

Clumped-Isotope Measurements on Small Carbonate Samples with a Kiel IV Carbonate Device and a MAT 253 Mass Spectrometer

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Introduction

Clumped-isotope thermometry (Ghosh et al., 2006; Eiler, 2007) has emerged as a new tool for paleotemperature reconstructions and is attracting growing interest in a variety of different applications in geology. The thermometer is solely based on thermodynamic properties and does not depend on the bulk carbon and oxygen isotope composition of the carbonate. Calculations of vibrational frequencies from different multiply substituted isotopologues based on statistical thermodynamics have shown that bonds between two rare isotopes are more stable. This is due to their lower zero-point energy at ambient temperatures (Eiler, 2007). This leads to a slightly higher abundance of these bonds than would be observed for a purely stochastic isotope distribution. As the abundance of these bonds is temperature-dependent, the difference between the measured and the stochastically expected bond abundance can be used as a thermometer. The best studied species for clumped-isotopes so far is CO₂. Ghosh et al. (2006) were the first to show that this excess bond abundance of ¹³C-¹⁸O in carbonates can be used as a thermometer for the formation of carbonate, where the carbonate is converted to CO₂ by reaction with phosphoric acid. This excess abundance is defined as

$$\Delta_{47} = \left(\frac{R_{\text{sample}}^{47}}{R_{\text{stochastic}}^{47}} - 1 \right) \times 1000$$

whereby R⁴⁷ refers to the measured and the calculated stochastic 47/44 ratio of the analyzed CO₂. As the clumped-isotope thermometer is based only on thermodynamics, the formation of ¹³C ¹⁸O bonds can be considered as a homogeneous reaction between carbonate ions. The simultaneous measurement of δ¹³C and δ¹⁸O allows the interpretation of three different proxies from one sample set and the calculation of the δ¹⁸O of the water, from which the carbonate precipitated.

Currently applied are the method by Ghosh et al. (2006), a manual preparation procedure to dissolve 10 to 12 mg of calcite and to purify the gas before the sample is measured and a custom built autosampler, based on the procedure by Ghosh, which allows completely automated measurements and has a minimum sample weight requirement of 5 mg (Tripathi et al., 2010). The advantage of a Thermo Scientific Kiel IV Carbonate Device is the completely automated sample analysis and the capability to measure small samples of less than 2 mg sample weight (Schmid and Bernasconi, 2010). This ability allows application of clumped-isotope studies in cases where the sample amount is very limited (e.g. foraminifera, cements, see Figure 2).

Heated Gases

The measurement of heated gases is necessary to determine the degree of fractionation and scrambling in the source of the mass spectrometer (Dennis et al., 2011). This effect is linear and slope and y-intercept can be determined on a Δ₄₇ vs. δ⁴⁷ plot (Huntington et al., 2009; Figure 1) to be used as correction factors of measured Δ₄₇ values.

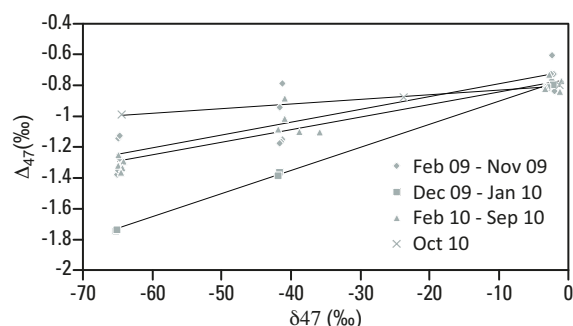


Figure 1. Heated gas measurements, showing changes in slope and intercept caused by new filaments.

Heated gases of different oxygen isotope composition can be produced by equilibrating tank CO₂ with H₂O of different δ¹⁸O compositions in quartz tubes. The produced CO₂ has to be separated from the water after having equilibrated and heated to 1000 °C for 2 h and immediately quenched afterwards in order to get a stochastic isotope distribution and to avoid re-equilibration during cooling. Reproducibility of heated gases is in the order of below 0.005 to 0.015 per mil.

