Boron isotope systematics of pH regulation in cold-water corals and resilience to ocean acidification

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Cold-water corals are thought to be especially vulnerable to CO_2-driven climate change and ocean acidification because they live close to the aragonite saturation horizon, which is now rapidly shoaling as anthropogenic CO_2 penetrates into the deep oceans. Due to the sensitivity of calcification to saturation state, this may not only lead to decreased calcification rates but also dissolution of deep-sea calcifiers.

Here we report boron isotopic measurements of cold-water corals representing a wide range of deep-sea and shallow-water environments. These zooxanthellate aragonite corals are all found to have relatively high $\delta^{11}B$ compositions, lying significantly above the seawater borate equilibrium curve. The internal pH of the solitary coral *Desmophyllum dianthus*, determined from the measured $\delta^{11}B_{carb}$ compositions, defines a highly correlated linear array with seawater pH. This relationship, indicative of internal (extracellular) up-regulation of pH at the site of calcification [1], corresponds to a differential pH (ΔpH) of ~0.7 to 0.8 units above ambient seawater. As a consequence the aragonite saturation state of the calcifying fluid is increased approximately two to five-fold, facilitating calcification in low pH environments. This contrasts with the hyper-calcifying tropical zooxanthanlate corals that operate within a significantly lower range of ΔpH values from 0.3 to 0.4 units [1], indicating the importance of temperature on the kinetics of inorganic calcification. These new observations suggest that the effect of declining carbonate saturation state in the deep-oceans may be partially offset by the combined effects of biological up-regulation of internal pH and enhanced rates of calcification from higher ocean temperatures.

[1] Trotter *et al.* (2011) *Earth Planet Sci Lett.* **303**, 163–173.

Origin and composition of LLSVPs in the lowermost mantle

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The structure of the lowermost mantle (D”) is dominated by spherical harmonics degree-2 variation with two anti-podal Large Low Shear-Velocity Provinces (LLSVPs) [1]. Their locally steep margins may be favourable sites for the generation of mantle plumes, giving rise to large igneous provinces, and even kimberlites, with ages covering the last 540 Ma [2-4]. The LLSVPs are probably thermochemical piles with sufficient density to resist thermal buoyancy and destruction. Steep margins could be promoted by elevated bulk modulus of the pile material [2].

The piles may be enriched in meta-basaltic material with high density caused by high Fe/Mg ratio in perovskite and high bulk modulus associated with the presence of stiff silica minerals and absence of soft ferropericlase [5, 6]. Peridotite or komatiite with elevated Fe/Mg may be alternative materials in the piles. The origin and age of the LLSVPs are probably linked to the nature of the material. Accumulation of basaltic rocks from subducted slabs could occur slowly in the plume generation zones near the LLSVP-margins over 3-4 Ga [7]. Emplacement of komatiitic or peridotitic material with elevated Fe/Mg, however, could have occurred early, either during the final solidification of a lowermost mantle magma ocean [8, 9] or by sinking of solidified material from a melt accumulation zone (by buoyancy) at 400 km depth [10]. Melting in hot Hadean or Archean plumes may have been widespread at 20-25 GPa where the peridotite solidus is at relatively low T [11, 12]. The psedo-invariant melt compositions at $p > 15$ GPa are poorly constrained and may be relatively silica-rich at 23-30 GPa, where ferropericlase is the liquidus phase [11-13]. A systematic melting study of a range of simplified compositions will provide further insights.

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