

Dual clumped isotope thermometry resolves kinetic biases in carbonate formation temperatures

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Introduction

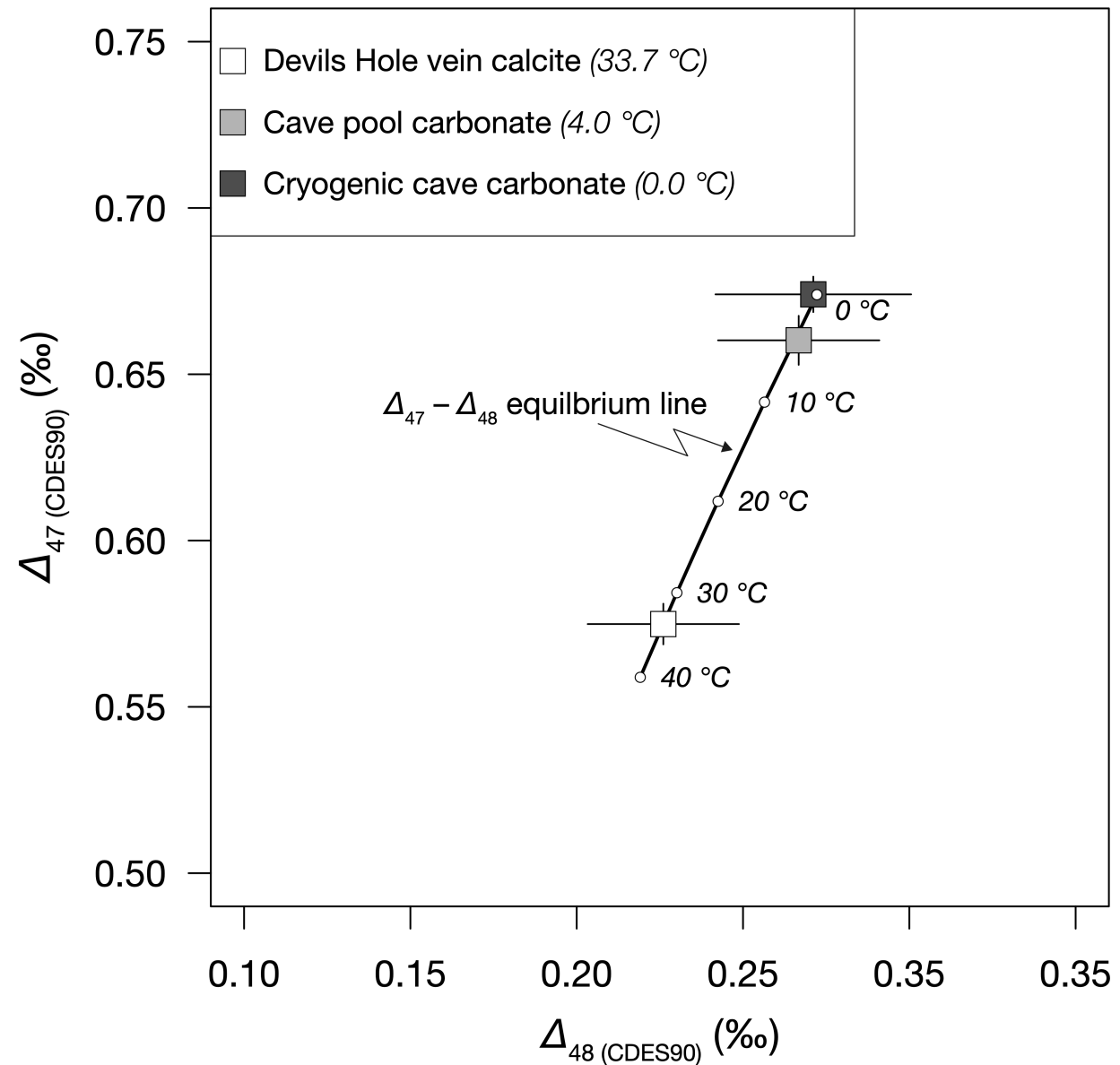
- **Problem:** Most carbonates precipitate out of clumped (Δ_{47}) and oxygen ($\delta^{18}\text{O}$) isotope equilibrium.
- The main reason for this are kinetic isotope fractionation processes that occur during carbonate precipitation. For example, kinetics occur when the carbonate precipitates faster from a solution before the DIC species reach isotopic equilibrium.
- This makes palaeothermometry complicated, because the extent of kinetic effects is often unknown:
 - speleothems with various growth rates
 - records consisting of multiple species
 - extinct organisms
- **Possible solution:** Combining Δ_{47} and Δ_{48} measurements in carbonates can help to resolve temperature from the kinetic information recorded in the single carbonate phase (Guo & Zhou 2019, Guo 2020).

