

**MÉMOIRE D'HABILITATION  
À DIRIGER DES RECHERCHES**

**Anomalies isotopiques dans le CO<sub>2</sub> et  
les carbonates: métrologie, interprétation  
et application aux sciences de la Terre**

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# Introduction

## Disclaimer

Here is a well-worn cliché: writing an HDR memoir is an opportunity to reflect on one's past and future research endeavors. I believe, however, that the worst possible way to convey the fruits of this introspection to a jury of peers is to write the memoir as if it were a funding proposal, painting a picture of triumphant progress towards solving pre-existing “important” questions. This storytelling is very rarely, in my opinion, a truthful picture of reality. Reporting on what we got right is the *recto*, half of the story, but the *verso* holds important, rarely acknowledged contradictions and difficulties. Where was I wrong, and what did being wrong teach me (or us, collectively)? What are the issues about which I disagree with my peers, or simply think about in a different way? When should I simply adjust my thinking to match others', hopefully understanding something new in the process, and when instead is this an itch that would be worth scratching, that could yield some new ideas? Because these topics are not the usual fare of science publications, in the present memoir I may occasionally leave aside some of the traditional academic decorum, favoring clarity over formality. I hope that the members of my HDR committee will find these attempts, if not inspired, at least tolerable.

## Acknowledgements

Speaking of them, I am truly thankful to all of the committee members for agreeing to sit on my jury. As I often warn students, grown-up researchers have to function under a constant bombardment of deadlines, pressing demands, and unhealthy expectations of multitasking. I am thus very grateful—and doubly so for my three reviewers—that six accomplished academics committed to carving out some time, essentially as a personal favor to me, to read this memoir and discuss/debate its contents in public.

I also wish to express my heartfelt gratitude to the people whose help, teachings and guidance over the years made it all possible, with particular thanks to the irresistible Paul Tapponnier; to Yann Klinger and Ata Elias, who dug holes alongside me; to Jean-Philippe Avouac who kindly

underwrote my first forays into stable-isotope geochemistry; to the so-called Caltech mafia of the late 2000's and to its godfather, John Eiler, for his willingness to take strays in; to Dominique Genty, for sharing his underground lair with me; to Daniele Romanini, Samir Kassi, and Erik Kerstel, for taking a chance on my unlikely proposal. Samir's contribution over the years, particularly, has been invaluable. I would be in a completely different place today if not for his scientific brilliance, relentless enthusiasm, and refusal to believe in hard deadlines. Thanks also to the past and present members of the Paleooceanography group at LSCE, with special thanks to Sébastien Nomade for countless good-natured disagreements, and to Jean-Claude Duplessy, whose savage critique of my CNRS audition presentation made a big difference. Last but not least, I am uniquely indebted to Dominique Blamart for his unabated support since my arrival at LSCE, his patient willingness to share his considerable scientific experience, and his thoughtful guidance over more than a decade.

## What I do

Any researcher faced with the question “what do you do?” first needs to stake stock of who's asking. To young children, I'm a weatherman for dinosaurs, working on really old weather reports. To most grown-ups I meet outside of work, I explain that an Earth science researcher is like a detective trying to solve geologic mysteries based on arcane clues, and that this is a worthwhile effort even when it is not materially useful. To other researchers, I am a stable-isotope geochemist whose work is primarily centered on developing new methods based on “isotopic anomalies” in carbonate minerals, and applying these methods to study our planet's history and the physico-chemical processes that shape it.

In this context, “anomalies” should be understood in its etymological sense as “deviation from the law”. For example, in most terrestrial materials, the isotope ratios  $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$  are very strongly covariant, so that, to the first order:

$$\frac{(^{17}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{17}\text{O}/^{16}\text{O})_{\text{VSMOW}}} \approx \left[ \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}} \right]^{\lambda} \approx 0.5 \quad (1)$$

Under this assumption, there is no new information to be gained by measuring  $^{17}\text{O}/^{16}\text{O}$ , which may be simply predicted to the first order based on  $^{18}\text{O}/^{16}\text{O}$ . However, assuming that we could make very precise measurements of the “triple oxygen isotope” composition of a sample, we could instead observe *deviations* from this phenomenological law:

$$\Delta^{17}\text{O} = \ln \left[ \frac{(^{17}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{17}\text{O}/^{16}\text{O})_{\text{VSMOW}}} \right] - \lambda \cdot \ln \left[ \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}} \right] \quad (2)$$

This tiny oxygen-17 anomaly (also called oxygen-17 “excess”), may be directly or indirectly measured in many molecules, including molecular oxygen, ozone, water, carbon dioxide, car-

bonates and sulfates, organic molecules... Considering  $\Delta^{17}\text{O}$  adds an extra dimension to the isotopic “observational space”, providing new information which may be used to solve previously under-determined problems.

