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# Clumped isotope analysis of carbonates: comparison of two different acid digestion techniques

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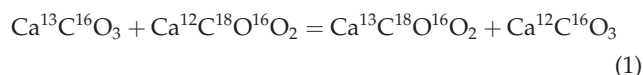
**RATIONALE:** The kinetic nature of the phosphoric acid digestion reaction enables clumped isotope analysis of carbonates using gas source isotope ratio mass spectrometry (IRMS). In most laboratories acid digestions are performed at 25°C in sealed vessels or at 90°C in a common acid bath. Here we show that different  $\Delta_{47}$  results are obtained depending on the digestion technique employed.

**METHODS:** Several replicates of a biogenic aragonite and NBS 19 were reacted with 104%  $\text{H}_3\text{PO}_4$  in sealed vessels at 25°C and at 90°C using a common acid bath. The sample size varied between 4 mg and 14 mg. Purification methods that are standard for clumped isotope analyses were applied to the evolved  $\text{CO}_2$  before measuring the abundances of masses 44 to 49 relative to a reference gas by IRMS.

**RESULTS:** A systematic trend to lower and more consistent  $\Delta_{47}$  values is observed for reactions at 25°C if the sample size is increased. We suggest that secondary re-equilibration of evolved  $\text{CO}_2$  or reaction intermediates with free water molecules preferentially occurs for relatively small samples (4–7 mg), finally yielding elevated  $\Delta_{47}$  values compared with >7 mg aliquots. In contrast, no such sample size effect on  $\Delta_{47}$  values is observed for carbonates that are digested at 90°C using the common acid bath.

**CONCLUSIONS:** The determination of  $\Delta_{47}$  values of carbonate samples smaller than 7 mg becomes more precise and accurate if digestions are performed at 90°C. Based on our results we propose that the difference in phosphoric acid fractionation factor between 25°C and 90°C is 0.07‰ for both calcite and aragonite. Copyright © 2013 John Wiley & Sons, Ltd.

Clumped isotope analysis has recently been advanced as a new tool to reconstruct carbonate formation temperature<sup>[1]</sup> (and references cited therein). The carbonate clumped isotope thermometer relies on the isotope exchange reaction involving the most abundant isotopologue containing two heavy isotopes  $\text{Ca}^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$ :



At thermodynamic equilibrium the abundance of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in  $\text{CaCO}_3$  is a function of the equilibrium constant of reaction (1). The equilibrium constant, in turn, largely depends on temperature<sup>[2]</sup> and, hence, the determination of the abundance of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in the carbonate provides information about its crystallization temperature. Currently, there is no technique sensitive and precise enough to directly measure the abundance of isotopologues in carbonates participating in reaction (1). Therefore, carbonates are digested with 103%  $\text{H}_3\text{PO}_4$ <sup>[3]</sup> or 105%  $\text{H}_3\text{PO}_4$ <sup>[4]</sup> and the abundance of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds within the evolved  $\text{CO}_2$  is measured instead.

Fortunately, the acid digestion reaction is kinetically controlled such that the concentration of  $^{13}\text{C}$ – $^{18}\text{O}$  bonds in the evolved  $\text{CO}_2$  remains proportional to the original abundance of corresponding bonds in the carbonate lattice.<sup>[3,5,6]</sup>

The temperature dependency of reaction (1) is expressed by  $\Delta_{47}$  which quantifies the deviation of the abundances of isotopologues of a sample gas from a theoretical random distribution. For this purpose, measured  $R^{47}$ ,  $R^{46}$  and  $R^{45}$  values are compared with their corresponding stochastic distribution ratios ( $R^{47*}$ ,  $R^{46*}$ ,  $R^{45*}$ ) where  $R^i = m_i/m_{44}$ :

$$\Delta_{47} = \left[ \left( R^{47}/R^{47*} - 1 \right) - \left( R^{46}/R^{46*} - 1 \right) - \left( R^{45}/R^{45*} - 1 \right) \right] \times 1000(\text{‰}) \quad (2)$$

A number of calibrations of the carbonate clumped isotope thermometer have been published, including those for synthetic and biogenic minerals,<sup>[3,7–10]</sup> as well as speleothems.<sup>[11,12]</sup> Several modern biogenic carbonates for which growth temperatures have been determined independently confirm the relationship between  $T_{\text{growth}}$  and  $\Delta_{47}$  of synthetic carbonates reported by Ghosh *et al.*<sup>[3]</sup> Amongst these are mollusks, brachiopods, corals, ooliths, foraminifera and coccoliths (see<sup>[1,13]</sup> for an overview). As a consequence, most authors refer to the Ghosh *et al.*<sup>[3]</sup> line when applying the  $\Delta_{47}$ -thermometer to fossil material (e.g.,<sup>[1,13,14]</sup>). However, discrepant results have also become

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