Δ47

Clumped isotope thermometry: basics, calibrations and applications

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Sketch of the talk

- Introduction
- Principles of the method
- Analytical methods
- Calibrations
- Applications
All we need is...the water temperature
Paleothermometry

- Conventional carbonate-water oxygen isotope thermometry

\[10^3 \ln \alpha_{c-w} = \frac{(18.03 \times 10^3)}{T} - 32.42\]

\[T \, [{}^\circ\text{C}] = 15.7 - 4.36 (\delta_{\text{calcite}} - \delta_{\text{water}}) + 0.12 (\delta_{\text{calcite}} - \delta_{\text{water}})^2\]

- \[\alpha_{c-w} = \frac{\delta^{18}\text{O}_{\text{calcite}} + 1000}{\delta^{18}\text{O}_{\text{water}} + 1000}\]

- assuming isotopic equilibrium

- Clumped isotope (Δ47) thermometry – a new method
  - it requires no assumptions on the δ^{18}\text{O} of the precipitating water

(Kim and O’Neil, 1997)

(Hays and Grossman, 1991)
Workshops

- 2010 University of Washington, Seattle
- 2011 Imperial College London
- 2013 Harvard University
- 2014 ETH Zürich
- 2016 University of Miami & University of South Florida
Number of papers/Institutes

(Rosenheim 2014)
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<th>Laboratories</th>
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Applications

Applications

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<th>Year</th>
<th>Atmospheric (trace gas budgets, CO₂ sources)</th>
<th>Planetary/Meteoritics</th>
<th>Geomorph/Tectonics (paleoaltimetry)</th>
<th>Geochem/Diagenesis</th>
<th>Bio and Paleobio</th>
<th>Technical or Review</th>
<th>Paleoclimate/paleothermometry</th>
<th>Paleo oceanography (foraminifera, etc.)</th>
<th>High temperature thermal histories of metamorphic rocks</th>
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Type of carbonates: Hydrothermal dolomites, carbonate veins, speleothems, soil carbonates, carbonatites, bioapatites, foraminifera, brachiopods, etc.

(Rosenheim 2014)
PRINCIPLES OF THE METHOD
Clumped isotope geochemistry

- Developed at Caltech, by John Eiler’s team (~2004)

'clumped isotopes’ (multiple-substituted isotopologues) refers to the natural abundance of molecules containing two heavy isotopes, such as $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ and is a measure of the preference of two heavy isotopes to clump together into a chemical bond.

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<th>Mass (AMU)</th>
<th>Isotopologue</th>
<th>Relative abundance</th>
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<tr>
<td>44</td>
<td>$^{12}\text{C}^{16}\text{O}_2$</td>
<td>98.4%</td>
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<tr>
<td>45</td>
<td>$^{13}\text{C}^{16}\text{O}_2$</td>
<td>1.11%</td>
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<td>$^{12}\text{C}^{17}\text{O}^{16}\text{O}$</td>
<td>748 ppm</td>
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<tr>
<td>46</td>
<td>$^{12}\text{C}^{18}\text{O}^{16}\text{O}$</td>
<td>0.40%</td>
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<tr>
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<td>$^{13}\text{C}^{17}\text{O}^{16}\text{O}$</td>
<td>8.4 ppm</td>
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<td>$^{12}\text{C}^{17}\text{O}^{2}$</td>
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<td>47</td>
<td>$^{13}\text{C}^{18}\text{O}^{16}\text{O}$</td>
<td>44.4 ppm</td>
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<td>$^{12}\text{C}^{18}\text{O}^{17}\text{O}$</td>
<td>1.50 ppm</td>
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<td>$^{13}\text{C}^{17}\text{O}^{2}$</td>
<td>1.60 ppb</td>
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<tr>
<td>48</td>
<td>$^{12}\text{C}^{18}\text{O}_2$</td>
<td>3.96 ppm</td>
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<td>$^{13}\text{C}^{17}\text{O}^{18}\text{O}$</td>
<td>16.8 ppb</td>
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<tr>
<td>49</td>
<td>$^{13}\text{C}^{18}\text{O}_2$</td>
<td>44.5 ppb</td>
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For example… for $\text{CO}_2$:

There are twelve isotopologues for $\text{CO}_2$, each of one has unique thermodynamic and kinetic properties.

Very low abundance $\rightarrow$ high analytical challenges
Clumped isotope geochemistry

- At low temperatures molecules containing more than one heavy isotope are more stable than singly-substituted relatives, because of their lower zero-point energy.

- Multiply-substituted isotopologues (clumped isotopes) are more abundant than predicted if the heavy isotopes were randomly distributed among all possible isotopomers.

