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Mg isotope fractionation during calcite precipitation: an experimental study.

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It has been shown that the oceanic Mg/Ca ratio varied significantly over geological times (Wilkinson et Algeo, *Am. J. Sci.* 1989 ; Hardie, *Geology* 1996 ; Stanley et Hardie, *Paleog. paleoclim. paleoeco.* 1998 ; Horita et al., *GCA* 2002), but no consensus exists to explain these variations. They could result of a combination of variations of (1) the hydrothermal inputs from alteration of the oceanic crust (Hardie, *Geology* 1996 ; Tipper et al. *EPSL* 2006b) and of (2) the dolomitization rate of sedimentary carbonates (Carpenter and Manella, *J. Geophys Res.* 1973 ; Horita et al, *GCA* 2002). Recent studies have shown the potential of Mg isotopes in carbonates to provide essential information on the Mg oceanic cycle (Carder et al., *GCA* 2005; de Villiers et al., *Chem. Geol.* 2005; Pogge von Strandmann, *EPSL* 2008; Higgins and Schrag, *GCA* 2009, 2010; Hippler et al., *GCA* 2009; Rose-Koga and Albarède, G^3 2010). However, it is necessary to better understand how carbonates record ocean Mg isotope composition. We have thus designed an experimental system to study Mg isotope fractionation during calcite precipitation, under various environmental conditions.

A precipitation system of inorganic calcite was developed, according to the experimental system of Lemarchand et al. (*GCA* 2004). 13 experiments were conducted under different experimental conditions (pH between 7.40 ± 0.07 and 8.51 ± 0.39, and Mg/Ca between 0.1 and 0.4 mmol/mol). Temperature was kept constant for all the experiments at a value of 25.25 ± 1.31 ˚C Precipitated crystals were characterised using different analytical methods (RAMAN, SEM, XRD). Mg and Ca concentrations were measured using ICP-AES and electron microprobe. Mg isotope compositions were measured using MC-ICP-MS (ENS-Lyon, France) after classical chemical separation (Bolou-Bi et al, *GGR* 2009).

In all the experiments performed, the most abundant precipitated phase is calcite. However, other minor crystal phases were also observed, mainly aragonite, and sometimes magnesite. Most of the experiments lead to a Mg isotope fractionation ($\Delta_{calcite-solution}$) of -2.2%¸ ± 0.2 ‰ (n=5), including some experiments resulting in the precipitation of three different phases (calcite, aragonite, magnesite). Our results show a negligible role of pH and of the mineralogy on the Mg isotope fractionation. For the aragonite, in situ measurements of Mg contents confirm very low Mg partition coefficients with our experimental conditions (D $<$ 0.005 ± 0.002). Simple mass balance shows that 80% of aragonite would be needed to change significantly the isotope composition of the bulk carbonate fraction. Such a proportion was never observed. The Mg isotope composition of the solution in four experiments, for which a large amount of dissolved Mg was removed by calcite precipitation, follows a Rayleigh trend with a Mg isotope fractionation of -2.2± 0.4 ‰This value is consistent, within errors, with values previously found (from -2.2 ± 0.1 ‰ to -2.7± 0.2 ‰ ; Galy et al., *EPSL* 2002; Hippler et al., *GCA* 2009; Kisakürek et al., *GCA* 2009; Immenhauser et al., *GCA* 2010). Four of our experiments lead to calcites with δ^{26}Mg higher than expected for $\Delta_{calcite-solution}$=-2.2‰ which would correspond to significantly reduced isotope fractionation (between -1.97%¸ ± 0.24 ‰ and -1.39%¸ ± 0.18 %¸). No direct correlation is observed with pH, Mg/Ca, or mineralogy. The δ^{26}Mg of these carbonates may be affected by the presence of fluid inclusions, or kinetic effects. These aspects still need to be investigated in more details.