A closely related notion is that of *clumped-isotope* anomalies. Generally, to a good approximation, isotopes are randomly distributed among molecules in most natural materials, so that the relative abundances of every isotopologue (e.g.  $^{16}\text{O}^{18}\text{O}$ ) can be predicted approximately by postulating a random (“stochastic”) distribution of isotopes:

$$\left(\frac{^{16}\text{O}^{18}\text{O}}{^{16}\text{O}^{16}\text{O}}\right) \approx 2 \cdot \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right) \quad \text{or} \quad \left(\frac{^{16}\text{O}^{13}\text{C}^{18}\text{O}}{^{16}\text{O}^{12}\text{C}^{16}\text{O}}\right) \approx 2 \cdot \left(\frac{^{13}\text{C}}{^{12}\text{C}}\right) \cdot \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right) \quad (3)$$

Clumped-isotope anomalies are defined relative to this stochastic prediction, for instance:

$$\Delta_{^{16}\text{O}^{13}\text{C}^{18}\text{O}} \equiv \frac{(^{16}\text{O}^{13}\text{C}^{18}\text{O} / ^{16}\text{O}^{12}\text{C}^{16}\text{O})}{2 (^{13}\text{C} / ^{12}\text{C}) (^{18}\text{O} / ^{16}\text{O})} - 1 \quad (4)$$

In the case of  $^{16}\text{O}^{13}\text{C}^{18}\text{O}$ , we usually measure its abundance by isotope-ratio mass spectrometry (IRMS), binning it along with other mass-47 isotopologues  $^{17}\text{O}^{12}\text{C}^{18}\text{O}$  and  $^{17}\text{O}^{13}\text{C}^{17}\text{O}$ . In that case,  $\Delta_{47}$  in a given sample is defined as the observed relative excess of mass-47  $\text{CO}_2$ , compared to a purely stochastic distribution of isotopes in that same sample<sup>[1, 2]</sup>. Clumped isotopes’ popularity comes in large part from carbonate clumped-isotope thermometry, which provides an estimate of a carbonate sample’s temperature of formation based on the  $\Delta_{47}$  value of  $\text{CO}_2$  produced by reacting the sample with phosphoric acid<sup>[3, 4]</sup>. Clumped-isotope geochemistry is not limited to carbonates, however, with many other molecules under investigation, including a growing number of organic macromolecules<sup>[5]</sup>.

Foregoing any pretense of originality, this memoir starts by summarizing the somewhat unorthodox path that led me to stable-isotope geochemistry in the first place, and to my current research interests. Chapter 2 outlines what I believe are my primary contributions to the field, with an emphasis on the collective nature of research and how various colleagues critically shaped my way of thinking over the years. A third and last chapter describes two prospective avenues of research that I would most like to explore next, keeping in mind that predicting my own future is perhaps not my strongest suit.

[1] Eiler & Schauble (2004).

[10.1016/j.gca.2004.05.035](https://doi.org/10.1016/j.gca.2004.05.035)

[2] Wang *et al.* (2004). [10.1016/j.gca.2004.05.039](https://doi.org/10.1016/j.gca.2004.05.039)

[3] Schauble *et al.* (2006). [10.1016/j.gca.2006.02.011](https://doi.org/10.1016/j.gca.2006.02.011)

[4] Ghosh *et al.* (2006). [10.1016/j.gca.2005.11.014](https://doi.org/10.1016/j.gca.2005.11.014)

[5] Eiler *et al.* (2017). [10.1016/j.ijms.2017.10.002](https://doi.org/10.1016/j.ijms.2017.10.002)

“La vie, pour la plupart des gens, c’est aller d’un point A à un point B. Tout ça est merveilleusement linéaire. Moi, donc, c’est pas comme ça.”

(*Casse-tête chinois*, 2013)

# 1 How we got here

## 1.1 From laser beams to rock hammers

My professional trajectory has been everything but a straight line. I started out wanting to study physics, with one my first “real research” projects having to do with a laser beam interacting with air molecules (i.e. a laser microphone, perhaps influencing or at least foreshadowing some of my choices twenty years down the line). Then, through circumstance, I changed course and got involved in Earth science as a graduate student, studying the neotectonics and paleoseismology of the Lebanese Restraining Bend under the guidance of Paul Tapponnier at the Institut de Physique du Globe de Paris.

