

## Carbonate clumped isotope fractionation during phosphoric acid digestion of calcite, dolomite and aragonite minerals

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Carbonate clumped isotope thermometry relies on the temperature-dependent extent of bonding of <sup>13</sup>C-<sup>18</sup>O within CO<sub>3</sub><sup>2-</sup> ion groups in solid carbonate minerals. The measure of the abundance of <sup>13</sup>C<sup>18</sup>O<sup>16</sup>O<sub>2</sub><sup>2-</sup> ion groups cannot be performed on the carbonate mineral itself and requires the analysis of CO<sub>2</sub> extracted from phosphoric acid digestion (expressed as Δ<sub>47</sub>, i.e., the excess of <sup>13</sup>C-<sup>18</sup>O bonds in extracted CO<sub>2</sub> relative to a random distribution). Theoretical studies predict variations in the degree of <sup>13</sup>C-<sup>18</sup>O clumping within the mineral lattice [1] and small but analytically resolvable difference in Δ<sub>47</sub> measured from CO<sub>2</sub> extracted from various types of carbonates equilibrated at a given temperature [2]. In contrast, published calibrations of the dependence of Δ<sub>47</sub> to growth temperature for various synthetic and natural biogenic and inorganic minerals (calcite, aragonite and carbonate-apatites [3]) show indistinguishable difference among different types investigated. However, some coexisting carbonate minerals supposed to have grown or re-equilibrate at the same temperature show different Δ<sub>47</sub> values [4].

We present here results from a series of experiments on natural carbonates as well as on carbonates for which their <sup>13</sup>C-<sup>18</sup>O bonds distribution have been experimentally driven to a stochastic distribution at very high temperatures (with a piston cylinder apparatus imposing required pressure-temperature fields). These results allow to experimentally determine that, for a given temperature of acid digestion, the isotope fractionation factor associated with phosphoric acid digestion of calcites, dolomites and aragonites are identical within uncertainties.

This study is relevant for key issues related to the use of Δ<sub>47</sub>, and in particular in refining application of the Δ<sub>47</sub> thermometry to the variety of carbonate minerals found in the geological record.

[1] Schauble *et al* (2006), *GCA* **70**, 2510-2529 [2] Guo *et al* (2009), *GCA* **73**, 7203-7225 [3] Eiler (2011), *Quaternary Science Reviews* **30**, 3575-3588 [4] Bonifacie *et al* (2013), *Mineralogical Magazine*, **77**, 735