



The Paleozoic $\delta^{88/86}\text{Sr}$ record of marine carbonates – Implications to ocean carbonate chemistry and mass extinction events

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Within the Phanerozoic Eon stratigraphic boundaries are often associated with the extinction of marine organisms. However, the reasons for these events are still discussed. Strontium (Sr) is one of the most important divalent cations in calcium carbonate minerals and an important carrier of proxy information. In terms of the Sr output flux of the ocean, isotopically light carbonates represent the major Sr sink. Therefore, the geochemistry and stable Sr isotope composition is strongly coupled to the marine carbonate system. Consequently, variations in [Sr] and $\delta^{88/86}\text{Sr}$ becoming a suitable tool to investigate in the global carbonate budget in earth's history including the biotic turnover of calcifying organisms at stratigraphic boundaries which are expected to have a large influence on Sr geochemistry and isotope composition of seawater. We extended the conventional radiogenic Sr isotope system ($^{87}\text{Sr}/^{86}\text{Sr}$) by a simultaneous measurement of radiogenic and stable Sr isotopes ($\delta^{88/86}\text{Sr} = ((^{88}\text{Sr}/^{86}\text{Sr}_{\text{sample}})/(^{88}\text{Sr}/^{86}\text{Sr}_{\text{NBS987}}) - 1) * 1000$). With that we are able to add new constraints to Strontium Isotope Stratigraphy (SIS) and the ocean chemistry of the past. By taking Sr isotope fractionation into account we add an additional dimension to the radiogenic Sr isotope system. This allows us to gain quantitative information about the Sr output of the ocean. Applying a $^{87}\text{Sr}/^{84}\text{Sr}$ -double spike (DS), we measured paired $\delta^{88/86}\text{Sr}$ - $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 100 modern and Paleozoic marine brachiopod samples which were screened for diagenetic alteration prior to the measurement [1]. Data reduction and DS denormalization follows an iterative routine [2]. External reproducibility of $\delta^{88/86}\text{Sr}$ based on an international coral carbonate standard (JCP-1) is 0.026‰ (2SD, n=26). We found that modern brachiopods have similar values independent of habitat location, species and water temperature with a mean of $0.18\text{‰} \pm 0.02\text{‰}$ (2SD, n=13). This provides further support that brachiopods provide a reliable carbonate recording phase for $\delta^{88/86}\text{Sr}_{\text{seawater}}$. In Paleozoic Eon we observe variations in $\delta^{88/86}\text{Sr}_{\text{seawater}}$ in the range of $0.25 - 0.45\text{‰}$. On longterm timescales (100 Ma) these variations in $\delta^{88/86}\text{Sr}_{\text{seawater}}$ follow the general distribution of "calcite seas" and "aragonite seas" [3], implying a control mechanism by $\text{Mg}/\text{Ca}_{\text{seawater}}$ ratios and further global spreading rates. On shorter timescales (residence time of Sr in the ocean of 5 Ma) we observe a positive correlation of $\delta^{88/86}\text{Sr}_{\text{seawater}}$ and the number of marine genera [4] during mass extinction events in late Ordovician and mid-Devonian. This indicates the strong influence of marine calcifiers on the Sr budget of the ocean and gives us the opportunity of tracing back major extinction events in the Phanerozoic with sudden drops in the $\delta^{88/86}\text{Sr}_{\text{seawater}}$ record. Furthermore, with changes in marine Phanerozoic [Sr] [5] and $^{87}\text{Sr}/^{86}\text{Sr}$ we are able to correlate these changes in Sr out- or influxes of the ocean. Ultimately, the combined measurement of radiogenic and stable Sr isotopes enhances our understanding of ocean chemistry of the past and increases the precision of SIS with the addition of a second Sr isotope reference curve.

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