What is Δ_{48} ?

- $^{18}\text{O}-^{12}\text{C}-^{18}\text{O}$ is the main CO_2 isotopologue contributing to the Δ_{48} signal.
 - (In comparison, $^{16}\text{O}-^{13}\text{C}-^{18}\text{O}$ is the main CO_2 isotopologue contributing to the Δ_{47} signal.)
- Carbonate Δ_{48} is measured along with Δ_{47} (see Fiebig et al. 2019).
- The Δ_{47} and Δ_{48} values of carbonates in equilibrium depend only on the precipitation temperature.
- Δ_{47} and Δ_{48} are independent of each other and of ambient water chemistry.

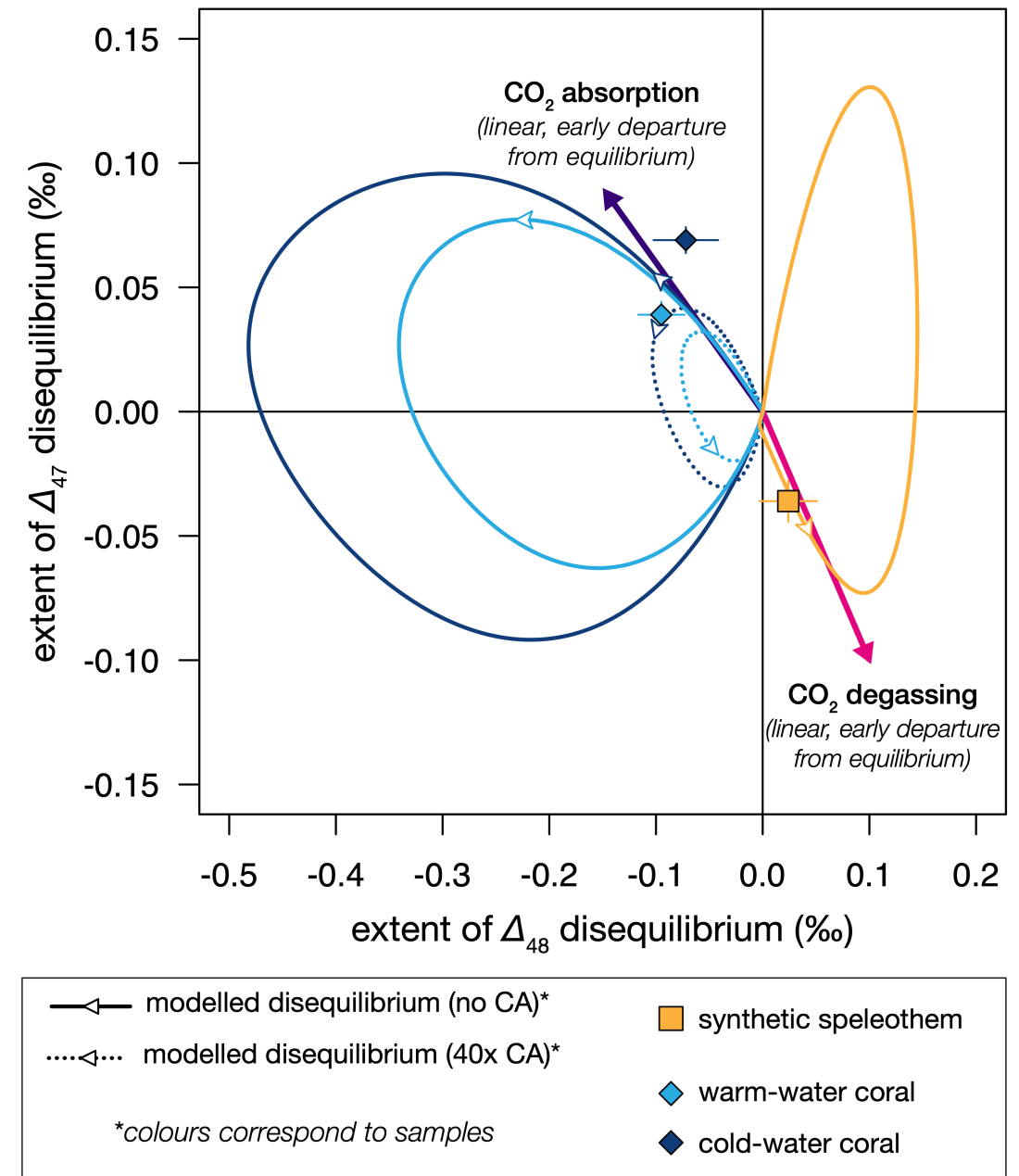
Where is equilibrium?