- The excess abundance of clumped isotopes is temperature-dependent.
Working principle

the clumping effect is based on thermodynamic properties

the molecule with the lowest energy potential needs more energy to reach the threshold that breaks the bond, and therefore, this molecule is more stable

This effect is most prominent at low temperatures and gets smaller with increasing temperature.
Traditional paleothermometry is based on the $^{18}$O-abundance in carbonates based on the heterogeneous exchange equilibrium:

$$\text{CaC}^{16}\text{O}_3 + \text{H}_2^{18}\text{O} \rightleftharpoons \text{CaC}^{18}\text{O}^{16}\text{O}_2 + \text{H}_2^{16}\text{O}$$

Which is temperature-dependent with a change of in $\delta^{18}$O of approx. $0.2\%/°C$

Notation: $\delta^{18}$O = $\left[\left(\frac{^{18}\text{O}}{^{16}\text{O}}_{\text{sample}}/\frac{^{18}\text{O}}{^{16}\text{O}}_{\text{standard}}\right) - 1\right] \times 1000 \%$
Clumped isotope thermometry of carbonates

Based on the homogeneous equilibrium: only one mineral phase is involved in the process of isotope exchange

\[
\frac{13}{16}O_3 + \frac{12}{18}O_2 = \frac{13}{18}O_2 + \frac{12}{16}O_3 \quad K > 1
\]

the abundance of $^{13}C-^{18}O$ bonds in carbonate minerals is proportional to their growth temperature and is independent of their bulk isotopic composition.

- clumping of heavy isotopes relative to stochastic distribution increases with decreasing temperature:
  - At high temperature $\implies \Delta_{47}$ is low
  - At low temperature $\implies \Delta_{47}$ is high
What is $\Delta_{47}$?

Clumped isotope analysis measures the excess abundance of $^{13}\text{C}^{18}\text{O}$ bonds and is based on measurements of the $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ isotopologue, with 47 atomic mass units, relative to mass 44 (the most abundant CO$_2$ isotopologue ($^{12}\text{C}^{16}\text{O}^{16}\text{O}$)).

$$\Delta_{47} \,(\%) = (([47]/[44]_{\text{measured}} / [47]/[44]_{\text{random}})-1) \times 1000$$

- Mass 47 consists of two additional isotopologues ($^{13}\text{C}^{17}\text{O}^{17}\text{O}$ and $^{12}\text{C}^{18}\text{O}^{17}\text{O}$) but they are too rare to make a significant contribution.

- $\Delta_{47} = 0 \,\%$, when the isotopes are randomly distributed (e.g. heating the CO$_2$ to 1000 °C)

Affek (2012)
Comparison of the two thermometers

**Clumped isotope thermometer**

Measurement of masses 44-47 in one phase (homogenous equilibrium) directly provides $\Delta_{47}$ value and temperature

$\rightarrow$ independent of fluid composition

$\rightarrow$ $\Delta_{47}$ value increases at decreasing temperature with $\sim 0.003$-$0.005$ ‰/1°C

**$\delta^{18}$O thermometer**

Temperature is inferred from fractionation between two phases: calcite-water (heterogeneous equilibrium)

$\rightarrow$ depends on knowledge of water $\delta^{18}$O

$\rightarrow$ can be ambiguous

(source: Tobias Kluge)
Challenges of clumped isotope geochemistry

- Small range of variation 0.78 (0°C) to 0.25 ‰ (600°C) in $\Delta_{47}$ requires extremely good precision and reproducibility (±0.005‰ would be desirable).

- Large sample sizes (3-15 mg in most laboratories) are generally necessary for a single measurement.

- Complex custom-built extraction lines required

- Time-consuming instrumental corrections involving gases of different composition heated to 1000°C and equilibrated at 25°C with water are necessary.

- Many calibrations with significant different slopes
ANALYTICAL METHODS
CaCO₃ is converted to CO₂ by reaction with phosphoric acid preserving the clumped isotope signature of the original carbonate (or modified in a consistent way).

CO₂ with masses 44,45,46, 47 is measured

From one measurement we obtain:

- δ¹⁸O, δ¹³C of the carbonate
- Δ₄₇: Excess abundance of $^{13}$C$^{18}$O$^{16}$O relative to a stochastic distribution
What kind of instruments can be used?

Kiel IV
MAT 253
MAT 252
Delta V plus

Research Article

Received: 7 July 2012 Revised: 2 October 2012 Accepted: 3 October 2012 Published online in Wiley Online Library

Precision and long-term stability of clumped-isotope analysis of CO₂ using a small-sector isotope ratio mass spectrometer

Naohiro Yoshida¹, Mikhail Vasilev¹, Prosenjit Ghosh², Osamu Abo³*, Keita Yamada¹ and Maki Morimoto⁴

CONCLUSIONS: The Delta XP gave results that were approximately as precise as those of the MAT 253 for clumped-isotope analysis. The temporal stability of the Delta XP seemed to be lower, although an advantage of the Delta XP was that no dependency of δ¹³C on δ⁴⁷ was found. Copyright © 2012 John Wiley & Sons, Ltd.
Analytical procedure – Heidelberg lab.

- Acid digestion of carbonates 5-10 mg (now: >1 mg)
- Cleaning of CO₂ 2-3 h per sample
- Cleaning line at Heidelberg
- Mass spectrometric analysis 3h per sample
  Precision of single analyses: 0.02-0.03 ‰

- Offline preparation system
- Acid digestion at 90 °C

(source: Tobias Kluge)
Analytical procedure – Imperial College

Qatar Stable Isotope Lab

- Offline preparation system
- 5-7 mg carbonate is needed
- Acid digestion at 90 °C for 10 minutes
- Gas cleaning with Porapak trap

The sample gas is measured against an Oztech reference gas standard. Heated gases (1000°C), water-equilibrated gases (25°C, 50°C, 80°C)

A normal measurement cycle is about 1.5 to 2 hours, and each sample is measured at least three times.
AIMS at ETH Zürich

- Reducing sample size
- Automating measurement to improve sample throughout, adaptation of **commercially available extraction line** (ThermoScientific Kiel IV)
- Developing alternative calibration scheme to reduce the repeated measurements of heated gases
- Improved and streamlined analytical procedures eliminating time-consuming gas measurements.
- Instrumental corrections for mass-spectrometric artifacts using a **background correction** and **carbonate standards**

(Schmid & Bernasconi (2010), Meckler et. al. (2014), RCMS)
Analytical procedure – ETH Zürich

- Automated system (Kiel IV Device), 46 aliquots

  CaCO₃ is converted to CO₂ by reaction with phosphoric acid preserving the clumped isotope signature of the original carbonate.