This was, unsurprisingly, a deeply formative experience in many ways. For one thing, I was immediately faced with a well-known but profound difference between physics and geology: studying the Earth system cannot rely primarily on well-designed controlled experiments. Instead, things are messy: we depend on the “experiments” offered by nature, and our reasoning and creativity is applied to *recognizing* these opportunities as opposed to *designing* experiments. You first have to convince yourself that you know which hashish field is crossed through by a fault line, then you dig a big hole and start looking for coseismic fractures and charcoal fragments that might ultimately help to date the corresponding earthquakes — if you somehow manage to get your Lebanese, hashish-contaminated charcoals past USA customs. This “foraging” approach is quite far from the traditional mythos of empirical science as a linear progression, from a testable hypothesis to a carefully-designed experiment yielding conclusive results. Yet, for many of us, this adaptive *modus operandi* is one of the appeals of geoscience, along with the deeply multi-disciplinary nature of our work.

Another lesson I took from my Lebanese adventures is the sheer fun and sense of freedom that comes with studying a “new”, still mostly unexplored topic. Here, I’m not (only) referring to my own ignorance: although the geology of Lebanon had been studied extensively for decades, the country had been almost entirely inaccessible to foreign researchers during the civil war from

1975 to 1990, at a critical time when modern geoscience was being deeply transformed by the general recognition of plate tectonics as a unifying theory of geology. As a result, many of the questions we were trying to answer during my PhD work were very open, first-order issues. In retrospect, exploring a *terra incognita* was a mixed blessing: since not many answers were to be found in the existing literature, it encouraged creativity, independent thought, and “big-picture” thinking. On the other hand, self-discipline, i.e. deciding what is worth pursuing and what to leave aside, was not our guiding principle. Because many things could be done, why not do them all? This is how you end up with a five-year-long PhD instead of the official three years. As an HDR candidate, I feel obligated to affirm that all my current and future students should finish their PhD project in three years and not a day longer. But in the context of these simpler times, I have no regrets about the duration of my Lebanese work, which allowed me to combine very diverse approaches ranging from geomorphology and structural geology to paleoseismology, to  $^{14}\text{C}$  and cosmogenic  $^{36}\text{Cl}$  dating, to digging up original 18<sup>th</sup> century diplomatic letters at the Archives Nationales<sup>[6-8]</sup>. What’s more, this is how I later found myself being a post-doc at Caltech at a particularly interesting time.

My first year at Caltech was mostly devoted to modeling the progressive deformation of geomorphic surfaces and stratigraphic markers in fold-and-thrust belts surrounding the Tien Shan range, in Central Asia. This project, initiated by Jean-Philippe Avouac, could be seen as a natural extension of my earlier research topics, still focusing on neotectonic deformation of the upper crust but at somewhat longer time scales (millions instead of thousands of years). Working at Caltech, particularly with Jean-Philippe, was quite stimulating and opened up many learning opportunities. It is while working on these Tien Shan folds that I had my first experience of using a numerical model linking *in situ* observations (field measurements and seismic profiles) to quantitative reconstructions (tectonic shortening as a function of time). In the resulting publication<sup>[9]</sup>, we described a simple kinematic model of fault-tip folding based on earlier analog experiments<sup>[10]</sup>. Adjusting the kinematic model to fit the field observations gathered at two Tien Shan localities yielded new constraints on the long-term evolution of local shortening rates, at the scale of each anticline. These results by themselves may not have been earth-shattering (pun intended), but they highlighted, in a tectonically simple setting, the interplay of tectonics, climate and orogeny. More specifically, we argued that combining the structural geometry of an anticline with its topographic expression provides constraints on the balance between local sedimentation, uplift and shortening.

This Tien Shan work was also my first lesson on the merits of open science. For one thing, my numerical tool of choice at the time I arrived in Caltech was Matlab, but the software licenses that I had used at IPGP and the hardware they ran on did not cross the Atlantic with me. Quite trivially, acquiring and setting up a modern version of Matlab at my new institution proved to be unexpectedly challenging for technical and administrative reasons. Without being tragic

[6] Daëron *et al.* (2004). [10.1016/j.epsl.2004.07.014](https://doi.org/10.1016/j.epsl.2004.07.014)

[7] Daëron *et al.* (2007). [10.1785/0120060106](https://doi.org/10.1785/0120060106)

[8] Daëron *et al.* (2005). [10.1130/g21352.1](https://doi.org/10.1130/g21352.1)

[9] Daëron *et al.* (2007). [10.1029/2006jb004460](https://doi.org/10.1029/2006jb004460)

