

## A critical review and recent advances in the boron isotope paleo-pH proxy

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Proxy development inevitably involves an initial success where a simple application seems to work perfectly, followed by many years of investigating the complications. After 16 years, the boron isotope paleo-pH proxy remains promising if carefully applied. It is clear that the first order control on the boron isotope composition of marine calcium carbonate is the pH of seawater. Other influences such as temperature, pressure, salinity, alkalinity, kinetics (vital effects and life cycle influences, precipitation rate), and preservation (diagenesis) need to be understood to use the proxy with confidence. Premature applications without consideration of these factors (as well as data quality), has only complicated proxy development.

Our group has focused on ground-truthing through survey studies of modern marine carbonates, core top studies<sup>1</sup>, culture experiments under controlled conditions (foraminifera and corals<sup>2</sup>), and synthetic carbonate mineral growth experiments (in progress). Core top studies have shown previously unknown dissolution and shell size effects which can be avoided with careful sample selection. With this knowledge, surface ocean pH (and aqueous PCO<sub>2</sub>) has been confidently determined in late Quaternary samples where the isotope composition of seawater can be assumed constant. A remarkable covariation of the foraminiferal boron isotope composition with climate records of atmospheric pCO<sub>2</sub> and marine oxygen isotopes bears this out.

### References

- [1] Hönisch, B. & Hemming, N.G. (2004). *Paleoceanography* **19**. doi:10.1029/2004PA001026
- [2] Hönisch, B. et al. (2004). *Geochim. Cosmochim. Acta* **68**. 3675-3685.

## Isotopes in Paleozoic carbonate components: An evaluation of proxies

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Brachiopods, trilobites, cement and whole rock were evaluated for their reliability as proxies of original seawater carbon, oxygen and strontium isotope chemistry. Coeval material was evaluated from horizons of formations spanning the Permian to Cambrian.

Unaltered shells of low-Mg calcite articulated brachiopods retain original seawater oxygen, carbon and strontium isotope compositions, as old as late Ordovician. Assessments of older specimens are hampered by a lack of suitable material (coeval brachiopod-whole rock sets). A definitive assessment of cement marine chemistry is difficult due to the paucity of material, but despite this caveat, cements hold some promise for retaining original carbon and possibly strontium isotope seawater values. The potential of whole rock material as a proxy of original seawater chemistry is quite complex. In some, but not all instances, the carbon isotopic composition of whole rock, after detailed scrutiny and evaluation, appears to represent an original seawater chemistry signal. In few instances their oxygen isotope compositions reflect original seawater values. Unlike the stable isotope compositions, strontium isotopes of all studied whole rock material (Permian to upper Cambrian) do not reflect original seawater chemistry values. Thus the potential for retaining original seawater isotope chemistry and serving as proxies, in order of decreasing reliability, are 1) unaltered low-Mg calcite brachiopods (C, O & Sr isotopes), 2) pristine marine cements (C & Sr isotopes), and 3) whole rock material (C isotopes ?).

Carbon, oxygen and strontium isotope compositions of Ordovician trilobites mirror those of coeval unaltered brachiopods. Cambrian trilobites hold significant promise as an important proxy of original-seawater isotope chemistry but further studies are needed to ascertain their full potential. The survey of isotopes in some Ordovician and Cambrian intermediate/low-Mg calcite trilobites demonstrates their potential as an important proxy of original seawater chemistry.