

Geochemistry of Lithium isotopes: recent applications and future directions

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Abstract

Here, we are aiming to illustrate different applications of lithium isotopes during water/rock interactions. The first example deals with the behavior of Li during river weathering at the scale of the Loire River Basin. The second example shows that Li isotope tracing can be very useful to decipher between natural and anthropogenic input like waste waters release in a small watershed. Finally, the last innovative example is focusing on Li isotopes in fracking fluids geochemistry and future direction deals with the implementation of Li isotope geochemistry into transport-reactive modeling.

Introduction

In Earth Sciences, the field of metal stable isotope geochemistry has greatly expanded over the past 25 years. Among the stable isotope systematics of metals studied so far, the geochemistry of lithium (Li) isotopes provides exceptional potential as a tracer of water/rock interactions within low- and high-temperature systems. Furthermore, Li has strategic importance for numerous industrial applications including its use in the production of batteries for mobile devices (computers, tablets, smartphones, etc.) and electric vehicles, and also in pharmaceutical formulations. BRGM (French Geological Survey) has been at the forefront of developing the field of Li isotope geochemistry in recent years with the use of multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) techniques.

Assessing the behavior of Li and its isotopes in Earth's surface and subsoil reservoirs (fluids, rocks) is crucial for constraining the origin and distribution of Li in geological and energy reservoirs. This highly mobile element has two isotopes with very different abundances (${}^6\text{Li}$ ~7.5% and ${}^7\text{Li}$ ~92.5%) and, due to the large relative mass difference between the two stable isotopes, significant mass fractionation is observed in geological materials. The resulting variations in isotope ratios (${}^7\text{Li}/{}^6\text{Li}$) observed in nature thus may provide key information on the origin, fate and processes affecting Li behavior.

Geogenic and Anthropogenic origin of Lithium in the Loire River Basin

First, we report data for lithium and its isotopes for river waters and suspended sediments at the scale of the Loire River basin. The Loire River in central France is approximately 1010 km long, drains a surface area of 117,800 km² and is one of the main European riverine inputs to the Atlantic Ocean.

Overall, lithium concentrations in river waters of the Loire River main stream span a wide range from 2 to 23 µg/L, whereas $\delta^7\text{Li}$ values are between +5.8 and +13.2‰. We can observe a clear contrast between the headwaters upstream and rivers located downstream in the lowlands, with a significant decrease of the $\delta^7\text{Li}$ with the distance from the source. This feature is observed for both high and low flow stages. In addition, one of the major tributaries in the Massif Central (the Allier River) is clearly influenced by inputs from thermo-mineralized waters resulting of hydrothermal activities having lower $\delta^7\text{Li}$ values. More generally, the Li isotopic composition measured in the rivers of the Loire Basin shows that ${}^7\text{Li}$ is enriched in the dissolved load when compared to suspended river materials. Indeed, lithium concentrations in suspended sediments of the Loire River at Montjean are comprised between 41 and 73 µg/g, whereas $\delta^7\text{Li}$ are very low, between -8.7 and -7.6‰. Suspended sediments are clearly ${}^6\text{Li}$ enriched ($\delta^7\text{Li}$ from -8.7 to -7.6‰) compared to river waters (+5.8 and +13.2‰), in agreement with the fact ${}^6\text{Li}$ is preferentially incorporated into suspended sediments during river weathering. Finally, the relationship between $\delta^7\text{Li}$ and Al/Li in suspended sediments also raises the question of the control by the different mineral phases (clay minerals...) during Li isotopic fractionation between water and solids.

From the other hand, the contribution of human activities such as industries, agriculture and various domestic inputs, becomes more and more significant in the chemical composition of the dissolved load of rivers. Human factors act as a supplementary key process. Therefore the mass-balance for the budget of catchments and river basins include anthropogenic disturbances. It is well known that Li has strategic importance for numerous industrial applications including its use in the production of batteries for mobile devices but also in pharmaceutical formulations. Here we investigate waste water releases by tracing its impact by the use of Li isotopes in a small river basin near Orléans in France (l'Egoutier, 15 km² and 5 km long). As case study, we

decided to monitor this small watershed which is poorly urbanized in the Loire river basin. Its spring is located in a pristine area (forested area), while it is only impacted some kilometers further by the releases rich in metals coming from a hospital water treatment plant. A sampling of these liquid effluents and dissolved load from upstream to downstream was realized and their concentrations and isotopic data were determined. Lithium isotopic compositions are rather homogeneous in river waters with $\delta^7\text{Li}$ values around $-0.5\text{‰} \pm 1$ along the main course of the stream ($n=7$). The waste water sample is very different from the natural background of the river basin with Li concentration being twice of the values without pollution and a significant heavy lithium contribution ($\delta^7\text{Li} = +4\text{‰}$).

This last example show the ability of Li isotopes to decipher between natural and anthropic origin at the scale of a small watershed.

Li isotopes in fracking fluids

Finally, identifying the geochemical fingerprints of fluids that return to the surface after high volume hydraulic fracturing of unconventional oil and gas reservoirs has important applications for assessing hydrocarbon resource recovery, environmental impacts, and wastewater treatment and disposal. Here, we report elemental and isotopic signatures (Li/Cl, and $\delta^7\text{Li}$) useful for characterizing hydraulic fracturing flowback fluids (HFFF) and distinguishing sources of HFFF in the environment.

However, in this context one of the major obstacles to using Li isotopes is the ability to obtain a clear distinction between primary effects associated with source/origin and the effects of secondary processes that can modify the isotopic signature (e.g., mineral alteration, dissolution, precipitation). The Li isotope fractionation related to such secondary processes can be investigated either by experimental studies designed specifically to determine the fractionation associated with secondary processes, or by theoretical models to understand the consequences of fractionation in order to predict them at laboratory and field scales.

At this point, a possible future direction to get a step further is to couple two very specific scientific approaches: 1/ Li isotope geochemistry and 2/ reactive transport modeling, in order to better understand the mechanisms of enrichment of Li in geological reservoirs with the goal of optimizing prospecting methods and improving our knowledge in the sustainable management of energy resources (geothermic, oil/gas exploitation).