  CO₂ with masses 44, 45, 46, 47 is measured

- Background correction (Bernasconi et al. 2013) and carbonate standard correction eliminating the need of regular heated gas measurements.

- Precision: 0.005-0.009‰ (±2°C)

- Small samples: 1.5 -2mg (8-10 aliq. of 100-200 μg) with 2-3 drops of c acid/vessel

- Output: 2 samples/day

(Schmid & Bernasconi (2010), Meckler et al. (2014), RCMS)
KIEL IV carbonate device

Figure 2-2. Heating Cabinet - Front View
KIEL IV carbonate device

Autosampler

Figure 2-36. Turret and Correct Vertical Placement of Vials
Gas cleaning with PoraPak

Scheme of the Kiel IV Carbonate Device

Custom Porapak trapping unit to reduce hydrocarbons/halocarbons and sulfur contaminants

Schmid et al. (2011)
**PBL correction:** eliminates the $D_{47}$ dependence from $d^{47}$

Changes in negative backgrounds through time

Bernasconi et al. 2013, Meckler et al. 2014, RCM
Reproducibility of our 5 internal standards over 15 months (n= 70-95):

0.012-0.016 ‰ (1 SD)

Meckler et al. 2014 RCM
Number of replicate aliquots to reach the best possible standard error:
A SE of 0.007-0.009 ‰ (~2 °C) can be achieved with 3 measurements of 1.5-2 mg carbonate each.

Output: 2-3 samples/day
Comparison of analytical approaches

CALTECH

• Analysis of 5-10 mg by reaction in a common acid bath at 90° C with 10 ml phosphoric acid
• Precision reached by using 1 large aliquot measured for a long time (c.a. 2 Hrs).
• Complex custom-built extraction line
• Instrumental corrections for mass-spectrometric artifacts using heated and equilibrated gases.

ETH

• Repeated analysis of small aliquots (150-200µg) with 2-3 drops of phosphoric acid in individual reaction vessels.
• Precision reached by repeated analysis of small aliquots.
• Adaptation of commercially available extraction line (ThermoScientific Kiel IV)
• Instrumental corrections for mass-spectrometric artifacts using a background correction and carbonate standards
Summary of analytical developments

Sample size reduced to 1.5-2mg per measurement, by repeatedly measuring small 150-200µg aliquots – clumped isotopes are applicable to paleoceanography. Further reductions are possible.

- Improved and streamlined analytical procedures eliminating time-consuming gas measurements.

- Sample reaction temperature with Phosphoric acid, influences the apparent T sensitivity of this proxy.

- Improvement of calibrations -> towards a common T calibration
CALIBRATIONS
The first calibration – Ghosh et al. (2006)

\[
\Delta_{47} = \frac{0.0592 \times 10^6}{T^2} - 0.02
\]

\[R = 0.94\]
Currently available calibrations – large range

- Came et al. (2013), Tripati et al. (2010, GCA), Fernandez et al. (2014)

Different reaction temperatures → different T-D$_{47}$ relationships → different T-sensitivity

Currently available calibrations – large range
acid digestion T vs. calibration slope

Fernandez et al. 2013

\[ \Delta_{\text{G-RF}} = \frac{(0.0385 \pm 0.0019) \times 10^6}{T^2} + (0.271 \pm 0.023) \]
different reaction $T$, different $T-D_{47}$ relationships

\begin{align*}
25 \, ^\circ C \text{ digestion} \\
y &= 0.0572x + 0.0445 \\
R^2 &= 0.96765 \\
70 \, ^\circ C \text{ digestion} \\
y &= 0.0432x + 0.184 \\
R^2 &= 0.95117
\end{align*}
Calibration at high temperatures

- Theoretical calculations are based on transition state theory, statistical thermodynamics.
- Due to non-linear dependence of D47 on T, analytical uncertainties equate to larger temperature errors at higher temperatures...
  - Analytical precision $\sim 0.01$ translate to the following T errors:
    - 50°C: ±4°C
    - 150°C: ±10°C
    - 250°C: ±18°C

Guo et al. (2009)
Blocking/closure temperature

- the crystal structure has formed sufficiently to prevent diffusion of isotopes

- Carbonatites have been used as a geologic test

None of the high temperature carbonates measured record signatures lighter than 0.31‰, implying isotope exchange continues during cooling until ca. 250–300 °C.

