# The clumped isotope fractionation for carbonates reacted with phosphoric acid at 70 °C in a KIEL IV – MAT 253 system

I. A. MÜLLER[1*], M. E. S. VIOLAY[1], M. BONIFACIE[2], A. KATZ [2], A. FERNANDEZ[1], J.VAN DIJK[1], C. MADONNA[1] AND S. M. BERNASCONI[1]

[1]ETH, Geological Institute, 8092 Zürich
[2]IPGP, Sorbonne Paris Cité, 75005 Paris, France
(*inigo.mueller@erdw.ethz.ch)

The application of the clumped isotope signature ($\Delta_{47}$) of carbonate minerals as proxy for temperature is increasingly used in studies ranging from paleoclimatology to low temperature diagenetic processes. Yet inter-laboratory comparison of $\Delta_{47}$ analyses suffers from small uncertainties, such as the isotopic fractionation during phosphoric acid digestion of the carbonate mineral ($^{13}C^{18}O^{16}O_2$) to gaseous $CO_2$ ($^{13}C^{18}O^{16}O$). Pioneer studies [1] [2] observed a positive isotope fractionation in $\Delta_{47}$ and determined its dependence on the acid digestion temperature.

We drove various carbonate minerals to a stochastic isotope distribution by heating them to 1000°C in a “Paterson apparatus” at ETH and a piston cylinder at IPGP. Samples were digested in phosphoric acid at 70°C in a Kiel IV carbonate device and the $\Delta_{47}$ analyzed with a MAT 253 isotope ratio mass spectrometer (Thermo Scientific, Bremen, Germany). The $\Delta_{47}$ values were pressure baseline corrected, transferred to the absolute reference frame and projected to an acid digestion temperature of 25°C [3].

Preliminary results for the acid digestion fractionation of calcite at 70°C in a Kiel IV system are consistent with the temperature dependent acid fractionation factor derived from interpolating data of [4] [5] and confirm the acid fractionation at 25°C determined by [2] [4].

[1] Ghosh et al. (2006), *GCA* **70**, 1439-1456. [2] Guo et al. (2009), *GCA* **73**, 7203-7225. [3] Meckler et al. (2014), *RCMS* **28**, 1705-1715. [4] Henkes et al. (2013), *GCA* **106**, 307-325. [5] Defliese et al. (2015) *Chemical Geology* **396**, 51-60.