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Alteration histories of fossil biogenic calcite as indicated by 87Sr/86Sr ratios

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The 87Sr/86Sr, δ18O and δ13C composition of biogenic calcite from stratigraphically well-defined marine fossils can be utilized to reconstruct paleoenvironments and the isotopic evolution of past seawater. A conceptual prerequisite for reliable results is a minimum of post-depositional alteration of the samples. In order to establish a measure of the degree of alteration it is common practise to check all biogenic calcite samples using cathodo-luminescence, SEM, and trace element concentration analysis. However, none of these screening techniques is fool-proof. A combination of these approaches is necessary to select the best preserved samples.
In this study we show that strontium isotope signatures can serve as an independent alteration indicator. Because the seawater 87Sr/86Sr ratio in fully marine environments is virtually constant during the lifespan (< 50 years) of the shelly organisms involved, and biofractionation of the 87Sr/86Sr ratio is corrected for by the recalculation to a constant 88Sr/86Sr of 0.1194, only altered samples exhibit variability of the 87Sr/86Sr ratio beyond analytical reproducibility and/or significant deviation from the strontium isotope curve for seawater.
We measured 87Sr/86Sr, δ18O, δ13C and element ratios from a Late Kimmeridgian belemnite from New Zealand, and a Late Triassic (Rhaetian) brachiopod from New Caledonia. The 87Sr/86Sr ratios for the belemnite vary from 0.706724 to 0.706928 (n = 5) with three values being compatible with coeval seawater and two values being less radiogenic than the lowest seawater value of the Phanerozoic seawater curve. The low 87Sr/86Sr ratios coincide with elevated Mn and low Sr concentrations, and light δ18O values indicate diagenesis that involved fluids leaching less radiogenic Sr from the surrounding rocks, and re-crystallisation of the belemnite guard at elevated temperatures. The 87Sr/86Sr ratios of the brachiopod vary from 0.707813 to 0.707934 (n = 8) and are strongly correlated with Mg/Sr ratios. In the shell, about 40% of the measured Mn values (n = 157) are higher than 250 μg/g indicating partial alteration. No δ18O value is < -4 ‰ and the stable isotope pattern is similar to those described for modern brachiopods as governed by vital effects. For the studied sample, low temperature alteration is most likely involving seawater-like fluids with DIC signatures involving oxidised organic matter.