

## Triple oxygen and clumped isotope equilibrium fractionation in synthetic carbonate-water systems

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The triple isotope fractionation exponent  $\theta$  relates fractionation in  $^{17}\text{O}/^{16}\text{O}$  to fractionation in  $^{18}\text{O}/^{16}\text{O}$  ( $\theta = \ln^{17}\alpha/\ln^{18}\alpha$ ). This parameter, yet to be measured for the carbonate-water system, is necessary for reconstructing parent water triple oxygen isotope compositions from measured carbonate triple oxygen isotope compositions. Thus knowledge of this parameter is central to emerging applications of carbonate triple oxygen isotopes to paleoclimate, paleoecology, paleoatmospheres, and petrology.

To determine this parameter, we synthesized carbonate in the laboratory at temperatures ranging from 5 to 60°C using a mostly passive CO<sub>2</sub> degassing method. Triple oxygen isotope compositions of the water were determined using the CoF<sub>3</sub> fluorination method [1], and of the carbonate (as CO<sub>2</sub> liberated from carbonate by 90°C phosphoric acid digestion) using a reduction-fluorination method [2]. We observe a mean  $\theta$  value of  $0.5243 \pm 0.0005$ , which is a composite value reflecting calcite-water fractionation, and 'acid fractionation' during phosphoric acid digestion of carbonate. The  $\theta$  value appears to have weak temperature dependency of  $\sim 0.00001/^\circ\text{C}$ , in agreement with theoretical predictions [3].

Clumped isotope compositions of the synthetic carbonates show a temperature dependency that is indistinguishable from previously published calibrations with typical 'low slope' pattern in  $\Delta_{47}$  vs.  $1000/T^2$  plot [*e.g.*, 4]. We also observed laboratory self-consistency between this new inorganic calibration and a previous calibration based on biogenic mollusk and brachiopod shells [5].

[1] Barkan & Luz (2005) *RCMS* **19**, 3737; [2] Passey *et al.* (2014) *GCA* **141**, 1; [3] Cao & Liu *GCA* (2011) **7**, 7435; [4] Defliese *et al.* (2015) *CG* **396** 51; [5] Henkes *et al.* (2013) *GCA*, **106**, 307.