The temperature dependence of $\Delta_{47}$ thermometers and the exchange of CO$_2$ oxygen in phosphoric acid baths

Albert S. Colman$^1$ and Gerard A. Olack$^1$

$^1$Dept. Geophysical Sciences, University of Chicago; Chicago, IL, USA
Email: asc25@uchicago.edu

As the number of thermometric $\Delta_{47}$ calibrations grows, the evidence has strengthened that the slope of the $\Delta_{47}$ vs. inverse temperature relationship clusters into two distinct groupings based on whether the carbonate minerals were digested at low temperature (25°C) vs. high temperature (generally 70 - 90°C). We show that small amounts of oxygen exchange between CO$_2$ liberated to phosphoric acid solution and trace water in that solution can result in modification of the $\Delta_{47}$ signal. This can occur with very little shift in $\delta_{47}$ and $\delta^{18}$O of the CO$_2$. We model this effect and provide initial experimental $\Delta_{47}$ measurements conducted using phosphoric acid produced with different $\delta^{18}$O compositions. The extent and effect of oxygen exchange following CaCO$_3$ dissolution is a complex function of the phosphoric acid’s temperature, water content, and viscosity. Conventional approaches to preparation of phosphoric acid (targeting a defined density range at room temperature) are likely inadequate for resolving the finer details of these dependencies. This stems in part from changes that can occur to acid water content and density during heating of the acid under vacuum. Secondary effects may also arise that relate to the grain and crystallite size of the carbonate minerals, intercalation of carbonate minerals with siliciclastic matrix in sediments or paleosols, and possibly the reactivity of hydrous components of a siliciclastic rich sample.