

## Volcanogenic massive sulfide deposits host the evidence for sulfate-rich Archean oceans

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Recent researchers have suggested that the Archean oceans were sulfate poor (<0.1 mM SO<sub>4</sub><sup>2-</sup>, compared to 28 mM today), because the atmosphere was supposedly poor in O<sub>2</sub> (pO<sub>2</sub> < 10<sup>-6</sup> atm) to completely oxidize the sulfur-bearing volcanic gases (H<sub>2</sub>S and SO<sub>2</sub>) and sulfide minerals in soils to SO<sub>4</sub><sup>2-</sup>. However, such a scenario cannot explain the abundance of pyrite of Archean ages, much like those of younger ages, because these pyrites most likely formed by bacterial (or thermochemical) reduction of seawater SO<sub>4</sub><sup>2-</sup>.

One of the strongest lines of evidence for SO<sub>4</sub><sup>2-</sup> rich Archean oceans comes from volcanogenic massive sulfide (VMS) deposits and alteration zones in their host rocks. VMS deposits, such as the black smoker deposits on MORs, formed on and beneath the seafloor by reactions between submarine hydrothermal fluids (typically ~50° to ~450°C) and the local seawater. The hydrothermal fluids evolved mostly through reactions between the underlying volcanic rocks and deep-circulating seawater, rather than derived directly from magmas. Therefore, the mineralogy and geochemistry of VMS deposits and their alteration zones reflect the chemistry of the contemporaneous ocean water. Phanerozoic VMS deposits are characterized by the abundance of pyrite and sulfate minerals, and by increased Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios in the alteration zones due to the involvement of sulfate-rich seawater: some of the H<sub>2</sub>S used to form the pyrite was generated by reduction of seawater sulfate by FeO components in rocks, resulting in the increases of Fe<sup>3+</sup>/Fe<sup>2+</sup> ratios. The ~3.2 Ga Panorama Formation of Western Australia hosts many VMS deposits with mineralogy, geochemistry, and associated alteration zones that are essentially identical to those of Phanerozoic ages, suggesting that the processes of submarine mineralization and the sulfate content of the seawater at 3.2 Ga were essentially the same as today.

Many other Archean VMS deposits and their alteration zones host barite (BaSO<sub>4</sub>), such as the ~3.46 Ga Big Stubby deposits in Western Australia, the 3.26 Ga Fig Tree deposit in South Africa, the 2.6 Ga Geco deposit in Canada, and the 2.7 Ga Hemlo deposits in Ontario, Canada, suggesting that the Archean oceans remained sulfate-rich. The only major difference between the sulfate in the Archean oceans and that in the Phanerozoic oceans was the δ<sup>34</sup>S values, between +2 and +5‰ during the Archean, but between +10 and +35‰ for the Phanerozoic. This difference has caused the δ<sup>34</sup>S values of sulfides in Archean VMS deposits to be less than +5‰, where as those of Phanerozoic ages could be higher than +5‰, because the H<sub>2</sub>S in the hydrothermal solutions came from the leaching of sulfides in igneous rocks (δ<sup>34</sup>S ≈ 0‰) and from the partial reduction of seawater sulfate. These data suggest that the Archean oceans were as sulfate-rich as today's oceans due to the weathering of pyrite in rocks under an O<sub>2</sub>-rich atmosphere.

## Oxygen isotopes & Mg content in brachiopod calcite: equilibrium fractionation and a new paleotemperature equation

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Modern brachiopods and ambient seawater were collected at fourteen localities from the Arctic to the Antarctic. The brachiopods were analysed for Mg, δ<sup>13</sup>C and δ<sup>18</sup>O, and their ambient seawater was measured for temperature, salinity and δ<sup>18</sup>O. Our materials were supplemented by those of Lowenstam [1]. δ<sup>18</sup>O values of marine carbonates increase by about 0.06 or 0.17 ‰ per mol% MgCO<sub>3</sub> [2,3], and failing to adjustment for this 'Mg-effect' has a profound impact on water temperatures determined with standard paleotemperature equations. This Mg-effect on δ<sup>18</sup>O values applies to all marine invertebrates secreting shells or tests made of calcite with variable amounts of MgCO<sub>3</sub>, such as articulated brachiopods, foraminifera and enchinoderms. The Mg content of our brachiopods varies from a low of 250 to a high of 30,660 ppm, which needs to be accounted for by the oxygen isotope impact of the Mg-effect. We propose a new paleotemperature equation that considers the pristine biogenic calcite (δc) and accounts for both the Mg-effect as well as the established seawater oxygen isotope (δw) correction:

$$T^{\circ}\text{C} = 14.5 - 3.5((\delta\text{c} - \text{Mg effect}) - \delta\text{w}) + 0.13((\delta\text{c} - \text{Mg effect}) - \delta\text{w})^2$$

The 'Mg effect' is defined as the MgCO<sub>3</sub> content of brachiopod calcite \* 0.17 ‰ (per mol% MgCO<sub>3</sub>, accepting the latest study results [3]). Without adjustment for the Mg-effect, paleo seawater temperatures and compositions may be different than actual ones.

Without considering the effect of MgCO<sub>3</sub> on the oxygen isotopic composition, most modern brachiopods were found to precipitate shell carbonate in equilibrium with ambient seawater [4,5]. To re-evaluate the exceptions, *Thecidellina* and *Hemithiris* were collected from several localities. After making allowance for the Mg-effect on their δ<sup>18</sup>O compositions and water-δ<sup>18</sup>O corrected, calculated seawater temperatures were significantly similar to measured ones. δ<sup>18</sup>O values of other modern brachiopods deemed problematic, after adjustment for the Mg-effect also offered up equilibrium water temperatures. Thus, we can state that modern, calcitic, articulated brachiopods incorporate oxygen isotopes into shell calcite in equilibrium with ambient seawater, and this will be of critical importance to other modern and fossil calcitic carbonates.

[1] Lowenstam (1961) *Journal of Geology* **69**, 241-260.

[2] Tarutani et al. (1969) *GCA* **33**, 987-996.

[3] Jiménez-López et al. (2004) *GCA* **68**, 3367-3377.

[4] Brand et al. (2003) *Chemical Geology* **198**, 305-334.

[5] Parkinson et al. (2005) *Chemical Geology* **219**, 193-235.