The $\Delta_{47}$ fractionation of different carbonate minerals digested with phosphoric acid at 70 °C in a Kiel IV – MAT 253 system

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The broader paleoclimate community is increasingly convinced that the clumped isotope signature ($\Delta_{47}$) in carbonate minerals may be the ideal proxy for reconstructing the formation temperature of carbonates, due to its independence of the isotopic composition of the ambient water in which the carbonate mineral formed. Yet, inter-laboratory discrepancies in $\Delta_{47}$-temperature calibrations and in the measurements of carbonate standards cast a cloud over the application of the $\Delta_{47}$ signature. One potential reason for inter laboratory discrepancies could be differences in the isotopic fractionation during phosphoric acid digestion of the carbonate molecule ($^{13}$C$^{18}$O$^{16}$O$^{22}$) to gaseous CO$_2$ ($^{13}$C$^{18}$O$^{16}$O) (Ghosh et al., 2006) caused by differences in sample preparation or the instrumental setup.

In this study we determined the acid fractionation of different carbonate minerals digested at 70 °C in a Kiel IV carbonate device coupled to a MAT 253 mass spectrometer setup (Thermo Scientific, Bremen, Germany). The carbonate minerals were heated for several hours to temperatures of approximately 1000 °C to reach stochastic isotope distribution. Heating of calcites was performed in a “Paterson apparatus”, because it enables heating of gram-size carbonate quantities, but has a relatively slow cooling to room temperatures of 45 minutes. Dolomite and siderite were heated in smaller quantities in a “piston cylinder”, which allows to reach the higher pressure necessary to stabilize the specific carbonate mineral and ensures rapid cooling within 30 sec. XRD measurements verified the purity of the heated carbonate mineral. Subsequently the carbonates were finely ground, dissolved with phosphoric acid at 70 °C in the Kiel IV and the evolved CO$_2$ gas analyzed for its mass 44 to 49 in the MAT 253. The intensities were pressure baseline corrected, converted into the absolute reference frame and projected to acid digestion at 25 °C (Meckler et al., 2014).

Preliminary results of the $\Delta_{47}$ fractionation for carbonate digestion with phosphoric acid at 70 °C in a Kiel IV device are consistent with results from other studies using different preparation methods (Guo et al., 2009; Defliese et al., 2015). Thereof the various carbonate mineralogies indicate small but significant differences in their acid fractionation, which has to be taken into account while interpreting their $\Delta_{47}$ signature.