- In Δ_{47} vs Δ_{48} space, a curve represents temperature-dependent equilibrium. We constrained this curve in multiple steps:
- First, we took the theoretical equilibrium relationships of Hill et al. (2014).
- Then, we anchored it to the measured Δ_{47} and Δ_{48} value of a Devils Hole carbonate at 33.7 °C.
 - Vein calcites from Devils Hole, Nevada, USA, is thought to best approach thermodynamic equilibrium isotope compositions due to their extremely slow growth rates (Coplen 2007).
- To verify whether this anchored line accurately represents equilibrium also at low temperatures, we analysed two low-temperature calcites that were thought to precipitated in or very close to equilibrium at 4 °C and at 0 °C, respectively.
 - The measured Δ_{47} and Δ_{48} values of these two carbonates fall precisely on the anchored equilibrium line, where expected.



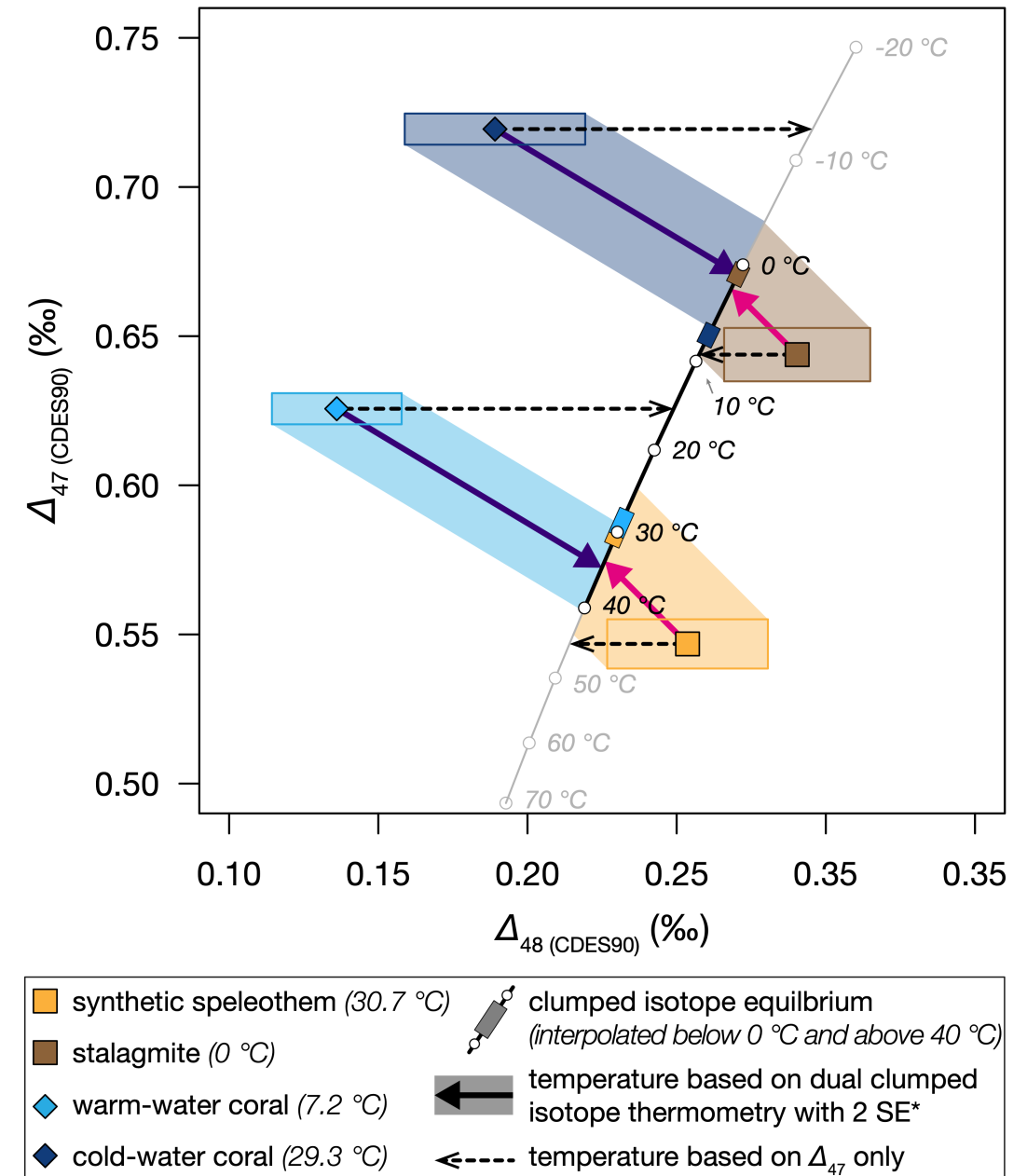
Modelling disequilibrium trajectories

