FINAL REPORT PROGRAM LEFE

Program LEFE CYBER / EC2CO	**Project Title** Unravelling the Mechanisms Controlling Li Incorporation in $CaCO_3$ minerals: Insights into Li Biogeochemical Cycles - MeLiCa	**Years** **2021 – 2022**

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Participating Laboratories : GET and IPGP

Contribution to

Other funding sources

Context

The main processes controlling chemical and isotopic composition of monovalent ions such as Li and Na in $CaCO_3$ minerals are underexplored, although these trace elements are routinely utilized as paleoenvironmental proxies. In this project, we examine the effect of mineral growth rate and temperature on the incorporation of Li, Na and Mg into aragonite.

Objectives / scientific questions:

The research has two main objectives:

1/ to quantify the mechanisms controlling the incorporation of Li and its isotopic composition in aragonite,

2/ to evaluate the use of Li ratios to other cations and Li isotopic composition of $CaCO_3$ minerals as proxies for paleoenvironmental conditions.

Main results

The main outcome of the project suggests that during aragonite formation under abiotic conditions the incorporation of Mg and Li is temperature dependent, but the temperature control can be considered negligible compared to that induced by mineral growth rate. As it can be seen in Fig. 1, the partition coefficients of Li and Mg between aragonite and forming fluid are strongly influenced by the growth rate. Interestingly, systematically higher distribution coefficients are observed at lower temperatures for both metals. This observation can likely be explained by the incorporation of Li and Mg in defects sites of the growing solid and not in the position of Ca. This is because Mg is unlikely to obtain a coordination of 9 required for an ideal replacement reaction with Ca, whereas Li is a monovalent ion, whose presence in the solid requires charge balance.

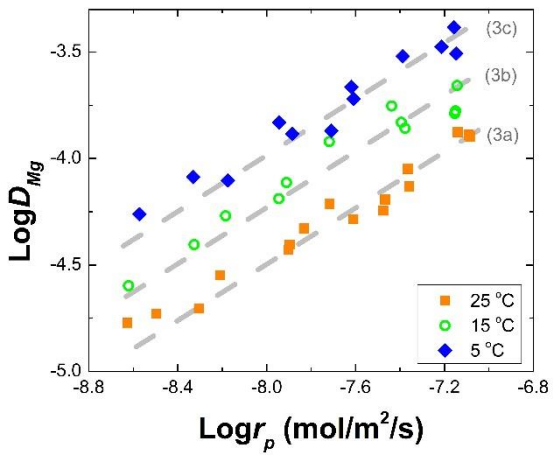

Fig.1. Dependence of Mg (top) and Li (down) distribution coefficients in aragonite as a function of mineral growth rate for experiments conducted at 5, 15 and 25°C.

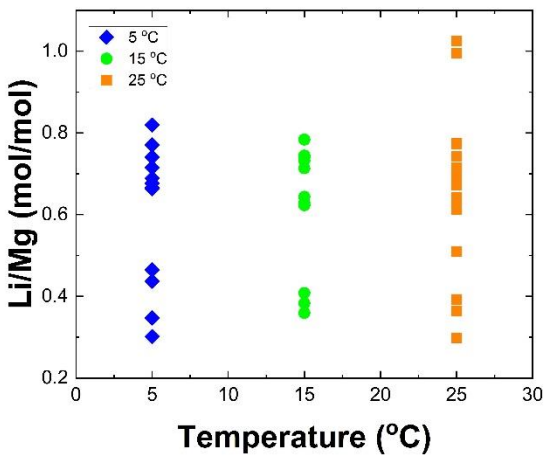

Fig.2. Dependence of Li/Mg ratio in aragonite as a function of temperature.

Notably, as it can be seen in Fig. 2, the Li/Mg ratio in inorganic aragonite cannot be used as a temperature proxy, because there is no relationship with temperature. This finding contradicts the results of field studies that arguing for the use of Li/Mg as a T proxy in coralline aragonite.

As it can be seen in Fig. 1 the main control on the distribution of Li and Mg between aragonite and forming fluid is the mineral growth rate. At the same time, although there is a temperature control, this is negligible compared to that imposed by the growth rate. Assessing the Li/Mg ratios in the precipitated solid, it can be seen in Fig. 2 that there is no temperature control and the results of experiments at 5, 15 and 25^{o}C overlap. This finding is not necessarily unexpected considering that the mechanisms controlling Li and Mg uptake in the solid are not the same.

Future of the project: The results obtained suggest that the growth rate has a significant impact on the distribution of Li and Mg in aragonite. The experiments performed in this study are the first step towards understanding the mechanisms controlling trace element composition in natural samples. Current and future work aims at investigating how mineral growth rate and temperature affect the isotopic composition of these solids as well, as the role of complexation with inorganic and organic ligands. These parameters are important for reconstructing formation conditions in natural environments.

Number of publications, communications and theses

Mavromatis V., Brazier J.-M., Goetschl K. (2022) Controls of temperature and mineral growth rate on Mg incorporation in aragonite Geochim. Cosmochim. Acta 317, 53-64.

Mavromatis V., Brazier J.-M., Goetschl K.E (2022) Controls of temperature and mineral growth rate on Mg incorporation in aragonite, Goldschmidt 2022, Hawaii, USA.

Brazier J.M., Harrison A. L., Rollion-Bard C., Mavromatis V. (2024) Controls of temperature and mineral growth rate on lithium and sodium incorporation in abiotic aragonite (ChemGeol under review)

<u>Conference session organization:</u>

Castillo-Alvarez M.C., Uchikawa J, Mavromatis V. (2022) Metal traces and their isotopes in carbonate minerals as tools for environmental reconstructions Goldschmidt Conference Hawaii, USA, 10-15/07/2022.

Harrison A, Mavromatis V. (2022) Mineral-fluid interactions at Earth's surface: Thermodynamics, kinetics and isotopes. International Mineralogical Association Meeting, Lyon, France 18-22/07/2022.

Data availability:

All data produced in this study are included in the associated publications. Note that following open-access policy the final text of the publications can be found in HAL.