Calibration and applications of the dolomite clumped isotope thermometer to high temperatures

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Carbonate clumped isotope paleothermometry is based on the temperature-dependent formation of $^{13}C^{18}O^{16}O_2^{2-}$ ion groups within solid carbonate minerals. This thermometer has now been calibrated for various synthetic and natural biogenic and abiogenic minerals (calcite, aragonite and carbonate-apatites [e.g., 1, 2]) at temperatures below ~ 50°C. Here we extend the use of the carbonate clumped isotope thermometer to shallow crustal environments by determining the Δ_{47} values of CO_2 extracted from natural and synthetic dolomites grown at know temperatures from 25 to 350ºC. The experimental temperature dependance is not linear in the Δ_{47} vs T^{-2} plot and resembles the predicted theoretical temperature dependence, both in shape and absolute value [3]. These data for synthetic dolomites overlap the previous calibrations for inorganic calcite and some forms of biogenic carbonates between 25 and 50°C, and are consistent with a single trend that also intersects data for synthetic calcite equilibrated at 1200°C. These observations suggest that a single temperature dependant relationship reasonably approximates the calibration for both phases. Data from a variety of slowly-cooled (i.e., over geological timescales) natural marbles and rapid (i.e., laboratory timescales) heating experiments provide insights into the kinetics of solid-state ^{13}C-^{18}O bond reordering in carbonates and its closure temperature. More generally, our new calibration and constraints on high-temperature kinetics have implications for the application of this technique to burial and metamorphic processes. These issues will be illustrated through estimates of the thermal history and oxygen isotopic compositions and abundances of pore fluids for several suites of late Neoproterozoic carbonates [e.g., 4].

[1] Ghosh *et al*. (2006) *GCA* **70**, 1439-1456. [2] Tripati *et al*. (2010) *GCA* 74, 569 [3] Guo *et al*., (2009) *GCA* **73** 7203 [4] Bristow *et al*., (2011) *Nature*, in press

Seasonal and tidal variations of dissolved thallium in coastal waters

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Little is known on the distribution and behaviour of Thallium (Tl) in oceanic and coastal waters, perhaps due to its very low concentration level (8-20 ng L^{-1} or 40-90 pmol L^{-1}). Thallium is as highly toxic as Hg and Cd and is involved in redox reactions, which makes it an interesting candidate for the study of environmental processes.

Here we present a method for the rapid and reliable determination of dissolved Tl in sea water using sector field inductively coupled mass spectrometry (SF-ICPMS) without any preparation except 10 times dilution. Our method is suitable for the measurement of large time series of sea water samples [1]. Precision is 7 % RSD except for samples below the quantification limit (0.3 ng L^{-1}). Validation was done using the standards CASS-4 and NASS-5. For both CASS-4 and NASS-5 (salinity of 30.5) we calculated a concentration of about 11 ng L^{-1} assuming a Tl concentration of 14±2 ng L^{-1} at a salinity of 35±1. For CASS-4 we measured 10.6±0.7 ng L^{-1}, for NASS-5 10.3±0.8 ng L^{-1}[1], the latter of which is close to the value of 9.37±0.02 ng L^{-1} determined by isotope dilution-ICPMS by Nielsen *et al*. [2].

We applied our method to surface waters from the Jade Bay (an embayment of the Wadden Sea in NW Germany) [1]. Sampling was done hourly for 48 h during January, April, July and November 2010 at a fixed station located close to tidal flats, with a subsequent offshore transect. Pore waters were taken from sediments close to the fixed station.

In general, the results of all transect measurements (9-12 ng Tl L^{-1}) indicated conservative mixing since Tl varied with salinity. The time-series at the fixed station, however, yielded Tl concentrations of 6-11 ng L^{-1}, which only in part correspond to determined salinities. Hence, the distinct tidal variations in the concentration of dissolved Tl are rather explained by changes in the contribution of pore waters low in Tl (below the quantification limit).

[1] Böning, P and Schnetger, B. (submitted) [2] Nielsen, S. G. *et al*. (2004) *Chem*. *Geol*. **204**, 109-124.