[10] Bernard *et al.* (2007). [10.1029/2005jb004149](https://doi.org/10.1029/2005jb004149)

in the long run, this added some completely unnecessary friction to my early post-doc days, and that experience was a strong motivation for switching to an open-source language shortly thereafter. As a final blow against proprietary software, I am not proud to confess that many years later, when a Chinese colleague contacted me, asking for the source of my folding model in order to re-use and/or improve it, I found myself technically unable to provide it to him, as my archives (on vintage CD-ROMs, naturally) contained various versions of the code which I was unable to test, having completely lost access to a compatible version of Matlab. Today, the modern solutions to such problems are well known (free open-source software, public code repositories...). For several years now I have found it quite interesting to explore how the tools used for the collaborative development of open-source software may change the ways in which we do science (reproducible code repositories, version control systems) and we publish our results (exploring alternative editorial processes, releasing results and/or models as software libraries, web applications, command-line utilities and/or API services...). Learning the basic use of these tools should now systematically be included in our students' curriculum, in my opinion.

## 1.2 From rock hammers to mass spectrometers

It is around that time, circa 2006, that I started looking into stable isotope geochemistry. By then, I had already applied twice for a CNRS position, with a rather narrow focus on paleoseismology and orogeny, a field that I felt was already crowded with brilliant young applicants. Looking around for something new and unique to Caltech at the time, I came across an article out of John Eiler's stable isotopes group, describing the first use of a new carbonate paleothermometer based on "clumped" isotopes to reconstruct the uplift history of the Altiplano plateau<sup>[11]</sup>. Paleo-altimetry, the ability to robustly constrain the uplift and/or topographic history of plateaus and mountain ranges, was — and remains — of interest to structural geologists and climatologists alike, for a number of reasons: (a) vertical motions of the crust are much more difficult to reconstruct than horizontal displacements; (b) the timing and rates of tectonic uplift should constrain the large-scale mechanisms in play, such as progressive crustal shortening versus delamination of the dense lower crust or mantle lithosphere; (c) as mentioned above, topography reflects a competition between tectonic uplift and erosion; erosion is influenced by tectonics and climate; uplift may also be sensitive to erosion; and finally, orogenic belts and large plateaux have a profound influence on climate patterns<sup>[12]</sup>.

Despite having virtually no prior experience with stable isotope geochemistry, I found the theoretical basis of clumped-isotope thermometry to be quite understandable from a purely physical point of view. With Jean-Philippe Avouac's generously continued financial support, I got more and more involved in the activities of John Eiler's group. Because of their potential applications to paleo-altimetry, my first targets were pedogenic carbonates. The aforementioned Altiplano paper<sup>[11]</sup> was based on such carbonates, but relied on general assumptions about when and where clumped isotopes may record soil temperatures in paleosols. I thus collaborated with

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[11] Ghosh *et al.* (2006). [10.1126/science.1119365](https://doi.org/10.1126/science.1119365)

[12] Ruddiman (1997). [10.1007/978-1-4615-5935-1](https://doi.org/10.1007/978-1-4615-5935-1)



Jay Quade (U. of Arizona) to collect pedogenic calcite coating the underside of clastic rocks from Late Holocene river terraces in the Southwestern United States, to analyze their clumped-isotope signatures ( $\Delta_{47}$ ) and compare them to local soil temperatures. What I learned then — and which would have been obvious to a more experienced geochemist — is that reliable paleothermometry depends critically on how well we understand the “carrier” phase (authigenic pedogenic calcite in this case), at least as much as how precisely we can analyze samples. As it turns out, the  $\Delta_{47}$  signatures of our pedogenic calcite samples at a given location varied systematically with depth, following the expected temperature profile around the end of the Southwest US Monsoon, consistent with calcite precipitation driven by the yearly onset of arid conditions and a decrease in soil  $p\text{CO}_2$ <sup>[13]</sup>. This clearly implied (a) that  $\Delta_{47}$  paleothermometry of pedogenic carbonates might record something quite different from mean annual temperatures, and (b) that applying this technique to reconstruct paleoclimates and/or paleoaltimetry would have to carefully consider the timing and driving processes of carbonate formation, both of which may vary through time in poorly constrained ways.