This suggests the temperature at which solid-state exchange ceases is in the range of 250–300 °C (an upper limit on temperatures recorded by the clumped isotope proxy in natural carbonates)

\[ T = 250–300 \, ^\circ\text{C} \]

\[ \Delta_{47} = 0.31 \, \text{‰} \]
Laboratory calibration at Imperial C. (25-250°C)

Kluge et al. (2015)
Laboratory calibration at Imperial C. (25-250°C)

- minerals were precipitated from a CaCO3 supersaturated solution at atmospheric pressure (23-91°C),
- second, from a solution resulting from the mixing of CaCl2 and NaHCO3 in a pressurized reaction vessel at a pressure of up to 80 bar (25-250°C).

Kluge et al. (2015)
**Temperature calibration**

**Inorganic calibration**
Summary of inorganic laboratory experiments, phosphoric acid reaction at 90°C

**Results:**
- agreement between different labs
- $\Delta_{47}$-T constrained over wide T range

\[
\Delta_{47} = 0.98 (\pm 0.01) \cdot (-3.407 \cdot 10^9/T^4 + 2.365 \cdot 10^7/T^3 - 2.607 \cdot 10^3/T^2 - 5.880/T) + 0.293 (\pm 0.004)
\]

Kluge et al. (2015)
CALIBRATION USING TRAVERTINES
**Aim**

**Calibration** of the clumped isotope thermometer on recent natural carbonates (travertine and tufa) in order to improve the confidence in paleotemperature reconstructions

1) They grow over a **wide temperature range**;

2) The **temperature**, **pH**, and **water chemistry** and **rate of deposition** can be measured

3) They are mainly inorganic deposits and show **no biological vital effect**;

4) They form **different polymorphs** of calcium carbonate (calcite, aragonite).

**Study of the possible effect of pH, precipitation rate, mineralogy on the Δ_{47} –values**
- Stable isotope analyses on 108 travertine & tufa samples
- Clumped isotope analyses on ~1000 aliquots of 51 recent carbonate samples
Travertines
Downstream sampling
Tufa

5.6 < T < 95 °C

5.7 < pH < 8.9

0.5 < EC < 20 (mS/cm)

0.05 < log R < 28.5 (mg/cm²/d)
DOWNSTREAM SAMPLES:  →  increasing DISEQUILIBRIUM

DOWNSTREAM SAMPLES are not involved into the calibration!
Strong T-dependence of vent and pool travertines

- Slightly lower $1000\ln\alpha$ values for tufa samples
- No effect of mineralogy
Conventional carbonate-water oxygen isotope thermometry

\[ y = (20 \pm 2.2)x - (36 \pm 6.8) \]

\[ R^2 = 0.96; \ N = 16 \]
STRONG T-DEPENDENCE OF $\Delta_{47}$ DATA OF VENT AND POOL SAMPLES

Devils Hole data fit to the calibration: travertines might represent equilibrium

- Tufa samples are also fit to the travertine calibration
- No effect of mineralogy

Kele et al. (submitted)
CALIBRATION OF THE CLUMPED ISOTOPE THERMOMETER

\[ y = (0.044 \pm 0.005)x + (0.20 \pm 0.05) \]

\[ R^2 = 0.96 \]
Offsets in $1000\ln\alpha$ and $\Delta47$ values → NO correlation

\[ y = (69.5 \pm 8.2)x - (17.4 \pm 5.1) \]
\[ R^2 = 0.96; N = 14 \]
EFFECT OF PRECIPITATION RATE

- Oxygen isotope fractionation between calcite and water can be affected by the precipitation rate (Dietzel et al., 2009), Day and Henderson, 2010, Gabitov et al., 2012)

  high carbonate precipitation rates drive $\delta^{18}O_{\text{carbonate}}$ to lower values

- Saenger et al. (2012): fast-growing hermatypic corals; higher than expected $\Delta_{47}$ values might be caused by fast calcification

- Tripati and Hill (2014): the crystal may inherit the $\Delta_{47}$ value of the DIC species and thus record a disequilibrium mineral composition, when the growth rate is high, while DIC speciation effects are likely to be negligible for slow-growing crystals

Tang et al. (2014), Kele et al. (submitted)
EFFECT OF PRECIPITATION RATE

Experimental approach

(b) $T=25\,^\circ\text{C}$ and pH=8.3

c) $T=40\,^\circ\text{C}$ and I=35 mM

Tang et al. (2014)
EFFECT OF PRECIPITATION RATE

Experimental approach

Tang et al. (2014)
EFFECT OF PRECIPITATION RATE → No effect for the $\Delta_{47}$
EFFECT OF PRECIPITATION RATE → NO EFFECT

Variable log R values: between 0.06 and 28.5 mg/cm²/day

Kele et al. (submitted)
EFFECT OF pH ON THE $\Delta_{47}$ VALUES

pH may influence oxygen and clumped isotopes through two ways:

- Equilibrium DIC speciation
- $\text{CO}_2$ hydration and hydroxilation

Zeebe (1999), Tang et al. (2014)
EFFECT OF pH ON THE $\Delta_{47}$ VALUES – LITERATURE REVIEW

- **In the earliest calibration studies** (e.g. Ghosh et al., 2006; Dennis and Schrag, 2010) the experimental conditions were **not investigated**

- Tripati et al. (2010) found **no evidence** for a relationship between pH and $^{13}$C–$^{18}$O bond order in foraminifera.

