Variable $\Delta_{47}$ acid digestion fractionation

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The extraction of CO$_2$ from CaCO$_3$ via digestion by phosphoric acid includes a fractionation factor that affects both $\delta^{18}O$ and $\Delta_{47}$. In both systems the fractionation factor is assumed to vary only with temperature and to be constant at a specific temperature. A correction factor is therefore derived to enable comparison of data that is produced under different acid digestion temperatures, reflecting the difference between 25°C reaction and a reaction at a higher temperature ($\Delta \delta_{25-90}$). Calcite samples having a wide range of $\Delta_{47}$ values (0.26‰ - 0.74‰) and of bulk composition ($\delta_{47}$ values between -40‰ and +20‰) were analyzed using acid digestion at either 25°C or 90°C. The difference in $\Delta_{47}$ values when digesting at 90°C versus 25°C ($\Delta \delta_{25-90}$) is highly variable, suggesting that the acid digestion fractionation is not constant at a given temperature. $\Delta \delta_{25-90}$ varies between the accepted value of 0.09‰ to as low as 0.03‰, and correlates with the bulk isotopic composition of the sample (either $\delta_{47}$ of the sum of $\delta^{13}C+\delta^{18}O$). This strong variability is observed in particular when phosphoric acid concentration is at the low end of commonly used concentrations (103%); weaker variability is observed when using higher acid concentration (105%). Such non-constant $\Delta \delta_{25-90}$ leads to potential systematic errors in $\Delta_{47}$ determination in experimental setups in which acid concentration is relatively low, or if concentrations change over time, as may often be the case in a common acid bath.