At this point, I could have chosen to delve deeper into pedogenesis-related issues, but after giving a presentation at LSCE in 2007 I was contacted by Karine Wainer, a graduate student of Dominique Genty, asking if I would be interested in reconstructing glacial-interglacial temperatures using  $\Delta_{47}$  in speleothems. As I was still without a permanent position at the time, collaborating with LSCE seemed like a pretty good opportunity and I was aware, from discussions with Hagit Affek, another Caltech post-doc, that speleothems were an appealing target for clumped-isotope paleothermometry. I thus started working with Karine and Dominique on a flowstone from Villars cave, in SW France, which recorded the termination of the penultimate glacial age and the start of the Eemian warm period. The outcome of this collaboration was threefold: (a) we eventually published a paper<sup>[14]</sup> confirming earlier observations<sup>[15]</sup> of  $\Delta_{47}$  disequilibrium in stalagmites/flowstones but showing that these disequilibria could vary strongly through time; (b) with Dominique Genty and Weifu Guo, another Caltech alumni, we started collecting different types of modern speleothems to study the factors influencing isotopic disequilibrium in speleothems<sup>[16]</sup>; (c) I successfully applied for a post-doctoral position at CEA, with a long-term objective of setting up a clumped-isotope lab at LSCE.

My first years back in France were mostly spent applying for funding to set up a new clumped-isotope facility, and shuttling between Paris and Los Angeles to analyze samples. I had the good fortune to be hired at CNRS in 2008, and to secure funding for a mass spectrometer in 2010. With the invaluable help of Dominique Blamart at LSCE, we were finally in a position to perform reasonably good  $\Delta_{47}$  measurements just a few years later. As it turned out, this was a perfectly wrong time to start a new clumped-isotope lab.

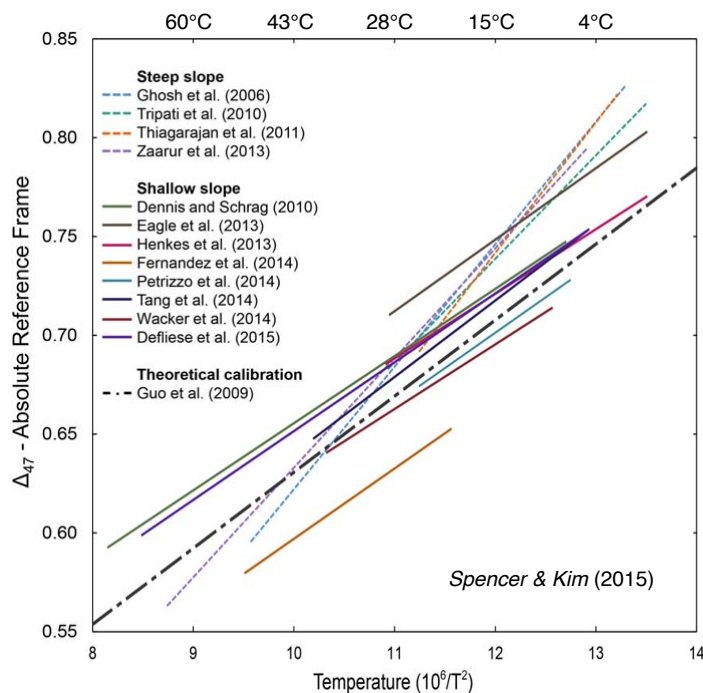
[13] Quade *et al.* (2011). [10.2475/02.2011.01](https://doi.org/10.2475/02.2011.01)

[14] Wainer *et al.* (2011).

[10.1016/j.quascirev.2010.07.004](https://doi.org/10.1016/j.quascirev.2010.07.004)

[15] Affek *et al.* (2008). [10.1016/j.gca.2008.06.031](https://doi.org/10.1016/j.gca.2008.06.031)

[16] Daëron *et al.* (2011). [10.1016/j.gca.2010.10.032](https://doi.org/10.1016/j.gca.2010.10.032)



**Figure 1.1 — Conflicting  $\Delta_{47}$  calibrations published between 2006 and 2015.** Modified from *Spencer & Kim* [18]. Many people would agree today that these large discrepancies resulted from a combination of data processing [19–21] and inter-laboratory standardization [22–24] issues, as well as underestimated analytical errors [25].

### 1.3 Timing is everything

Over the period from 2008 to 2011, the clumped-isotope landscape changed profoundly: instead of a single machine analyzing samples backed up by a shared set of reference material measurements, half a dozen new labs started performing  $\Delta_{47}$  analyses. Dan Shrag’s group at Harvard was the first one attempting to replicate Caltech’s original  $\Delta_{47}$  calibration<sup>[4]</sup>, yielding a calibration relationship linking  $\Delta_{47}$  and carbonate formation temperatures which differed markedly from the original one<sup>[17]</sup>. As years went by, the number of conflicting calibrations increased steadily, yielding disagreements equivalent to  $\pm 10^\circ\text{C}$  on  $\Delta_{47}$  predictions for ambient temperatures (fig. 1.1).

