. They are all fluid-mobile, non-subject to redox processes and they present large relative mass differences (from 7.69% for Mg to 16.66% for Ca) between their

different stable isotopes. In contrast to Li, B or Mg isotopes that have no radiogenic isotopes, one part of ⁴⁰Ca originates from the β⁻ radioactive decay of ⁴⁰K leading to ⁴⁰Ca excesses compared to other isotopes (Marshall and DePaolo, 1982) but only in case of old samples (> 1 Ga) showing high K/Ca ratios (Nägler and Villa, 2000). They form either ionic (Ca) or covalent bonds with their atomic neighbors, and show variable coordination in solutions and solids, which are the main factors that determine isotope fractionation between solids, complexes and liquids. As a result, Li, B, Mg and Ca are subject to significant low temperature mass fractionations which can provide key information on the nature and quantification of weathering and/or biological processes.

On continents, the weathering of Ca- and Mg-silicates directly influences the carbon cycle by CO₂ consumption and releases Ca²⁺ and Mg²⁺ cations into the hydrosphere according to the two following reactions (Berner et al., 1983):



These two major alkaline-earth elements are essential nutrients and have physiological and structural key functions in plants. In particular, Ca is necessary for the cell wall stability and acts as an intracellular messenger (Marschner, 1995; McLaughlin and Wimmer, 1999; Taiz and Zeiger, 2010). Mg participates in the activation of more than 300 enzymes for the synthesis of organic molecules and the functioning of chlorophyll (Wilkinson et al., 1990). However, the bio-availability of these two elements can be rapidly limited in soils which developed on base cation-poor bedrocks like granites. Their transfer from the parent mineral to surface water as well as their integration in vegetation tissues is therefore highly sensitive to the nature and extent of the water-soil-plant interactions. In contrast, the alteration of Li- and B-rich minerals does not directly influence the carbon cycle, but these two trace elements are particularly enriched in silicate minerals relative to carbonates, which makes them suitable proxies for quantifying alteration rates of silicate phases at the scale of large mixed lithology basins, or even at the global scale.

Several studies have focused on soil profiles, monolithological and mixed-lithology watersheds for each of these four isotopic systems. They have especially shown isotopic differences of various magnitudes between rivers, silicate rocks and minerals (Chaussidon and Albarède, 1992; Chaussidon and Marty, 1995; Huh et al., 1998; Tipper et al., 2006a, 2010a). Flux-weighted riverine isotopic signatures of these elements are lighter for Ca and Mg (Fig. 1), and heavier for B and Li, compared to the bulk silicate earth value. This suggests that fractionation

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