Can Li isotopes help detect leakage in future CCS sites? The example of a natural analogue in France

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Introduction

Natural analogue sites where geologic CO_2 is leaking to the surface provide excellent opportunities to test approaches suitable for monitoring potential CO_2 leakage at carbon capture and storage sites. We tested here the possibility of completing the classical CO_2 chemical/isotope monitoring approach with the study of the Li isotope systematic, at a CO_2 analogue site near Sainte-Marguerite in the Massif Central (France).

Study site

The Sainte-Marguerite area is located in the southern part of the Limagne graben (French Massif Central). The basement, composed of highly fractured granite, outcrops toward the west of the study area, notably around the Saladis spring. An intercalated arkosic permeable interval between fractured granite and Oligocene marls and limestones acts as a stratiform drain for fluid migration while the overlying thick Oligocene interval is impermeable and acts as a seal. The Allier river bed is located near the contact between the basement and the sedimentary rocks. Deep CO_2-ladden fluids migrate through the arkose interval toward the Sainte-Marguerite area and sustain a number of local springs (Figure 1). The Sainte-Marguerite area is known for the travertine deposits associated with the CO_2-rich natural springs

Results

The previous characterisation of $\delta^{13}C$ and $\delta^{18}O$ from dissolved CO_2[1] indicated some water samples are in isotope equilibrium with degassing mantle CO_2 while other are not. The study of the corresponding δ^7Li isotope compositions (Figure 1) confirm that Li is explained by a binary mixing relationship between a ^7Li-depleted endmember originating from a deep thermal source, and Li originating from the Allier river.

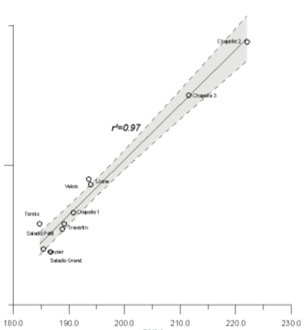

Figure 1: Li concentrations and isotope compositions covariations.

[1] Widory *et al.* (2011) *AGU Fall Meeting*, **H23B-1251**.

ZIRCON AS A PROBE OF PLANETARY IMPACT HISTORY

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The impact history of the early solar system remains controversial. The longstanding paradigm of a Late Heavy Bombardment (LHB) at 3.8-4.0 Ga that largely resurfaced the Moon (and by implication, ~30% of Earth) is to a significant degree supported by highly problematic interpretations of $^{40}Ar/^{39}Ar$ ages. Recent studies indicate that zircon has the potential to preserve evidence of impact events on Earth and possibly other solar system bodies. For example, LHB-era Jack Hills zircon grains and epitaxial rims grown between 3.85-3.95 Ga both show evidence of temperature excursions possibly due to impacts. Lunar zircons have also been interpreted to result from large-scale impacts on the Moon. However the geochemical signatures of zircons produced within impact events are poorly understood and caution must be used when assigning an impact as opposed to igneous origin. Ion microprobe U-Pb ages, Ti-in-zircon thermometry and trace element geochemistry of impact-produced zircon obtained from four preserved terrestrial craters reveal broadly similar thermal conditions of formation and provide a basis of comparison with which to distinguish zircon crystallized within an impact event from grains that formed by endogenic igneous processes. A zircon saturation model of hypothetical target rock compositions undergoing thermal excursions associated with the LHB was developed to predict the Ti-in-zircon temperature spectra expected from impacts. Modeled impact zircon production is a function of ambient temperature, Zr content, target composition, and impact energy. Impacts need to be sufficiently large to permit decompression melting of uplifted middle to upper crust (i.e., low energy bolides will not produce melt sheets and thus impact zircon). Target compositions were estimated from large geochemical databases (including meteorites for other solar system bodies such as the Moon and Mars) and selected through a Monte Carlo process allowing a spectrum of compositions to be randomly accessed. Model results for impact produced zircon yield a zircon crystallization temperature distribution significantly higher than that, for example, from Hadean Jack Hills zircons, but considerably lower than the temperature spectrum of lunar zircons. For modern terrestrial crustal target compositions, modeled results yield zircon formation temperatures remarkably similar to Ti-in-zircon crystallization temperatures for recent, large terrestrial impacts. Importantly, the model predicts that zircon growth in response to impacts form in dominantly felsic melts, with little to no zircon formed in mafic melts. This result appears to rule out most lunar zircons documented for both U-Pb age and [Ti] as having formed in response to impact melting and provides an explanation for the apparent absence of impact zircon from Mars samples.