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High variability in boron isotopes of deep-sea corals (*Lophelia pertusa*): implications for biomineralization processes and for paleo-pCO_2 reconstruction.

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The deep-sea coral *Lophelia pertusa* is a scleractinian coral (azooxanthellate) found on the continental margins of the major world oceans. Its aragonite skeleton can be precisely dated and measured for stable isotope composition (C-O) to reconstruct past oceanic conditions. O-C isotopic data obtained at a micrometer scale using either Secondary Ion Mass Spectrometry (SIMS) (Rollion-Bard et al., 2003; Blamart et al., 2005) or micromilled samples (Adkins et al., 2003) and taking into account the skeleton microstructures, i.e. centres of calcification (COC) and surrounding fibres, exhibit large O-C isotopic variations. These variations have been interpreted in term of pH variations during and/or at the site of calcification. To document the boron isotopes behaviour in deep-sea coral we have performed several SIMS delta-11B profiles cross cutting the two main microstructures of the skeleton. With this technique the precision is about 0.5‰.

Within the entire data set δ^{11}B ranges from 28.5 to 38.5‰, which is twice the variation obtained from TIMS or MC-ICPMS on similar samples. The δ^{11}B values of COC

range from 27.1 to 33.6 with a mean value of 31.2 (n=19). The δ^{11}B values for the surrounding fibres are systematically heavier, ranging from 33.2 to 38.5‰ with a mean value at 35.8‰. Delta-11B values appear strongly correlated with the microstructure of the coral skeleton. This conclusion was also reached by Rollion-Bard et al. (2003), based on analyses of zooxanthellate corals. From the δ^{11}B values, we have calculated the pH value at the site of calcification. We used a value of delta-11B of seawater of 39.5‰, a fractionation factor (3-4) of 0.974 and a pKA of 8.8. If a fractionation factor (3-4) of 0.981 is used in the calculation the resulting pH values are lower by about 0.2‰. We calculate a mean pH value of 9.2 ($\pm$0.1) for the COC and 9.6 ($\pm$0.2) for the surrounding fibres. These calculated values are within the range measured with microelectrode (Vengosh et al. 1991) or by microsensor on calicoblastic layers (8.2 and 9.3; Al-Moghrabi et al. 2001) of zooxanthellate corals.

As is the case for the C and O isotopes, the boron isotopic composition of the COC appears to have a narrow range of variation and the lowest associated pH values compared to surrounding fibres. If we assume that the pH is the only parameter driving the C-O-B isotopic variations, then COC should be characterized by the highest pH values during their formation, which is not observed. This implies that COC and surrounding fibres are precipitated by different mechanisms, which are controlled by specialized domains of the calicoblastic cell-layer. With respect to biomineralization model, the two distinct δ^{11}B values in COC and surrounding fibres provide additional evidence of a sharp limit between two specialized domains of the calicoblastic cell-layer. Such a limit could not exist if the subectodermal space was a wide volume of fluid with homogenous composition close to sea water, as usually admitted .

From these results it is clear that the use of δ^{11}B in biocarbonates and especially in (deep-sea) coral to reconstruct paleo-pCO_2 is not straightforward. Delta-11B values derived from bulk samples will correspond to the proportion of COC and Surrounding fibres rather than a proxy for paleo-pCO_2 reconstruction.