The future of marine calcifiers in a high CO₂ world: Boron isotope systematics of pH up-regulation

M.T. MCCULLOCH^{1,2}, J.A. TROTTER¹, J. FALTER^{1,2} AND P. MONTAGNA³

 ¹The University of Western Australia Oceans Institute and School of Earth and Environment, Western Australia
²ARC Centre of Excellence in Coral Reef Studies, UWA
³Laboratoire des Sciences du Climat et de l'Environnement, Av. de la Terrasse, 91198, Gif-sur-Yvette, France

Rising atmospheric CO_2 is not only causing global warming, but also lowering the oceans pH and hence carbonate ion concentration upon which many marine organisms depend to calcify their skeletons. Declining calcification rates combined with an increased frequency of coral bleaching from unusually high seawater temperatures has the potential to cause major disruption to marine ecosystems. Which marine calcifiers can sustain skeletal development as pCO_2 increases is however highly uncertain. Here we present new boron isotopic constraints on the degree of physiological control of the pH of the calcifying medium. Biological up-regulation of pH is linked to abiotic calcification rates using the inorganic kinetics of carbonate precipitation.

Boron isotope systematics of aragonitic corals show a species dependent ability to up-regulate the pH at their site of calcification, with changes in internal pH being approximately one-half of those in ambient seawater [1]. This pH buffering capacity is present in both non-symbiont and symbiont bearing aragonitic corals and serves to raise the saturation state of the calcifying fluid, thereby increasing their potential rate of calcification. The ability of biogenic calcifiers to raise the internal saturation state via pH up-regulation is not however ubiquitous, being absent for example in many key species of calcitic foraminifera. Ocean acidification and global warming are thus likely to cause a major bi-polar shift in the abundance and distribution of marine calcifiers. Those that lack internal pH regulation will continue to undergo rapid declines, while in cold-water corals enhanced rates of aragonite precipitation from pH elevation and rising temperatures has the potential to counter the effects of decreasing seawater pH. However the ability of tropical corals to maintain calcification rates by pH up-regulation will mainly depend on their capacity to adapt to thermal stress caused by rapid increases in ocean temperatures.

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

Interfaces and exchange coupling

S.A. $MCENROE^1$, P. $ROBINSON^1$, K. FABIAN¹, R.J. HARRISON², N. MIYAJIMA³ AND F. LANGENHORST³

 ¹Geological Survey of Norway, Trondheim 7041 Norway (*correspondence, suzanne.mcenroe@ngu.no)
²Cambridge University, Cambridge, UK
³BGI, Universitaet Bayreuth Bayreuth Germany

Natural oxides in the ilmenite-hematite system are now known to have contact layers [1] at the interface between the two phases. Contact layers, reduce charge imbalance at interfaces [2] and result in magnetic properties that are different from the bulk host or lamellae. Magnetic coupling across interfaces provide a mechanism for the stability of extremely small lamellae. These samples with lamellae < 1nm thick show exchange bias with shifted hysteresis loops more than 13, 000 Oe. This shift is the largest that has ever been measured in any material, natural or synthetic.



Figure 1: Shifted hystereis loop measured at 5 K. [3]

Combined TEM analyses and images with lowtemperature magnetic studies are powerful tools to describe the chemical, structural and electronic nature of the interfaces. To date these are the smallest stable magnets ever known. There is wide interest in under-standing these natural samples and their interfaces, which may well provide blueprints for future technological designs.

[1] Robinson *et al.*(2002) *Nature* **418**, 517–520. [2] Robinson *et al.*(2006) *Am Min.* **91**, 67–72. [3] McEnroe *et al.*(2007) *Nature Nanotechnology* **2**, 631–634.

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