Lithium in Brachiopods – proxy for seawater evolution?

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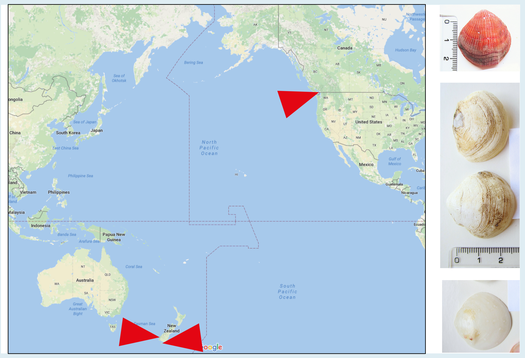
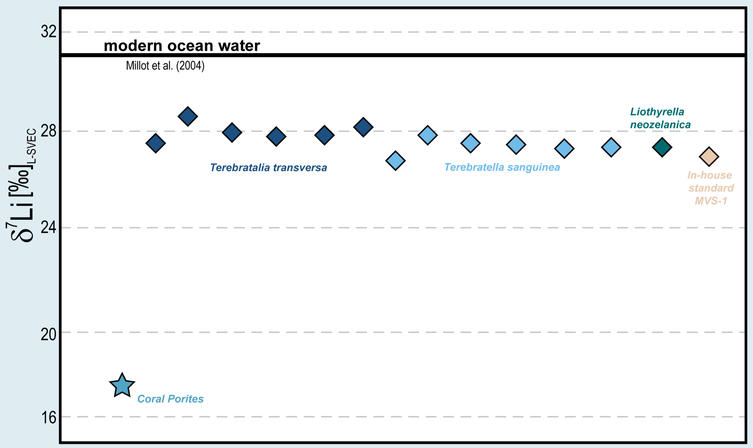
INTRODUCTION

Marine biogenic carbonates have the potential to serve as a proxy for evolution of seawater chemistry. In order to compile a record of the past and recent δ^7Li in the oceans, foraminifera shells, scleractinian corals and belemnites have been used. However, only a foraminifera-based record appears to more accurately reflect the Li isotope composition of ocean water. At present, this record is available for the Cenozoic with implications for major events during this period of time, including K/T event [1]. A record for the entire Phanerozoic has not yet been obtained. In order to extend this record to the more distant past, Lithium elemental/isotope systematics of brachiopods were investigated.

WHY BRACHIOPODS?

Brachiopods have one of the longest and richest geological record of marine invertebrates, first documented findings date back to the Early Cambrian. The phylum has been divided into three subphyla: the Linguliformea, Craniiformea and Rhynchonelliformea. However, only the last two build carbonate shells, the shells of the Linguliformea, with the famous recent representative Lingula, are phosphatic. The carbonate shells consist of low-Mg calcite which is less sensitive to diagenesis-induced modifications than other carbonates.





METHODS

SAMPLES

The samples included calcitic shells from recent brachiopods collected near the San Juan Islands (San Juan Channel) and in New Zealand (Doubtful Sound/Tricky Cove, Paterson Inlet) as well as fossil shells from the J. Veizer collection at the GEOMAR. The recent samples comprise three different species: Terebratalia transversa, Terebratella sanguinea and Liothyrella neozelanica.

SAMPLE PREPARATION

The recent brachiopod shells were cleaned with H_2O_2, ground to powder and dissolved with HCl and HNO_3. Lithium was separated from matrix elements by a single-step column chemistry following [2]. Fossil shells were already cleaned from previous work, and were processed directly for column separation.

MEASUREMENTS

Trace element measurements were carried out using an Agilent 7900 ICP-MS and Li isotope measurements using a Neptune MC-ICPMS connected to an Aridus 2 desolvating nebulizer.

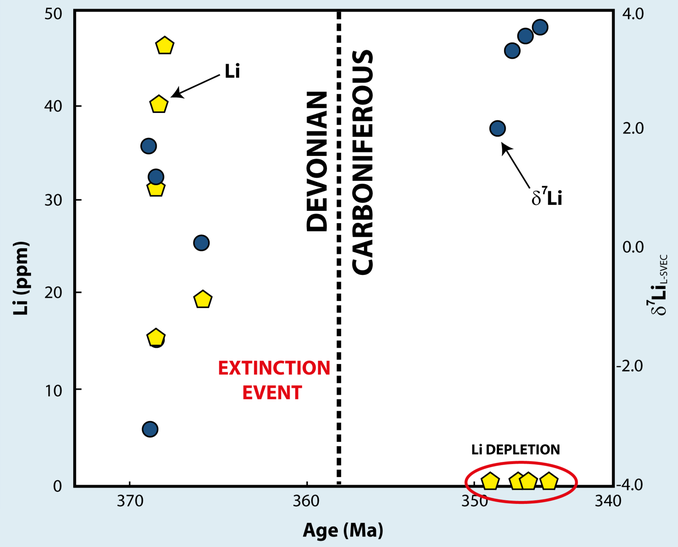
RESULTS

MODERN BRACHIOPODS

Lithium is a trace element that is marginally incorporated into brachiopod shells. The analyzed modern shells show ~2 ppm Li, with only Liothyrella neozelanica having ~1 ppm Li, which perhaps reflects a large proportion of tertiary layer. The δ^7Li values of modern brachiopods were consistent at ~27-28‰, irrespective of depth, pH and temperature and with no intra-shell variability. This value is in agreement with the ≈3‰ difference between growth solution and inorganic calcite [3].

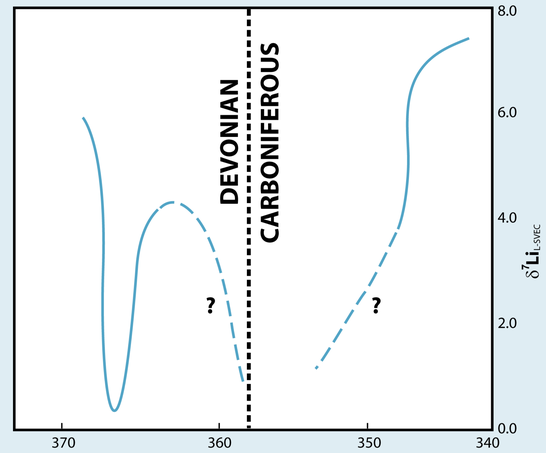
FOSSIL BRACHIOPODS

Fossil brachiopods show a significant variation in Li contents – Devonian samples have >15 ppm Li whereas Carboniferous brachiopods have systematically low Li <1 ppm. Large variations in ^{7}Li/^{6}Li ratios are observed towards the end of the Devonian whereas a systematic recovery of δ^7Li values in the Carboniferous is observed.



IMPLICATIONS

- The enrichment of Li in brachiopods compared to seawater is approximately tenfold (0.18 ppm seawater – 2 ppm brachiopods). The high Li contents in the Devonian brachiopod shells suggest that the seawater also had much higher Li contents (40 ppm brachiopods – 4 ppm in seawater?). The depletion in the Carboniferous points to low Li concentrations in ocean water.
- High Li contents in Devonian seawater could be linked to extensive weathering through the warm climate with sea surface temperatures 10-15°C higher and atmospheric CO_2 levels 14-24 times greater than today [4].
- Increased weathering rates are possibly related to continental plant evolutionary events.
- Uniformly low Li contents in Carboniferous ocean water could reflect a decreased influx of continental material



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