Latitudinal gradient in $\delta^{18}O$ of Permian brachiopods

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Oxygen isotope values of calcareous shells of articulated brachiopods are often utilised to estimate paleoseawater temperatures because the secondary layer of these organisms are rather resistant to diagenetic alteration, and the degree of alteration can be evaluated by optical and chemical techniques [e.g., 1, 2]. Although, Auclair et al. [3] in one modern intertidal specimen observed deviations of several permil for oxygen isotopes, the norm for the secondary brachiopod layer are $\delta^{18}O$ values mostly within ±1‰ of isotopic equilibrium with ambient seawater [4, 5].

Here we present new oxygen isotope data of Permian articulated brachiopods from Pakistan and Australia which were deposited at latitudes greater than 45°S. These high-latitude brachiopods were compared to coeval low latitude and warm water counterparts [2]. The $\delta^{18}O$ values of high-latitude late Permian brachiopods from Pakistan are between −1.0 and −3.0‰, and, on average, are 0.8‰ heavier than coeval low latitude counterparts. Calculated temperatures of Permian seawater of Pakistan were on average 3-4°C cooler than that of coeval low latitudes. The high-latitude Australian brachiopods yield oxygen isotope values ranging from +1.0 to −2.6‰. These values are about 2.0‰ heavier than those of their low latitude counterparts suggesting that high latitude paleoseawater was up to 9°C cooler. Moreover, the temporal early Permian melting of continental ice and consequent ice-volume impact on the oceans of about 2.0‰ $\delta^{18}O$ documented by low latitude brachiopods [2] is also observed by their high latitude counterparts.

The Permian brachiopod datasets demonstrate for the first time significant differences in oxygen isotope values between low and high latitude seawater.

References

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Oxygen isotope exchange between calcite and water: An experimental study

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Analysis of oxygen isotope composition in carbonate fossils is a widely used method to quantitatively estimate palaeotemperatures. Considerable information about oxygen isotope fractionation between calcite and water already exists in the literature but there is still no consensus on equilibrium fractionation magnitude and on the role of calcite precipitation rate. The aim of this work was to study oxygen isotope fractionation between water and precipitated calcite under strictly controlled experimental conditions. Precipitation experiments were carried out using the constant addition technique at 25° C.
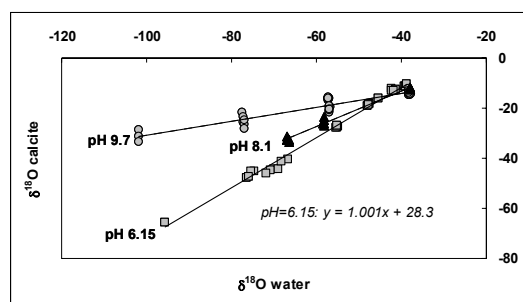

Fig 1 shows the equilibrium relation between calcite and water $\delta^{18}O$ compositions at different pH.

1) the lines have nearly one intersection point ($\delta^{18}O_{cc}$ ~ -14‰) that corresponds to $\delta^{18}O$ of Na_2CO_3 in the source input solution;

2) the slope of the lines representing fraction of isotopic exchange increases as pH decreases and approaches 1 (equilibrium) at pH close to 6;

3) line with the slope 1 corresponds to the value $\Delta_{(cc-w)} \approx$ 28.3 ‰ that is very close the equilibrium value.

Disequilibrium at higher pH means that calcite precipitation outpaces oxygen isotope equilibriation with water, that is, precipitation is fast enough that CO_3^{2-} units in the crystal are buried before they isotopically equilibrate with H_2O. Because the calcite surface is largely equilibrated isotopically with CO_3^{2-} in the solution, isotope equilibration is likely prevented by slow isotopic exchange between dissolved CO_3^{2-} and H_2O.