

# The effects of Porapak™ trap temperature on $\delta^{18}\text{O}$ , $\delta^{13}\text{C}$ , and $\Delta_{47}$ in preparing samples for clumped isotope analysis

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Preparation of  $\text{CO}_2$  for clumped isotope analysis requires additional cleaning steps beyond those used for traditional stable isotope measurements ( $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}$ ) because the clumped isotope measurement is susceptible to isobaric interference from a wider range of contaminants, including hydrocarbons, halocarbons, and sulfur compounds [Eiler and Schauble, 2006]. To reduce the effects of these contaminants, the  $\text{CO}_2$  is cleaned prior to sample introduction into the mass spectrometer in one of two ways: by passing  $\text{CO}_2$  through either 1) a gas chromatography column with a helium carrier gas [Ghosh *et al.*, 2006 and others] or 2) a “static” U-trap filled with a similar adsorbing agent (such as Porapak™ Q, or “PPQ”) using the pressure gradient produced by liquid nitrogen to facilitate the transfer [Dennis and Schrag, 2010]. Of the labs using the static PPQ trap configuration, the dimensions of the trap, the temperature to which it is cooled, and the duration of transfer have all been empirically determined on a lab-by-lab basis, possibly through assessing yield (% of starting gas collected on the far side of the PPQ trap) or by testing measured  $\Delta_{47}$  values of standards calibrated by other labs.

We tested the effects of PPQ trap temperature on the measured stable isotopic and clumped isotopic composition of carbonate standards. We found that, on the University of Michigan sample preparation line, at PPQ trap temperatures below  $-20^\circ\text{C}$ ,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and raw  $\Delta_{47}$  are fractionated, with the magnitude of the fractionation increasing linearly as temperature decreases below  $-20^\circ\text{C}$ . The rate of fractionation is  $0.0097\text{‰}/^\circ\text{C}$  below  $-20^\circ\text{C}$  for  $\delta^{13}\text{C}$ ,  $0.0392\text{‰}/^\circ\text{C}$  below  $-20^\circ\text{C}$  for  $\delta^{18}\text{O}$ , and  $0.0037 \pm 0.0019\text{‰}/^\circ\text{C}$  for raw  $\Delta_{47}$ , in all cases making the measured values lighter at colder temperatures. Reference-frame-corrected  $\Delta_{47}$  values ( $\Delta_{47\text{-RFAC}}$ ) were unaffected as long as standards gases and samples were prepared identically. Contaminant removal, determined by monitoring  $\Delta_{48}$ , was equivalent at all PPQ trap temperatures between  $-10^\circ\text{C}$  and  $-40^\circ\text{C}$ . Interestingly, measured yield through the PPQ trap was consistently  $>99\%$  at PPQ trap temperatures as low as  $-30^\circ\text{C}$ , resulting in a temperature interval ( $-20^\circ\text{C}$  to  $-30^\circ\text{C}$ ) in which high yields were achieved but fractionation was occurring. This suggests that an ideal PPQ trap temperature cannot be determined by monitoring yield alone (or  $\Delta_{47\text{-RFAC}}$ ). We find that a PPQ trap temperature above  $-20^\circ\text{C}$  is required to avoid fractionation, and  $-10^\circ\text{C}$  to  $-15^\circ\text{C}$  is ideal for the University of Michigan apparatus. Other labs should determine their own ideal PPQ trap temperature by monitoring not only yield and  $\Delta_{47\text{-RFAC}}$ , but also changes in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  with temperature.

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