

The isotopic composition of trace sulphates in Palaeozoic biogenic carbonates: Implications for coeval seawater and geochemical cycles

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The isotopic composition of biogenic calcites (e.g. belemnites, brachiopods) can be utilised as a proxy for the isotopic composition of coeval seawater. This is well established for carbon, oxygen and strontium isotopes, but has only recently been applied to $\delta^{34}\text{S}$ studies of the Mesozoic. In biogenic calcites, portions of the CO_3^{2-} group can be structurally replaced by SO_4^{2-} , (Structurally Substituted Sulphate), accounting for up to several thousand ppm of sulphate (e.g. Kampschulte and Strauss, 1996). However, for any meaningful interpretation of ancient isotope records it is important to know the natural $\delta^{34}\text{S}$ variability. This can best be assessed by studying modern marine biota and dissolved sulphate from seawater. A second important aspect relates to a possible diagenetic influence on the $\delta^{34}\text{S}$ values of ancient shells as well as means to determine such alteration. The aim of this study is threefold: first, we like to compare $\delta^{34}\text{S}$ values for modern biogenic carbonates with those from dissolved seawater sulphates; second, we compare the $\delta^{34}\text{S}$ from well preserved fossils from Phanerozoic strata with those from coeval evaporites and whole-rock carbonates and, finally, we would like to discuss temporal sulphur isotopic variations during the Palaeozoic, as derived from SSS.

Analytical techniques

For sulphur isotope analysis of SSS, brachiopod shell containing whole rock samples were broken into small pieces and cleaned in distilled water. Dried shell splinters, not contaminated with any sulphides, were picked manually under binocular microscope. Between 0.7 and 1 g of shell or 100 g of whole rock material were pulverized and subsequently leached in NaCl-solution to remove any water-soluble true sulphate minerals. Subsequently, these samples were filtered, the carbonate residue dissolved in HCl and any insoluble residue removed through final filtration. Finally, the dissolved sulphate was precipitated as BaSO_4 and combusted with a

mixture of vanadium pentaoxide and silica glass to SO_2 (Yanagisawa and Sakai, 1993) for mass-spectrometric measurements of the sulphur isotope ratio.

Modern biota and seawater $\delta^{34}\text{S}$

For a set of modern seawater samples ($n = 16$) collected in different parts of the world, sulphur isotope values scatter around $20.8 \pm 0.25\text{‰}$ (1σ) and are in good agreement with previously published data for seawater sulphate (Longinelli 1989). However, seawater from restricted environments, such as the Baltic or Black Sea, are slightly depleted in ^{34}S . Additionally, the latter are characterised by lower sulphate and magnesium concentrations relative to normal marine environments, both most probably indicating mixing with meteoric waters. In addition to seawater, we also collected different modern marine biota with skeletons/shells composed of calcite or aragonite from a wide range of habitats ($n = 31$). With the exception of sea urchin spines, the species-dependent average $\delta^{34}\text{S}$ values either agree with the range of seawater values or are slightly enriched in ^{34}S . Furthermore, the entire range of measured $\delta^{34}\text{S}$ values for biogenic carbonates from normal marine environments scatters no more than $\pm 1.2\text{‰}$ around the mean for modern seawater.

Biogenic carbonates vs evaporite and whole rock carbonate data

For the Mesozoic, we already documented that the $\delta^{34}\text{S}_{\text{SSS}}$ correlates well with sulphur isotope data for contemporaneous evaporites (Strauss, 1996). New data for the Palaeozoic presented in this study confirm this observation. However, due to the limited stratigraphic control for the ancient evaporites, the resulting correlation is relatively poor for each period.

For a subset of ancient samples, we additionally measured the sulphur isotopic composition of whole

rock carbonates (matrix and shell material). A comparison with well preserved shell material from similar stratigraphic positions shows a very good correlation of both data sets, but whole rock samples are on average slightly enriched in ^{34}S by 1.2%. This difference, however, is within the reproducibility of brachiopod data ($\pm 1\%$). The shift to slightly more positive values observed in the whole rock data most likely points to pore waters which were already affected by bacterial sulphate reduction during carbonate diagenesis prior to structural substitution of sulphate ions into the carbonate lattice (Popp 1986). It will be necessary to extend this comparison to pure matrix samples, as the latter might be a helpful alternative for very detailed $\delta^{34}\text{S}$ records and, particularly for time intervals lacking suitable biota (e.g. Cambrian).

Palaeozoic $\delta^{34}\text{S}$ record

New sulphur isotope data from brachiopod as well as whole-rock carbonate samples for parts of the Palaeozoic (Ordovician, Silurian and Carboniferous) define a structured temporal isotope record with a (bio-)stratigraphic resolution frequently better than a stage (i.e. less than ± 5 Ma). This is in marked contrast to our current knowledge of the sulphur isotopic composition of Palaeozoic seawater, which is based on 18 published evaporite values for the Ordovician (with a stratigraphic assignment of simply 'Ordovician' or at best 'Upper Ordovician'), 5 published evaporite data for the Silurian (stratigraphic control listed simply as "Silurian"), and 54 published evaporite values for the Carboniferous

(with a stratigraphic resolution of an 'Epoch' at best). Furthermore, not only the stratigraphic resolution has been significantly improved, but also a more or less continuous time record for these periods has been established. This shows a long term evolution of the sulphur isotopic composition with superimposed higher frequency oscillations. Prime causes for the observed long term variations in $\delta^{34}\text{S}_{\text{SSS}}$ include fluctuations in the depositional rates of oxidized vs. reduced sulphur. The greatly improved time resolution, however, allows as well a more detailed interpretation of causes and consequences for the global sulphur cycle in relation to shorter-term events which have affected the geosphere, hydrosphere and biosphere.

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