This glaring problem did not have any obvious short-term solution, and the default assumption was that you were better off interpreting  $\Delta_{47}$  measurements based on a “local” calibration established in the same research group. As the proud proprietor of a new clumped-isotope facility, I was thus facing two bad options: either focus on geo-applications, mostly disregarding calibrations issues—in other words, throwing in my lot with a existing calibration, selected more or less arbitrarily— or attempt to establish my own local calibration, knowing full well that this was not a robust way forward. In the end, I found myself looking deeper and deeper into metrological issues, with three key lines of enquiry: characterizing unrecognized effects of our data processing methods, establishing a reliable inter-laboratory metrological scale for  $\Delta_{47}$ , and providing a robust models of analytical error propagation.

[4] Ghosh *et al.* (2006). [10.1016/j.gca.2005.11.014](https://doi.org/10.1016/j.gca.2005.11.014)

[17] Dennis & Schrag (2010).  
[10.1016/j.gca.2010.04.005](https://doi.org/10.1016/j.gca.2010.04.005)

The results of these efforts are summarized in section 2.1. Granted, our small group was far from the only one concerned with metrological issues, and we used an older generation of mass spectrometer, but it is fair to say that our ability to routinely perform carbonate  $\Delta_{47}$  measurements with state-of-the-art precision and traceability attracted a number of French and international collaborators. On one hand, I was primarily invested in solving methodological issues; on the other, I found myself in an excellent position to collaborate with experts on varied topics, working on very diverse time scales and geo-archives including speleothems<sup>[16, 26]</sup>, foraminifera<sup>[27–30]</sup>, bivalves<sup>[31–33]</sup>, brachiopods<sup>[34]</sup> and hydrothermal carbonates associated with seafloor basalt alteration<sup>[35]</sup>.

## 1.4 Back to lasers

In my first years as a CNRS researcher, I was acutely aware that I was “competing”, however collegially, with brilliant minds backed by substantial funding. The clumped-isotope community in its first decade comprised plenty of young/talented/ambitious scientists, many of whom were hired in top institutions. This early community was largely shaped by a series of international clumped isotope workshops, the first of which was organized in 2010 by Kate Huntington and her colleagues at the University of Washington, right at the time of the Eyjafjallajökull eruption which temporarily disrupted air travel worldwide (another bit of poor timing for a round-trip flight from Paris to Seattle). That first workshop included a presentation by Aaron van Pelt, of Picarro Instruments, describing the principle of Cavity Ring-Down Spectroscopy (CRDS) and how it could potentially be used to measure clumped isotopes in CO<sub>2</sub>.

As a former physicist, I was immediately curious about the true potential for spectroscopic measurements of CO<sub>2</sub> isotopologues. A Nier-type gas source ionizes less than 1 % of the CO<sub>2</sub> molecules you throw at it, pumping away the rest, and isotope-ratio mass spectrometry (IRMS) is a mature technology refined over seven decades. IRMS analyses of  $\Delta_{47}$  (and  $\Delta_{48}$  even more so) are already mostly limited by counting statistics, so that large further gains in analytical precision are unlikely. By contrast, molecular spectroscopy is a non-destructive measurement based on several rapidly evolving techniques, and offers specific advantages such as the ability

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- [18] Spencer & Kim (2015). [10.1007/s12303-015-0018-1](https://doi.org/10.1007/s12303-015-0018-1)
  - [19] Daëron *et al.* (2016). [10.1016/j.chemgeo.2016.08.014](https://doi.org/10.1016/j.chemgeo.2016.08.014)
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  - [23] Anderson *et al.* (2021). [10.1029/2020gl092069](https://doi.org/10.1029/2020gl092069)
  - [24] Daëron & Vermeesch (2023). (in press). [10.31223/x5k394](https://doi.org/10.31223/x5k394)
  - [25] Daëron (2021). [10.1029/2020gc009592](https://doi.org/10.1029/2020gc009592)
  - [16] Daëron *et al.* (2011). [10.1016/j.gca.2010.10.032](https://doi.org/10.1016/j.gca.2010.10.032)
  - [26] Daëron *et al.* (2019). [10.1038/s41467-019-08336-5](https://doi.org/10.1038/s41467-019-08336-5)
  - [27] Peral *et al.* (2018). [10.1016/j.gca.2018.07.016](https://doi.org/10.1016/j.gca.2018.07.016)
  - [28] Peral *et al.* (2020). [10.1016/j.palaeo.2020.109603](https://doi.org/10.1016/j.palaeo.2020.109603)
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  - [30] Daëron & Gray (2023). [10.1029/2023PA004660](https://doi.org/10.1029/2023PA004660)
  - [31] Huyghe *et al.* (2022). [10.1016/j.gca.2021.09.019](https://doi.org/10.1016/j.gca.2021.09.019)
  - [32] Briard *et al.* (2020). [10.1016/j.palaeo.2019.109582](https://doi.org/10.1016/j.palaeo.2019.109582)
  - [33] Letulle *et al.* (2022). [10.5194/cp-18-435-2022](https://doi.org/10.5194/cp-18-435-2022)
  - [34] Letulle *et al.* (2023). [10.5194/bg-20-1381-2023](https://doi.org/10.5194/bg-20-1381-2023)
  - [35] Coogan *et al.* (2019). [10.1016/j.epsl.2018.12.014](https://doi.org/10.1016/j.epsl.2018.12.014)