- Thiagarajan et al. (2011): **differences in $\Delta_{47}$ between DIC species can lead to pH effects** in the $\Delta_{47}$ and $d^{18}$O values

- Saenger et al. (2012): fast-growing **hermatypic corals**; pH-related changes in DIC speciation alone cannot explain the observed offsets in their $\Delta_{47}$ and $d^{18}$O values
THEORY SUGGESTS pH EFFECT

- **Guo (2008)**: CO₃²⁻ is estimated to be ~0.018 ‰ lower in Δ⁴⁷ than HCO₃⁻, while the d¹⁸O value of the CO₃²⁻ is ~7 ‰ lower at 25ºC.

- **Hill et al. (2014)** suggest that pH and salinity can have an effect on Δ⁴⁷ values of the carbonate minerals if the growth rate is high. Δ⁴⁷ values can be up to 0.03 ‰ higher at low pH compared to neutral pH 8.

The Δ⁴⁷ value of carbonates rapidly formed by dehydration of HCO₃⁻ is expected to be ~0.03 ‰ higher than from CO₃²⁻, but ~0.03 ‰ lower than that of H₂CO₃ (Hill et al. 2014).
EFFECT OF pH ON THE $\Delta_{47}$ VALUES

- Well-controlled experimental conditions
- Study of the effects of precipitation rate ($\log R$), pH and ionic strength

There is no clear effects of pH, ionic strength and growth rate effects on the measured $\Delta_{47}$ values

Tang et al. (2014)
EFFECT OF pH ON THE $\Delta_{47}$ VALUES ➔ NO EFFECT (?)

- Study of four vent travertines from Italy, Turkey and Hungary from the acidic (6.1-6.8) pH range (Kluge et al.)

- **AIM:** to test the theoretical predictions of the pH effect on the $\Delta_{47}$ values
EFFECT OF pH ON THE $\Delta_{47}$ VALUES

Kluge et al. (submitted)
EFFECT OF pH ON THE $\Delta_{47}$ VALUES

Positive $\Delta_{47}$ offset (corresponding to theoretical calculations) may indicate that the $\Delta_{47}$ value is generally determined in the DIC and directly inherited in the mineral during fast growth.

- pH-related effects could be relevant in sub-surface environment if linked with high mineral growth rates at moderate temperatures (<70 C).

Positive $\Delta_{47}$ offset can lead to an under-estimation of the formation temperature!

Kluge et al. (submitted)
EFFECT OF pH ON THE Δ_{47} VALUES → NO EFFECT

Kele et al. (submitted)
Different materials, different calibrations

All ETH precipitates: \[ Y = 0.04526 \times X + 0.1989, N = 7, R^2 = 0.99 \]
ETH biogenic: \[ Y = 0.04216 \times X + 0.2160, N = 6, R^2 = 0.996 \]
ETH travertines: \[ Y = 0.04288 \times X + 0.2071, N = 31, R^2 = 0.94 \]
Leeds: \[ Y = 0.04423 \times X + 0.1757, N = 7, R^2 = 0.98 \]
Hagit surface: \[ Y = 0.04289 \times X + 0.1891, N = 3, R^2 = 0.99 \]
Hagit surface: \[ Y = 0.04282 \times X + 0.1751, N = 4, R^2 = 0.998 \]
KIEL calibration in Grauel et al. (2013)

Consistent with the slope of Ghosh et al., 2006,

- Tripati et al., 2010

- Not in absolute reference frame (Dennis et al. 2011)

- Limited temperature range

- Based on core-top foraminifera

- Without using the new standard correction (Meckler et al., 2014)
ETH calibration based on synthetic calcites

Previous calibration studies using synthetic calcites:

• Ghosh et al. (2006), Zaarur et al. (2013): Growing synthetic calcite by active removing of CO$_2$ (N$_2$ bubbling) from calcite-saturated solutions, using a method similar to that described by Kim and O’Neil (1997)

• Dennis et al. (2010): Passive degassing of calcite-saturated solutions

• Kluge et al. (2015): Laboratory calibration of the calcium carbonate clumped isotope thermometer in the 25-250 °C temperature range
Mixing of 20 ml of 0.1M NaHCO$_3$ and 200 ml of 0.1M CaCl$_2$ solutions (equilibrated over several days)

I. Rapid mixing, with rapid (s to hrs) and near-quantitative precipitation (ETH)

I. Constant slow addition of solutions to achieve relatively slow (several days) precipitation of calcite (Leeds University)

Temperature range: 3 to 70°C

Ziegler et al. (in prep)
ETH: comparison of the two experiments

ETH synthetic CC, fast growth
\[ y = 0.0444x + 0.207 \]
\[ R^2 = 0.996 \]

ETH synthetic CC, slow growth
\[ y = 0.0440x + 0.179 \]
\[ R^2 = 0.984 \]

Offset:
- pH?
- precipitation rate?

