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How ^{17}O excess in clumped isotope reference-frame materials and ETH standards affects reconstructed temperature

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Carbonate clumped isotopes have been widely applied as a paleothermometer, but various errors limit their application. Calculation of Δ_{47} requires a correction for mass interference from ^{17}O, which traditionally assumes all analytes follow a linear relationship between ^{17}O/^{16}O and ^{18}O/^{16}O with a slope of 0.528 and a ^{17}O excess (Δ^{17}O) of zero. Here, we evaluate these assumptions by measuring Δ^{17}O in Δ_{47} reference-frame gases and waters, our mass spectrometer working gas, and ETH standards 1, 2, 3 and 4. We systematically evaluate how the Δ^{17}O of these materials influence Δ_{47} values, and the magnitude of Δ_{47} error introduced by assuming a Δ^{17}O of zero. We find most Δ_{47} reference-frame materials and ETH standards have negative Δ^{17}O values, ranging from -300 to +38 permeg, which can largely be explained by equilibration with surface water at Earth surface temperature. Exceptions include CO_2 equilibrated with evaporatively enriched water and CO_2 derived from fossil fuel combustion. CO_2 heated to 1000ºC in quartz glass tubes shows a small, 5-10 permeg, increase in Δ^{17}O that may reflect contamination in the quartz. CO_2 evolved from ETH standards exhibits mean Δ^{17}O values of -151 to -123 permeg, similar to most natural carbonates, but ETH 2 and 4 have greater variance. Our results show that assuming Δ^{17}O = 0 can overestimate or underestimate measured Δ_{47} values, with the direction of change dependent on whether sample Δ^{17}O falls above or below the Δ^{17}O of the working gas. Similarly, assuming Δ^{17}O = 0 can also overestimate or underestimate Δ_{47} in the carbon dioxide equilibration scale (CDES), with the direction of change dependent on whether sample Δ^{17}O falls above or below reference-frame materials. The magnitude of this effect is significant, and is equivalent to an error on reconstructed temperature of 0.6-1.7ºC for Earth surface conditions and 1.9-5.8ºC in the shallow crust. While analytical and calibration errors are also important, the effect of Δ^{17}O needs to be considered for Δ_{47} thermometry to achieve its highest possible accuracy. The same is true for the recently introduced dual clumped isotope thermometer. We provide suggested laboratory protocols that best account for Δ^{17}O when measuring Δ_{47}.