to painlessly separate isobar molecules, potentially providing a way to characterize CO<sub>2</sub> isotopes in a 5-dimensional space ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ ,  $\Delta_{47}$ ,  $\Delta_{48}$ ).

Back in Paris, I cold-emailed the leading French lab working on CRDS techniques, the Laboratoire de Spectrométrie Physique (now Laboratoire Interdisciplinaire de Physique, or LIPhy) which eventually led to collaborating with Samir Kassi and others, despite the fact that I was asking for something that was an order of magnitude beyond what was technically achievable at the time. We were able, based on early proof-of-concept results, to secure funding from INSU, then from ANR’s early-career program, which allowed us to seriously start developing new VCOF-CRDS instruments (V-Cavity Optical Feedback CRDS) dedicated to high-precision isotopologue measurements in CO<sub>2</sub>. For strategic reasons, we decided that our primary objective should be oxygen-17 excess ( $\Delta^{17}\text{O}$ ), a quantity describing small departures from phenomenologic relationships between the  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$ , with many potential applications to hydrology, geology, and biochemistry<sup>[36]</sup>. At the same time, Amaëlle Landais (LSCE) was starting a collaboration of her own with LIPhy, focused on  $\Delta^{17}\text{O}$  in water vapor. Our two complementary projects involved many of the same people, which proved very helpful over the years, with each technical breakthrough benefitting both projects.

My ongoing, decade-long collaboration with LIPhy has been quite quite exciting. Once again, we find ourselves exploring a *terra incognita*, trying out new analytical approaches using a one-of-a-kind instrument of our own design. Tellingly, the commercial instrument designed by Aerodyne Research with the same objectives as ours (TILDAS, for Tunable Infrared Laser Differential Spectroscopy<sup>[37]</sup>) turned out to be based on a radically different technical choices (high-absorption spectral region; multipass optical cell instead of CRDS; continuous flow instead of a static gas...), making these two instruments almost perfect technical opposites despite comparable analytical performance. This sense of freedom goes beyond the purely technical aspects of instrument design, as detailed in section 2.2. What I had not anticipated, however, is how much time it would takes to go from an instrumental concept to a usable prototype, and from a prototype to a reliable “workhorse” instrument. In our case, it took ten long, frustrating years to get there: the latest VCOF-CRDS prototype has been more-or-less-routinely churning out top-quality  $\Delta^{17}\text{O}$  measurements at LIPhy for the past year now and, thanks to SESAME regional funding, the first production version of this instrument dedicated to CO<sub>2</sub> isotopologues is about to be assembled at LSCE in the next few months.

Because neither time nor resources are limitless, we must come to terms with the fact that we are only able to investigate a small subset of what we would like to understand. It is thus particularly gratifying that other groups, such as that of Joël Savarino at IGE, have been picking up on VCOF-CRDS with other molecules and completely different applications in mind. One of my goals in the years to come is to help build a diverse community of scientists interested in applying novel spectroscopic techniques to solve old and new geochemical problems.

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[36] Reviews in Mineralogy and Geochemistry, 86:1,  
ISSN 1529-6466

[37] Wang *et al.* (2020).  
[10.1021/acs.analchem.9b04466](https://doi.org/10.1021/acs.analchem.9b04466)

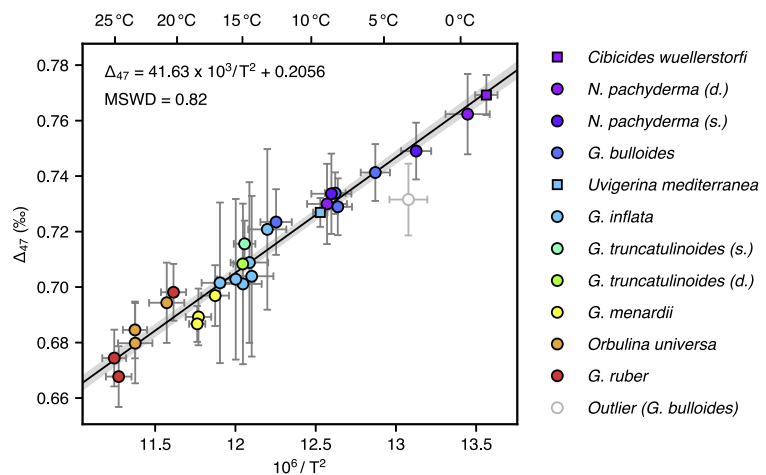
## 1.5 Student supervision over the years