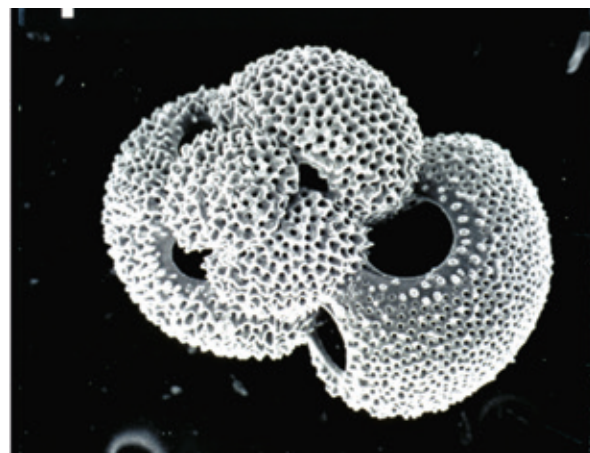


Figure 2. Scanning electron microscope photograph of a cleaned *Globigerinoides ruber* foraminifer ready for measurement (photo: H. Thierstein).

Key Words

- MAT 253
- Kiel IV
- Clumped Isotopes
- High Precision Carbonate CO₂ Clumped Isotope Analysis
- High Resolution Carbonate CO₂ Clumped Isotope Analysis
- Isotope Ratio MS

Kiel IV Sample Preparation

The Kiel IV Carbonate Device uses the principle of individual acid baths. Storage, transfer and chemical reaction of phosphoric acid at elevated temperatures operate under full temperature control. CO₂ evolves in septum-free vials and is transferred into a cryogenic trapping system. Water, evolved during phosphorolysis and non-condensable gases are removed from the CO₂ under high vacuum in the first Liquid Nitrogen (LN₂) trap.

The trapping system of the Kiel IV Carbonate Device inlet system consists of two LN₂ traps, two pneumatic valves, an expansion volume and a vacuum gauge. The first trap quantitatively cleans the CO₂ by removing non-condensable gases (e.g. O₂, N₂), H₂O produced during the carbonate-phosphoric acid reaction, and traces of water contained in the nominally anhydrous ortho-phosphoric acid (104% of H₃PO₄, > 1.93 g/cm³ phosphoric acid). During the acid reaction all CO₂ gas is produced into the first trap at -190°C. Afterwards CO₂ is transferred into the second trap (microvolume) where it is trapped at -190°C, leaving all of the water in the first trap.

In addition to the commercial Kiel IV Carbonate Device, a newly developed trap was added to remove organic contaminants (e.g. hydrocarbons and halocarbons), released during the sample preparation process. The trap was inserted between the two cold fingers of the Kiel IV Carbonate Device and consists of a 6 mm o.d. stainless-steel tube filled with PoraPak Type Q 50-80 Mesh (Figure 3). It is cooled to -20°C with two Peltier elements attached to a copper block encasing the stainless steel tubing during a run. The trap is baked out for at least one hour at about 100°C after each run. This additional part was developed at ETH Zurich and is currently not available from Thermo Fisher Scientific (Bremen).

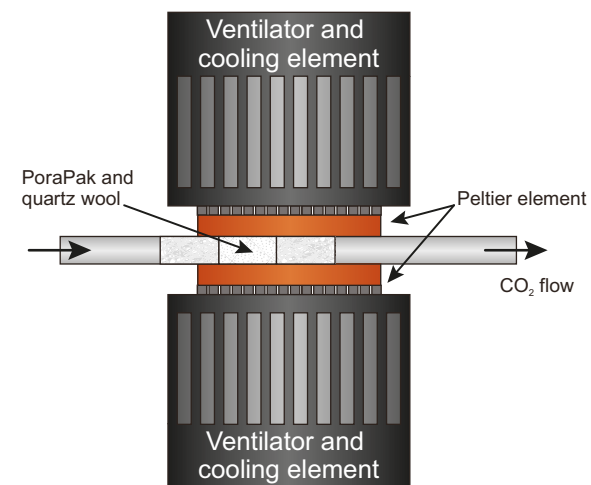


Figure 3. Custom Porapak trapping unit to reduce hydrocarbon contaminants.