Ziegler et al. (in prep)
Comparison with natural samples - travertines

ETH synthetic CC, fast growth
\[ y = 0.0444x + 0.207 \]
\[ R^2 = 0.996 \]

ETH synthetic CC, slow growth
\[ y = 0.0440x + 0.179 \]
\[ R^2 = 0.984 \]

Travertines
\[ y = 0.0445x + 0.1927 \]
\[ R^2 = 0.96 \]

Ziegler et al. (in prep)
Comparison with natural samples - biogenic

ETH synthetic CC, fast growth
\[ y = 0.0444x + 0.207 \]
\[ R^2 = 0.996 \]

ETH synthetic CC, slow growth
\[ y = 0.0440x + 0.179 \]
\[ R^2 = 0.984 \]

Travertines
\[ y = 0.0445x + 0.1927 \]
\[ R^2 = 0.96 \]

Ziegler et al. (in prep)
Comparison with natural samples - speleothems

- ETH synthetic CC, fast growth
  \[ y = 0.0444x + 0.207 \]
  \[ R^2 = 0.996 \]

- ETH synthetic CC, slow growth
  \[ y = 0.0440x + 0.179 \]
  \[ R^2 = 0.984 \]

- Travertines
  \[ y = 0.0445x + 0.1927 \]
  \[ R^2 = 0.96 \]

Ziegler et al. (in prep)
Comparison with other calibrations

ETH synthetic CC, fast growth
\[ y = 0.0444x + 0.207 \]
\[ R^2 = 0.996 \]

ETH synthetic CC, slow growth
\[ y = 0.0440x + 0.179 \]
\[ R^2 = 0.984 \]

Travertines
\[ y = 0.0445x + 0.1927 \]
\[ R^2 = 0.96 \]

Ghosh et al., 2006

Dennis et al., 2011

Ziegler et al. (in prep)
Three new calibration datasets, based on measurements of synthetic calcites and natural travertines using the Kiel Carbonate Device ($r^2$ in all cases >0.96)

All three calibrations have a very similar slope (0.044) but different intercepts

Additional biogenic samples appear to be consistent with travertine line, speleothem samples with slow growth synthetic calcites line

Intermediate slope supports the idea, that the acid digestion temperature determines the calibration slope

Ziegler et al. (in prep)
Conclusions – travertine calibration

- Both δ¹⁸O and Δ₄⁷ data of samples close to the vents and in pools show a strong correlation with temperature suggesting precipitation close to „equilibrium” conditions

- Vent travertines and tufa deposit show strong Δ₄⁷-T relationship between 5-95 °C:

  \[ \Delta_{47} = \frac{(0.044 \times 10^6)}{T^2} + 0.20 \quad (r^2= 0.96) \]

- NO clear effect of pH, mineralogy and precipitation rate on the Δ₄⁷ values!

- The slope of our Δ₄⁷-T calibration confirms the relationship with the acid digestion temperature (high digestion T – shallow slope)
Applications

This is the most robust calibration of the clumped isotope thermometer from inorganically precipitated carbonates from nature and extends the temperature range of empirical calcite calibrations to 95 °C.

Our empirical travertine vent+pool calibration can be used to calculate the T of deposition (and also the $\delta^{18}O$) of both travertine and tufa precipitating waters.

Applications: paleoclimate research, diagenesis, temperature of deposition of cement phases, reservoir geology... etc.
Deep Time Paleoclimate

APPLICATIONS
Thermometry - Deep time paleoclimate

Case study: Deep time paleoclimate

Ordovician-Silurian paleoclimate and paleogeographic reconstruction

$\Delta_{47}$ thermometry of fossils to constrain ocean temperatures, in order to estimate ice-volumes through the Late Ordovician-Early Silurian glaciation

far more is known about the most recent glacial age in the Pleistocene than about older glacial episodes...

Finnegan et al., 2011
This glaciation of the Gondwana is unusual:

- It occurred during a period when atmospheric partial pressure was generally \((8-16 \text{ times})\) higher than today.
- It was short-lived compared to subsequent Gondwanan glaciations.
- It is the only glacial episode that appears to have coincided with a major mass extinction of marine life.

The Late Ordovician–Early Silurian icehouse represents a climate mode distinct from more recent glaciations (duration?, peak ice sheet volume? Tropical SST?)

Finnegan et al., 2011
Reconstructed temperatures are nearly indistinguishable from each other and consistent with a narrow range from 32°C to 37°C throughout the ~20 mill. ys.
Relative contributions of temperature and $\delta^{18}O_{\text{water}}$ to changes in $\delta^{18}O$

$\Delta_{47}$ measurements place independent constraints on how much of the temporal variation in d18O can be explained by T changes

For much of the study interval, d18O variation is driven almost entirely by changes in d18O$_{\text{water}}$
Evidence for ice sheets spans much of the study interval, but the cooling coincided with a glacial maximum during which ice volumes likely equaled or exceeded those of the last (Pleistocene) glacial maximum. This cooling also coincided with a large perturbation of the carbon cycle and the Late Ordovician mass extinction.

- **tropical ocean temperatures of 32° to 37°C** except for short-lived cooling by ~5°C during the final Ordovician stage.

- Initial glaciation of Gondwana occurred with little or no cooling of the tropical oceans, that tropical SSTs exceeded the present-day range except during the Hirnantian glacial maximum, and that they warmed rapidly after the Hirnantian maximum despite the persistence of substantial continental ice volumes for several million years.

- **Nonlinear relationship** between tropical ocean temperatures and continental ice volumes.

Finnegan et al., 2011
APPLICATIONS

Search for equilibrium
Search for equilibrium – Devils Hole

Case study: Equilibrium vs. Kinetics

- fault zone, slowly opening fractures
- tectonic cave

- large aquifer
- slightly super-saturated ($\text{HCO}_3^-$)
- stable T and chemistry (?)

