

Boron isotope measurements of marine carbonate using MC-ICPMS

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Atmospheric CO₂ (pCO₂) plays a critical role in regulating the Earth's climate on geological timescales. Atmospheric pCO₂ is set by oceanic carbonate equilibria which both control and track its evolution. A reliable proxy for the state of the ocean carbonate system is thus highly desirable for understanding the evolution of the Earth's climate. Of particular importance in this regard is the boron isotopic proxy for ocean pH. This powerful tracer can be further combined with measurements of boron concentration (B/Ca) to fully constrain ocean carbonate equilibria.

The B isotope pH proxy has previously been explored, but its reliability has been questioned. The pH dependence of the boron isotope ratio of marine carbonate is firmly based in inorganic chemistry and a clear-cut test of its accuracy can be made given a knowledge of the isotopic fractionation between the two aqueous boron species. Such a test has been hindered so far by uncertainty in the fractionation factor in seawater (estimates ranging from 1.016 to 1.030). Recent experimental work, however, has determined the value to be 1.0272 [1]. This now provides a valuable independent means to test the fidelity of the proxy.

At the same time, advances in multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) allow a new approach to boron isotopic analysis that overcomes many of the problems associated with thermal ionisation (TIMS) measurements. Our new MC-ICPMS technique is rapid (10-20 analyses per analytical session), precise (better than 0.25 ‰ on full procedural replicates at 95 % confidence) and has relatively small sample size requirements (~10 ng per analysis). MC-ICPMS analysis requires B separation chemistry prior to analysis which also serves to remove any possible bias between samples with different matrices.

In contrast to previous work we find that the measured isotopic compositions of a variety of Holocene foraminiferal species from a number of locations are very close to that of the dissolved B(OH)₄⁻ predicted using the fractionation factor of 1.0272 [1]. This result greatly simplifies the use of the proxy and confirms that δ¹¹B, particularly when coupled with B/Ca, may provide valuable constraints on the ocean's carbonate system in the past.

[1] K. Klochko, A.J. Kaufman, W. Yao, R.H. Byrne & J.A. Tossell (2006) *Earth Planet. Sci. Lett.* **248**, 261-270.

Cubomedusae statoliths: Potential recorders of environmental change?

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Sclerochronology is a rapidly growing field for climate and environmental reconstruction. The use of trace elements in biogenic precipitates especially carbonates (e.g. corals and sclerosponges) for climate reconstruction is well documented. Increasingly, trace element fluctuations in carbonates of non-sessile organisms are being used to understand their behaviour and life cycle. For example otoliths from fish are being used as tracers for seasonal migration [1].

In contrast to many other medusae (e.g. *Aurelia aurita*) cubomedusae form statoliths which deposit daily growth rings [2] and thus have the potential for high resolution environmental reconstruction. Statoliths from cubomedusae are composed of calcium sulfate hemihydrates [3]. Calcium sulfate and its hydrates are generally extremely rare in biomineralization [4]. Jellyfish have been present in the marine planktonic ecosystem for >500 Ma [5] and are considered among the most primitive organisms that concentrate calcium at the cellular level [6]. Studies on various marine biominerals, which contain Ca as a major cation, could be of particular benefit to research on the effects of ocean acidification.

In this poster we present the first results of trace element variation in statoliths from cubomedusae, which may provide information about the behaviour and migration of the organism. This is important due to increasing dominance of jellyfish in ecosystems [7] and their ecological niche as predators. Electron microprobe chemical mapping indicates that there are significant changes in K, P and Na across the statoliths at specific growth bands. These preliminary findings indicate that the controls on trace element variation may be complex and requires further study.

[1] Campana *et al.* (2007) *Can. J. Fish. Aquat. Sci.* **64** 6-18.
[2] Ueno *et al.* (1995) *J. Plankton Res.* **17(6)** 1381-1384.
[3] Tiemann *et al.* (2006) *Zool. Anz.* **245(1)** 13-17. [4] Becker *et al.* (2005) *Dalton Trans.* **8** 1545-1550. [5] Cartwright *et al.* (2007) *PLoS ONE* **2(10)** e1121. [6] Spangenberg *et al.* (1968) *J. Exp. Zool.* 169 487-500. [7] Lynam *et al.* (2006) *Curr. Biol.* **16(3)** R492.s