- Based on available resources (Guo & Zhou 2019, Guo 2020) and the known precipitation conditions of three samples, we modelled the disequilibrium effects of **CO₂ degassing** and **CO₂ absorption** on the DIC of a solution starting from isotopic equilibrium.
- The evolution of the clumped isotope composition of the DIC follows nonlinear trajectories in Δ_{47} vs Δ_{48} space, dependent on T , CA activity, $p\text{CO}_2$, etc.
- Offsets from equilibrium observed in two scleractinian corals and a synthetic speleothem fall close to the **linear segment** of the model-predicted early departure from isotopic equilibrium.
- The initial linear segments of the model-predicted deviations from clumped isotope equilibrium (Δ_{47} and Δ_{48}) display slopes of **-1.0** and **-0.6** for carbonates formed during the early stages of CO₂ degassing and CO₂ absorption, respectively.



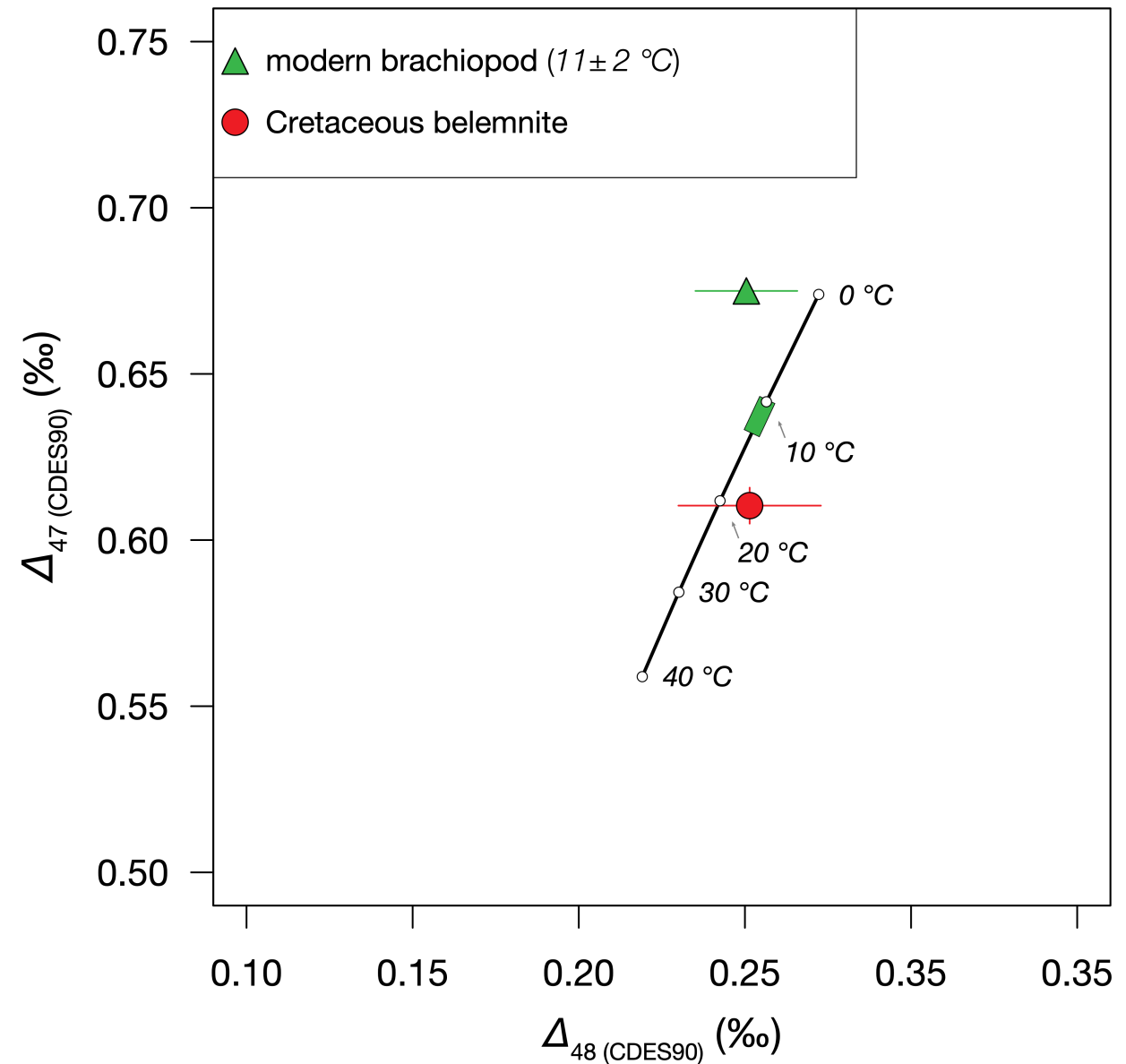
How does dual clumped isotope thermometry work?