Mammillary calcite
Devils Hole #2

- calcite
- very slow growth
- 1 mm/1000 a
- long record (700 ka)

Drill core
(Picture: C.Spötl, Y. Dublyansky)

Kluge et al., 2014
Search for equilibrium – Devils Hole

(Coplen, 2007): Fractionation factor H₂O-calcite for oxygen greater than so far accepted. Independent proof? Implications?

Assuming is that the δ¹⁸O water was constant throughout in the Holocene.

Kluge et al., 2014
Search for equilibrium – Devils Hole

Sample ages: 27-179 ka

- $\Delta_{47}$ values of glacial and interglacial periods are indistinguishable → aquifer temperature constant
- Devils Hole $\Delta_{47}$ value consistent with laboratory calibration → indication for equilibrium in the DIC

Kluge et al., 2014
Search for equilibrium – Devils Hole

Kluge et al., 2014
Kluge et al. (2014) ‘...confirmed a constant aquifer temperature and calcite formation in isotopic equilibrium for at least the last 180 kyr. Consequently, the Devils Hole calcite is a faithful recorder of the isotopic composition of the regional groundwater and therefore constitutes a valuable paleohydrological archive. Beyond paleoclimate research, Devils Hole calcite may serve as a reference material for isotopic equilibrium...’
CLUMPED ISOTOPES IN SPELEOTHEMS: useful or not...?

...only seven papers have been published...
Applications

Aim: extraction of terrestrial climatic information from speleothems

- **Reconstruction of paleotemperatures** using glacial-interglacial variations in the $\Delta_{47}$ values (Affek et al. 2008, Wainer et al. 2011)

- Reconstruction of $\delta^{18}$O of **paleo-drip-water** (Kluge et al. 2012)

- Quantification of **kinetic fractionation** (Daëron et al., 2011; Kluge and Affek, 2012)
Might NOT be useful...

...since the $\Delta_{47}$ of speleothems is sensitive to kinetic fractionations arising during CO$_2$-degassing from drip water films and fast carbonate precipitation

$\Rightarrow$ $\Delta_{47}$ is lower

$\Rightarrow$ $\delta^{18}O$ is higher

...than...

Daëron et al. (2011)
Soreq cave (Israel) speleothems: old (Holocene, Pleistocene) samples and modern samples to assess the importance of kinetic effects

**AIM:** Calculation the $\delta^{18}O$ of the precipitating water using the $\Delta_{47}$-based water temperatures, the measured $\delta^{18}O_{\text{carbonate}}$ and using the T-dependence of the calcite-water $^{18}O$ fractionation

$\Delta_{47}$-values of modern samples recorded apparent temperatures with +8 °C offset from the real temperature.

**Empirical correction** for a non-equilibrium artifact observed in a modern speleothem is needed, assuming that the offset is constant for older samples.
**Reason for the offset**

*Kinetic isotope effect* occurs during rapid degassing of CO$_2$ from calcite saturated aqueous solutions (Hendy, 1971)

- If, **degassing is rapid** compared to the rate of isotopic exchange between DIC and water, this will leave a **relative deficit of $^{13}$C–$^{18}$O bonds** in residual DIC species, and thus **lower than equilibrium $\Delta_{47}$ values (higher than equilibrium apparent temperatures)** in carbonates grown from that DIC.

- When degassing and precipitation are **slow** enough, the DIC can undergo a full $^{18}$O exchange with water leading to **equilibrium values in both $\delta^{18}$O and $\Delta_{47}$**.

- At equilibrium there is a correlation between the $\delta^{18}$O and $\Delta_{47}$ values assuming a constant $\delta^{18}$O value of drip water

Affek et al. (2008)
The ‘corrected’ $\Delta_{47}$ temperatures are consistent with the previous, independent estimates.
Study of KIE (kinetic isotope effect)

Carbonate precipitation from **bulk solution** – typically used for calibration of the $\delta^{18}O$ and $\Delta_{47}$ thermometers (e.g. Kim and O’Neil 1997, Zaarur et al. 2013)

Carbonate precipitation at the surface of the solution – amplifying the thin film characteristics of speleothem formation (passive degassing)

Soreq Cave speleothems are intermediate between these thermometers, providing a cave specific thermometer calibration
The Δ47-δ18O co-variance is strongly temperature dependent!

This suggests an influence of additional fractionation in fast growing minerals, between DIC and calcite, that affects δ18O.
APPLICATIONS

Cryogenic cave carbonate
Cryogenic cave carbonates (CCC) – useful or not?

Precipitation from oversaturated freezing cave pool water

- \( \text{CCC}_{\text{fine}} \): rapidly freezing thin water films result in the fast precipitation of fine-grained powder (rapid physicochemical changes, \( \text{CO}_2 \) degassing, etc.)

- \( \text{CCC}_{\text{coarse}} \): slow carbonate precipitation in ice-covered cave pools results in coarse crystalline CCC

Kluge et al., 2014
$\text{CCC}_{\text{coarse}}$ – useful or not?
CCC_{coarse} – useful or not?

Kluge et al., 2014
CCC\textsubscript{fine} – useful or not?