Settings of Measuring Procedure

The analysis of small amounts of carbonates requires the use of fully evacuated and contaminant free stainless steel tubing. The process timing, amount of H₃PO₄, leak test threshold and dual inlet parameters are set to optimize the removal of H₂O, non-condensable gases and other contaminants (e.g. hydrocarbons), while optimizing utilization of sample gas. In contrast to traditional stable isotope measurements, the integration time of an acquisition was maximized six cycles of 26 s integration time in order to minimize the statistical noise (shot-noise limit) as can be seen in Table 1.

Kiel IV Carbonate Device Settings

| | |
|---|------------|
| Acid temperature | 70 °C |
| Acid dosing | 3 drops |
| Trap pump out | 120 s |
| Reaction time | 210 s |
| Transfer time | 150 s |
| Reaction time 2 (Removal on non-condensable gases) | 120 s |
| Expansion equilibration delay | 60 s |
| Expansion pump time | 60 s |
| VM2 leak threshold | 150 µbar |
| VM1 leak threshold | 1,000 µbar |
| VM1 expansion threshold | 1,300 µbar |
| Trap heat out temperature | +140 °C |
| CO ₂ freeze temperature | -190 °C |
| CO ₂ release temperature | -110 °C |
| CO ₂ measurement temperature | +30 °C |

Dual Inlet and IRMS Settings

| | |
|------------------|------|
| Integration time | 26 s |
| Cycles | 6 |
| Idle time | 10 s |
| Signal up | 2 % |

Table 1. Method settings.

Analysis of Samples

Under routine conditions, through-put per day is six to eight samples, including two to three internal standards, which have a well known clumped-isotope composition. A sample analysis consists normally of six individual aliquot acquisitions, whereas standards vary from four to eight individual aliquot acquisitions.

Sets of standards are measured at the beginning, at the end and between different samples. The reproducibility of carbonate samples is normally in the range of 0.01 to 0.02‰, greatly dependent on the homogeneity of the sample, as the reported error represents a true external precision as shown in Table 2.

