An improved sampling method for coral P/Ca as a nutrient proxy

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The geochemical composition of the aragonite exoskeleton of corals is a valuable tool for paleoceanographic studies. Cold-water corals are particularly promising archives for sub-decadal scale resolution of intermediate and bathyal depth oceanic variability.

Recently, the P/Ca ratios have been proved to be a direct seawater nutrient proxy in azooxanthellate [1] and zooxanthellate corals [2], opening new perspectives to quantify the fluxes of nutrients and past ocean productivity.

Further studies on the phosphorus speciation in inorganic and coral aragonite [3] identified the presence of small quantities of hydroxylapatite inclusions, which could potentially complicate the P/Ca intepretation. Based on these findings we decided to investigate the skeleton of the cold-water species *Desmophyllum dianthus* following a new sampling strategy.

We analysed the P/Ca ratios for different coral specimens using a high sensitivity laser ablation ICPMS. A 105 µm diameter spot was focused both on the outer septal surface and along the cross-section of the septum, considered the most pristine portion not affected by hydroxylapatite. Adjacent septa of the same specimen dislay similar P/Ca variation pattern, both along the cross-section and on the outer septal surface, but with lower values for the former. The P concentrations obtained by sampling the fibrous aragonite of the cross-section are more consistent with a P incorporation as phosphate defects in aragonite [3].

The application of this improved sampling strategy offers the possibility to avoid hydroxylapatite inclusions or any additional crystalline phosphate phases present in the outer surface, yielding most accurate paleo-environmental reconstructions.

[1] Montagna *et al*. (2006) *Science* **312**, 1788-1791. [2] LaVigne *et al*. (2008) *Geophys Res Letters* **35**, 10.1029/2007GL031926. [3] Mason *et al*. (2007) *EOS Trans. AGU* **88**(52).

Reconstructing atmospheric $p\mathrm{CO}_2$ in the deep-time: Constraints and limitations

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As our climate system departs from the well-studied Pleistocene glacial-interglacial cycles, a 'deep-time' perspective of $p\mathrm{CO}_2$-climate-glaciation linkages during past icehouse-to-greenhouse transitions is required in order to fully explore potential linkages between atmospheric CO_2 and feedbacks and other forcings of the global climate system. Reconstructing deep-time atmospheric CO_2 is challenging given the applicability of proxy methods given complications of diagenetic overprinting and the lack of appropriate calibrations. Here the evolution of atmospheric CO_2 over the ~75 million year period of the Late Paleozoic Ice Age is constrained using the carbonate mineral paleobarometer – a technique with lower resolution but the only one applicable to intervals with $p\mathrm{CO}_2 \geq 500$ ppmV. The potential of this approach is documented by allowing input parameters to vary temporally, using populations of contemporaneous paleosols to constrain interval values. To estimate soil $p\mathrm{CO}_2$, a variable to which the paleobarometer model is very sensitive and which has limited past applications of the mineral paleobarometer, we apply the $\delta^{13}\mathrm{C}$ values of pedogenic carbonates and their occluded fossil organic matter to a two-component mixing equation to solve for changes in soil CO_2 during soil formation. Resulting estimates are used to independently constrain a conservative range of soil $p\mathrm{CO}_2$ for our modeling of atmospheric $p\mathrm{CO}_2$ that effectively corrects for large changes in soil conditions and productivity. The Late Paleozoic reconstruction reveals repeated fluctuations in atmospheric CO_2 contents, with increases from present-day levels to ≥1000 ppmV associated with glacial minima or intermittent periods of greenhouse conditions.