The estimated $\Delta_{47}$-based formation temperature of the samples ranged between 11-18 °C

non-equilibrium fractionation during precipitation in case of the fine-grained CCC as-well, similarly to the recently reported results from coarse-grained CCC (Klüge et al. 2014).

$\Delta_{47}$-based temperatures significantly above expected freezing temperatures indicate incomplete isotopic equilibration during precipitation of CCC

Figure 1.
Location of the Scărişoara Ice Cave (star).
APPLICATIONS

Soil carbonates

Quade et al. (2007, 2013), Garzione et al. (2008), Huntington et al. (2010), Passey et al. (2010), Peters et al. (2013), Hough et al. (2014)
Soil carbonates—useful for what?

- **Soil carbonate** is abundant and widely distributed in the geologic record and has proved useful in **paleoenvironmental reconstruction**.

\[ \text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O} = \text{Ca}^{++} (aq) + 2\text{HCO}_3^- (aq) \]

- $\delta^{13}C$: paleoecology, paleo-pCO$_2$, plant respiration rates (aridity), ..
- $\delta^{18}O$: reconstruction of $\delta^{18}O$ of meteoric water

$\delta^{18}O$: paleoaltimetry
Paleoaltimetry

- $\delta^{18}O_{\text{rainfall}}$ and surface temperatures vary as a function of elevation ($\sim 2.8 \% / \text{km decrease}$ of rainfall due to rainout).

- $\delta^{18}O$ of pedogenic carbonate and carbonate cement should reflect the $\delta^{18}O$ of soil water and shallow groundwater, which is a reflection of $\delta^{18}O$ of rainfall and near surface temperature.

- The effect of elevation will be archived in the $\delta^{18}O_{sc}$ provided that:
  - Temperature of formation can be estimated (e.g. from $A_{47}$ data)
  - The effects of evaporation are small
  - The effects of climate change can be accounted for
  - The carbonate is not diagenetically altered

Sampling from deep (> 50 cm) in paleosols can help
Clumped isotope thermometry, combined with conventional stable isotope geochemistry, provides:

- comparison of the record of carbonate growth temperatures with inferred altitudinal gradients in surface temperature

- comparison of calculated $\delta^{18}O_{sw}$ values with inferred altitudinal gradients in the $\delta^{18}O_{mw}$ values
Soil carbonates – problems

- **ground heating** is related to **seasonality** of soil carbonate formation, site shading, and site aspect (Quade et al. 2013)
- $\delta^{18}O$ of soil water can differ from the $\delta^{18}O$ of meteoric water due to **evaporative** enrichment
- **Diagenesis** (recrystallization of micrite to spar is a warning sign)
- Local cooling by **shade/vegetation**

![Graph showing $\delta^{18}O$ values for different soils](image-url)
Modern soils and buried paleosols

- Soil temperature varies diurnally and seasonally in soils. Depending on soil depth, $T^\circ C(47)$ will depend on the average time of day and year that it forms.

- Carbonate precipitation happens in summer, when soil water content is at its lowest.

Only extreme summer temperatures will be recorded.

- Below 300 cm, soil temperature is nearly invariant seasonally.

Quade et al. (2013)
Soil carbonates – Rise of the Andes

- Earth’s second largest mountain belt
- active plate margin where oceanic lithosphere is subducted beneath continental lithosphere.

Rise of the Andes
Carmala N. Garzione, et al.
Science 320, 1304 (2008);
DOI: 10.1126/science.1148615
Soil carbonates – Rise of the Andes

- T estimates from fossil-leaves suggest that paleoelevations were <1.3 km at ~15 to 20Ma (20) and <2 km by ~10 Ma (21).

- $\Delta_{47}$ data are consistent with elevation estimates from fossil leaves.

- Despite increasingly arid climate, the combined $\delta^{18}O_{c}$ and dD data show trends toward more negative isotopic compositions of meteoric water.

**Fig. 4.** Multiple proxies of elevation versus time for the central Andean plateau over the past 30 My. Paleoelevation estimates are derived from oxygen isotopes (17, 23), both $\Delta_{47}$ and oxygen isotopes (17, 22), and fossil-leaf physiognomy (20, 21).

Decrease in $\delta^{18}O_{c}$ reflects a change in surface elevation
Soil carbonates – Rise of the Andes

• Before 25 Ma, d18Oc values and high paleotemperature estimates → close to sea level

• minimal surface elevation change between 25-10 Ma

• Between 10-6 Ma → rapid surface uplift

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Fig. 4. Multiple proxies of elevation versus time for the central Andean plateau over the past 30 My. Paleoelevation estimates are derived from oxygen isotopes (17, 23), both $\Delta_{47}$ and oxygen isotopes (17, 22), and fossil-leaf physiognomy (20, 21).
Conclusions

Clumped isotopes are a promising new tool for a large range of geological problems from paleoclimatology to low T hydrothermal/metamorphic conditions.

Analytical improvements and a better understanding of the causes of discrepancies in the different calibrations, are improving the applicability of this tool.

Original clumped isotope signatures are preserved as long as burial temperatures do not exceed 200-250°C.
Challenges and open questions

- Improving analytical methods
  - Improving analytical methods
  - Further decreasing required sample size
  - Improving precision
  - Interlaboratory calibrations

- Experimental calibrations at higher temperatures