Isotopic behavior over the aragonite-calcite transition: implications for sampling methods and proxy interpretations

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At elevated temperatures, aragonite will readily convert to calcite, a process known to facilitate changes in the C and O isotopic composition. This transition can also occur during the frictional heating caused during the drilling of an aragonitic sample such as a coral, speleothem, or a sclerosponge. We have investigated this process using the clumped isotope temperature proxy combined with conventional C and O stable isotopes. The $\delta^{13}C$ and $\delta^{18}O$ values of the aragonite alter during the inversion as a result of exchange with available CO_2 and possibly trapped skeletal water. The clumped isotope composition of the aragonite is extremely succeptible to alteration by these processes, as Δ_{47} value is able to change without involvment of another medium, and will alter at lower temperatures than those needed to facilitate the mineral transition. Sampling aragonite archives using drilling can easily produce the temperatures neccesary to partially convert aragonite to calcite, which can contaminate bulk $\delta^{13}C$ and $\delta^{18}O$ values as well as offsetting the paleotemperatures predicted by clumped isotopes by as much as 20°C, thus representing a significant systematic bias in the analytical process; one which, if overlooked, could dramatically affect the interpretation of reconstructed climates. In addition, because this process facilitates exchange between atmosphere and sample, it is likely to introduce isotopically “young” atmospheric carbon into materials sampled for radiocarbon dating, biasing them towards younger values. Because the alteration of isotopic composition correlates with the transition from aragonite to calcite during drilling, we propose that the mineralogy can be used to test wether a given sampling technique is likely to substantially alter the isotopic composition prior to analysis.