| | | # | δ ¹³ C VPDB (‰) | δ ¹⁸ O VPDB (‰) | Δ ₄₇ (‰) | Temp (°C) | |
|----------------------|-------------|---|----------------------------|----------------------------|---------------------|--------------|-------|
| MS2 | Standard | 8 | 2.160 ±0.06 | -1.760 ±0.11 | 14.203 ±0.060 | 0.365 ±0.016 | 119.3 |
| Candoglia Marble | Standard | 4 | 1.267 ±0.06 | -12.141 ±0.08 | 2.561 ±0.080 | 0.369 ±0.020 | 117.3 |
| Hunza Valley Calcite | Standard | 4 | 4.761 ±0.04 | -4.814 ±0.08 | 13.639 ±0.085 | 0.439 ±0.023 | 86.3 |
| Roklum 560 II | Belemnite | 5 | 0.651 ±0.06 | -1.568 ±0.09 | 13.172 ±0.064 | 0.615 ±0.012 | 32.3 |
| Roklum 590 I | Belemnite | 6 | 0.674 ±0.06 | -2.009 ±0.11 | 12.768 ±0.067 | 0.647 ±0.005 | 24.8 |
| Roklum 590 II | Belemnite | 6 | 0.214 ±0.06 | -1.757 ±0.10 | 12.583 ±0.058 | 0.650 ±0.015 | 24.3 |
| Roklum 650 | Belemnite | 6 | 1.428 ±0.05 | -1.268 ±0.07 | 14.314 ±0.055 | 0.687 ±0.010 | 16.3 |
| MS2 | Standard | 7 | 2.160 ±0.06 | -1.760 ±0.11 | 14.308 ±0.066 | 0.363 ±0.019 | 120.1 |
| Candoglia Marble | Standard | 4 | 1.270 ±0.06 | -12.135 ±0.13 | 2.629 ±0.095 | 0.385 ±0.032 | 109.5 |
| Hunza Valley Calcite | Standard | 4 | 4.770 ±0.05 | -4.755 ±0.08 | 13.801 ±0.082 | 0.431 ±0.016 | 89.1 |
| 13345 Orb | Foraminifer | 6 | 2.689 ±0.19 | 0.521 ±0.25 | 17.485 ±0.083 | 0.654 ±0.010 | 23.3 |
| 13351 Orb | Foraminifer | 6 | 1.928 ±0.23 | 0.466 ±0.11 | 16.726 ±0.097 | 0.707 ±0.016 | 12.4 |
| 13436 Orb | Foraminifer | 6 | 1.667 ±0.06 | 0.099 ±0.13 | 16.079 ±0.079 | 0.700 ±0.005 | 13.8 |
| 13338 Orb | Foraminifer | 3 | 1.149 ±0.29 | 1.016 ±0.33 | 16.533 ±0.110 | 0.707 ±0.060 | 12.4 |
| 13466 Orb | Foraminifer | 3 | 1.409 ±0.09 | 1.182 ±0.04 | 16.920 ±0.013 | 0.662 ±0.035 | 21.5 |
| MS2 | Standard | 8 | 2.160 ±0.05 | -1.760 ±0.11 | 14.318 ±0.059 | 0.363 ±0.017 | 120.3 |
| Candoglia Marble | Standard | 4 | 1.299 ±0.04 | -12.084 ±0.04 | 2.697 ±0.045 | 0.359 ±0.015 | 122.3 |
| Hunza Valley Calcite | Standard | 4 | 4.721 ±0.05 | -4.858 ±0.09 | 13.671 ±0.084 | 0.449 ±0.022 | 82.2 |
| 13380 Rub | Foraminifer | 6 | 1.361 ±0.12 | 0.332 ±0.20 | 16.014 ±0.050 | 0.682 ±0.014 | 17.3 |
| 13414 Rub | Foraminifer | 6 | 1.254 ±0.07 | 0.397 ±0.10 | 15.988 ±0.066 | 0.694 ±0.015 | 15.0 |
| 13420 Rub | Foraminifer | 6 | 0.972 ±0.07 | 0.017 ±0.14 | 15.309 ±0.066 | 0.690 ±0.023 | 15.8 |

Table 2. Δ₄₇ values of standards (MS2, Candoglia Marble and Hunza Valley Calcite), belemnites (Roklum) and foraminifera (*Orbulina*, *Globigerinoides ruber*, Figure 1) # denotes the number of individual acquisitions. Errors are reported as standard error (S.E.). Temperatures are calculated with the Ghosh et al. (2006) calibration.

Three examples of runs are presented in Table 2. MS2 (Carrara Marble), Candoglia Marble and the Hunza Valley Calcite are internal standards, which are included in every run to monitor the system performance. The general reproducibility of these standards on long term is 0.005‰, 0.005‰ and 0.014‰ (Schmid and Bernasconi, 2010).

The samples in the first run are Cretaceous belemnites with reproducibilities in the range of 0.005 to 0.015‰ in Δ₄₇. Run two and three consist of standards foraminifera samples. However, these samples exhibit higher external errors attributed to not homogenized foraminifera samples. The samples 13338 *Orbulina universa* spp. and 13466 *Orbulina universa* spp. demonstrate the importance of at least six sample acquisitions, indicated by the extremely high standard errors of 0.06 and 0.35 per mil. These two results have to be interpreted very cautiously.

Conclusions

The Kiel IV Carbonate Device with the Thermo Scientific MAT 253 Isotope Ratio Mass Spectrometer is capable of fully automated measurement of carbonate clumped-isotopes with a routine precision of 0.01 to 0.02‰ and simultaneous measurement of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. The large number of samples that can be measured completely automated, provide a very user-friendly approach for measuring large sample sets (e.g. high resolution profiles). Furthermore it opens up new possibilities for addressing geological questions where available sample amounts are limited and therefore the method of Ghosh et al. (2006) cannot be applied.



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