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# 1 Mg isotopes fractionation processes in marine calcareous skeletons: methodology developments and preliminary results on echinoderms (sea urchin and starfish)

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Mg incorporation into marine biogenic carbonates is associated to a pronounced mass dependent Mg isotopic fractionation. Favouring light isotopes uptake compared to the bulk seawater and showing large differences between various species producing calcitic or aragonitic skeletons, the few available Mg isotopic signatures for marine biominerals tend to suggest that both environmental and biological parameters are influencing the Mg fractionation processes. Such influences are still to be clearly understood and deciphered in order to better constrain Mg isotopes as potential paleoceanography proxies and also to help identifying Mg assimilation pathways into marine organisms.

In the frame of both CALMAR II and PALEOSALT projects, we have successfully developed the methodology for precise and accurate analyses of Mg isotopes in a diversity of environmental samples such as seawater, freshwater, biogenic and inorganic carbonates, and biological samples. Special attention was given to set up a sample preparation protocol dedicated to low size and Mg content. Using ultra clean laboratory conditions, adequate cleaning procedures and reagents preparation, we have developed a one step resin extraction for Mg purification. The blanks in the range of $\sim$100 picograms are consistently lower than published methodologies and allow us

working with a critical Mg mass of 100 ng. In addition, significant analytical improvements were also performed on the Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS, Nu instruments). Equipped with a desolvation sample introduction unit (Aridus, Cetac) and a high performance interface pump, we got a precision of 10 ppm in terms of relative standard error on the measured ratio $^{26}Mg/^{24}Mg$ for a 50 ng/g Mg concentration. Such a running concentration appears to be one order of magnitude lower than literature analytical conditions. Using the bracketing technique with the isotopic certified reference material DSM3, the determination of the relative isotopic composition of a seawater sample expressed in ($\delta^{26}$Mg in per mil) shows a good accuracy ($\delta^{26}$Mg: -0.84 ‰ compared to the published value of -0.82 ‰) and also a good reproducibility (0.1 ‰ on $\delta^{26}$Mg for 10 measurements).

The analytical procedure is currently applied to the isotopic composition of different biogenic carbonates such as starfishes and sea urchins as part of the CALMAR II project. Preliminary results on their Mg isotopic composition will be presented and discussed.