- Take the linear slope, characteristic for the dominant kinetic reaction pathway:
 - CO₂ absorption for biogenic carbonates (**-0.6, blue**)
 - CO₂ degassing for speleothems (**-1.0, pink**)
- Fit the line through the measured data point.
- Its intersection with the equilibrium line yields the growth temperature, unbiased by kinetics.
 - For the samples investigated here, the real growth temperatures are within 95% confidence interval of the dual clumped isotope temperatures.
- In comparison, Δ_{47} -only thermometry (dashed lines) would under- or overestimate the carbonate precipitation temperatures significantly.



Belemnites vs brachiopods

- Belemnites and brachiopods are both important palaeoceanographic archives.
- Brachiopods are known to exhibit disequilibrium Δ_{47} signatures (Bajnai et al. 2019).
- In this study, we also see disequilibrium Δ_{47} and Δ_{48} values for a fast-growing, modern brachiopod.
- Dual Δ_{48} – Δ_{47} thermometry for the brachiopod yields too cold temperatures.
 - The CO₂ absorption model may not have captured the primary source of isotopic disequilibrium in brachiopods.
 - Causes of kinetics in brachiopods have to be further investigated.
- A belemnite, in contrast, seems to have precipitated its rostra in or near clumped isotope equilibrium.
 - Belemnites, thus, can be used to determine palaeotemperatures.



This work is based on:

Bajnai, D., Guo, W., Spötl, C., Coplen, T.B., Methner, K., Löffler, N., Krsnik, E., Gischler, E., Hansen, M., Henkel, D., Price, G.D., Raddatz, J., Scholz, D. and Fiebig, J. (in review) Dual clumped isotope thermometry resolves kinetic biases in carbonate formation temperatures. *Nature Communications*.

References

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- Coplen, T.B. (2007) Calibration of the calcite–water oxygen-isotope geothermometer at Devils Hole, Nevada, a natural laboratory. *Geochimica et Cosmochimica Acta*, 71, (16), 3948-3957. <https://doi.org/10.1016/j.gca.2007.05.028>
- Fiebig, J., Bajnai, D., Löffler, N., Methner, K., Krsnik, E., Mulch, A. and Hofmann, S. (2019) Combined high-precision Δ_{48} and Δ_{47} analysis of carbonates. *Chemical Geology*, 522, 186-191. <https://doi.org/10.1016/j.chemgeo.2019.05.019>
- Guo, W. and Zhou, C. (2019) Patterns and controls of disequilibrium isotope effects in speleothems: Insights from an isotope-enabled diffusion-reaction model and implications for quantitative thermometry. *Geochimica et Cosmochimica Acta*, 267, 196-226. <https://doi.org/10.1016/j.gca.2019.07.028>
- Guo, W. (2020) Kinetic clumped isotope fractionation in the DIC-H₂O-CO₂ system: Patterns, controls, and implications. *Geochimica et Cosmochimica Acta*, 268, 230-257. <https://doi.org/10.1016/j.gca.2019.07.05>
- Hill, P.S., Tripathi, A.K. and Schauble, E.A. (2014) Theoretical constraints on the effects of pH, salinity, and temperature on clumped isotope signatures of dissolved inorganic carbon species and precipitating carbonate minerals. *Geochimica et Cosmochimica Acta*, 125, 610-652. <https://doi.org/10.1016/j.gca.2013.06.018>