

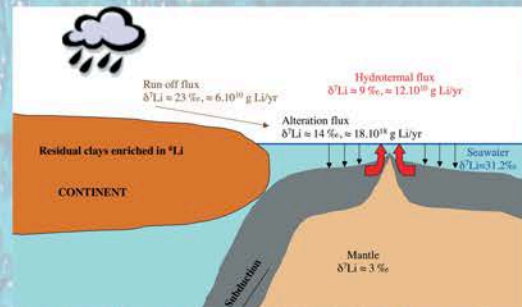
Lithium Isotopes in Coral Skeletons

Claire Rollion-Bard¹, Nathalie Vigier¹, Anders Meibom²,
Dominique Blamart³ and Stephanie Reynaud⁴
(1) CRPG-CNRS, Nancy-University, France
(2) LEME, Paris, France
(3) LSCE, Gif-sur-Yvette, France
(4) CSM, Monaco



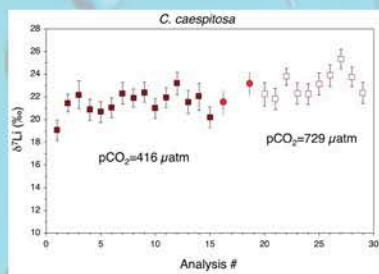
An important challenge towards reaching a better understanding of the global CO₂ cycle is to better quantify the weathering rate of continental silicates. Lithium has two stable isotopes, ⁶Li (7.52%) and ⁷Li (92.48%), that fractionate significantly during silicate weathering (e.g. Chan et al., 1992; Vigier et al., 2008). Despite its potential to become a proxy for the rate of continental weathering throughout a significant part of geologic time, only few studies have reported Li isotopic compositions in carbonates and only foraminifera have been used in attempts to reconstruct the paleo-δ⁷Li of the oceans

In this study, we report in situ δ⁷Li measurements for one shallow-water zooxanthellate species (*Porites lutea*), and two deep-sea azooxanthellate species (*Lophelia pertusa* and *Desmophyllum cristagalli*) grown under natural conditions. Additionally, the shallow-water zooxanthellate coral *Cladocora caespitosa* was grown experimentally under two different CO₂ partial pressures (pCO₂) to test if δ⁷Li in fossil corals would be affected by pCO₂ variation in the past. The possible dependency of Li isotopic fractionation on the ultrastructure of corals (i.e. EMZ or CRA versus fibres) was also investigated. The results were explored in order to determine the role of environmental conditions controlling Li isotopic fractionations.



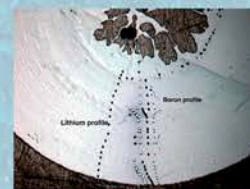
RESULTS IN CORALS AND DISCUSSION

The two experimental *Cladocora* corals grown under two pCO₂: 416 ± 29 and 729 ± 30 μatm. In consequence, they also grew at different pH (8.06 ± 0.03 and 7.86 ± 0.01, respectively), and different carbonate chemistries. The average δ⁷Li values for these two corals are very close (21.5 ± 1.0 ‰ and 23.1 ± 1.1 ‰, respectively) lending support to the conclusion that changes in seawater pH or pCO₂ do not induce a large change in the Li isotopic composition of the skeletons. At the level of precision obtained in this study, the Li isotope fractionation during coral formation is not pCO₂-dependent (nor pH-dependent).

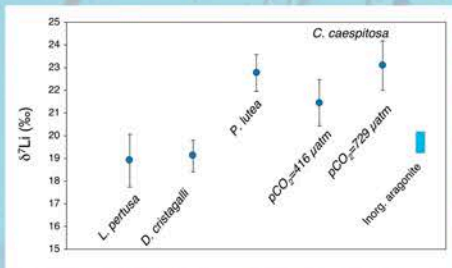
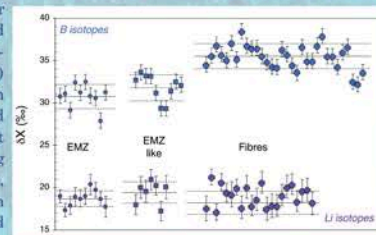


Lophelia pertusa was chosen for studying the impact of ultrastructure on Li isotope composition because it is characterized by a well-organized ultrastructure (EMZ/CRA vs fibres). There is no obvious change, within the analytical precision, in the δ⁷Li values in the various skeletal zones investigated. The δ⁷Li profile is therefore different from the δ¹¹B profile. Indeed, all boron isotopic analyses of the EMZ/CRA are characterized by distinctly lower δ¹¹B values compared with adjacent fibrous aragonite skeleton

Distinct the EMZ/CRA explained (i) mechanisms of (Meibom et al., et al., 2007; al., 2007), (ii) the seawater (essentially pH) fluid reservoir 2003; Cohen and 2003, Rollion-2003a) or (iii) fractionation in calcifying fluid 2006; Gagnon et Considering value of 31.2‰, fractionation seawater and ranges between and -8.1±1.1 al., 2004a; this study). As the δ⁷Li measurements performed in coral skeleton are in agreement with the lithium isotopic fractionation of inorganic aragonite (-11.7‰, Marriott et al., 2004b) and do not vary, the Rayleigh fractionation model is not compatible with the Li isotopic data presented here.



signatures in and fibres were by different biomineralisation 2006; Blamart Rollion-Bard et by changes of chemistry in a calcifying (Adkins et al., McConaughy, Bard et al., by a Rayleigh a semi-closed (Cohen et al., al., 2007), a seawater δ⁷Li the Li isotope between coral aragonite -12.8±0.4 ‰ (Marriott et



We observe a small but significant difference (~3‰) between deep-sea corals and shallow-water corals. This systematic difference could be due first to the presence of the symbiotic algae (zooxanthellae) in shallow-water species. Nevertheless, we can note that Marriott et al. (2004) measured two shallow-water corals (*Acropora* and *Porites*) and observed a difference of about 2‰ between these two zooxanthellate corals.

Increasing the number of coral species investigated is critically needed to better constrain the species effect and identify the cause of inter-specific differences in δ⁷Li. This effect will have to be taken into account in future paleo-weathering studies.

CONCLUSION

This is the first in situ extensive study of Li isotopic composition in corals. We find that the Li isotopic composition is species-dependent. There is a systematic difference between deep-sea azooxanthellate corals and shallow-water zooxanthellate corals. No relationship was found between the δ⁷Li and the coral microstructure. This implies that (1) the mechanisms of biomineralization do not influence the Li isotopic composition of coral, i.e. there is no vital effect, and (2) Rayleigh fractionation in a semi-closed calcifying fluid is unlikely to occur during CaCO₃ precipitation in corals.

The lack of temperature, pH, pCO₂ and ultrastructure dependence of Li isotope fractionation in corals indicates that they could be a good proxy for reconstruction of paleo-δ⁷Li of seawater and potentially, a proxy for past continental weathering.