In my attempts above to summarize a decidedly non-linear scientific trajectory, I left out one critical component: the diverse group of hard-working, talented young people who worked under my supervision at one point or another. This includes a number of people from other groups, most of them students, who visited LSCE to learn the ropes of  $\Delta_{47}$  analyses: Safana Sellman, Tim Pollard, Damien Huyghe, Justine Briard, Thomas Letulle, Loïc Marlot, Tiphaine Choteau, Héloïse Barathieu, Calla Gould-Whaley, and Aniès Zeboudj. Many of them initially underestimated their ability, as non-specialists, to fully master the theoretical and experimental details of the technique they came to learn, and I always made it a point of honor to disabuse them. I believe they all left LSCE with a solid understanding of the uses and limitations of clumped-isotope thermometry.

Notoriously, you first have to DR before you are HDR. So far I have directly co-advised four graduate students:

From 2015 to 2018, with CEA funding, I co-supervised the work of **Marion Peral**, who studied clumped isotopes in foraminifera with the longer-term goal to study the Mid-Pleistocene climate transition. My co-advisors were Dominique Blamart and Franck Bassinot, both from LSCE. At a time when  $\Delta_{47}$  calibrations were a flammable topic, Marion did a considerable amount of work to establish a robust foraminifer calibration based on the latest best practices. Her foraminifer calibration paper<sup>[27]</sup> was the first of a few which are still widely cited today, and a very recent attempt to revisit these data, among others, further confirmed the validity and usefulness of her original work<sup>[30]</sup>. Marion went on to be a post-doctoral fellow at the University of Melbourne and then Vrije Universiteit Brussel. Last year, she successfully applied for an IODP post-doctoral grant to conduct her own research project on the Mid-Pleistocene transition at EPOC (Environnements et Paléoenvironnements Océaniques et Continentaux, Université de Bordeaux). Marion and I co-signed six articles together, three on which she was the lead author, and one more manuscript is in late draft stages.

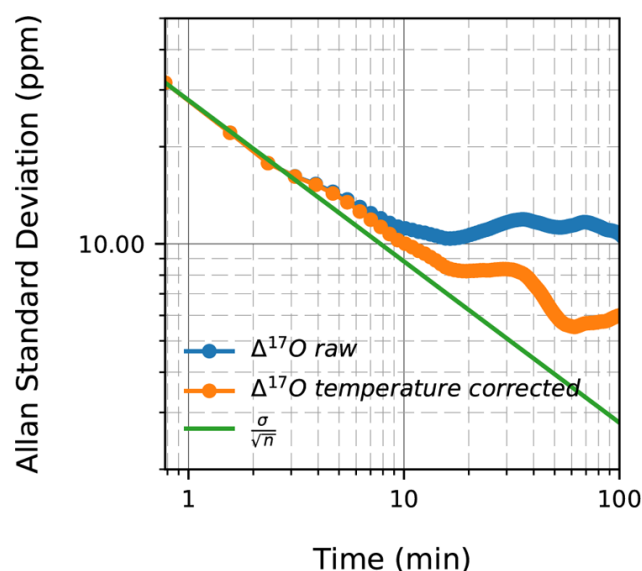
**Figure 1.2 — Calibration of  $\Delta_{47}$  as a function of calcification temperature estimates for planktic and benthic foraminifera.** Plot from Marion Peral's PhD results [27]. A recent article [30] revisiting foraminifer calibration data from several studies concluded that the  $T$ - $\Delta_{47}$  relationship in foraminifera does not appear to deviate significantly from calibrations based on inorganic calcite. These data are also included in the combined calibration shown in fig. 2.3.



[27] Peral *et al.* (2018). [10.1016/j.gca.2018.07.016](https://doi.org/10.1016/j.gca.2018.07.016)

[30] Daëron & Gray (2023). [10.1029/2023PA004660](https://doi.org/10.1029/2023PA004660)

From 2014 to 2017, I co-supervised the work of **Tim Stoltmann** on the development of VCOF-CRDS. Tim’s PhD was funded by my early-career ANR grant, and co-supervised by Samir Kassi and Erik Kerstel. The original plan was for him to spend half of his time working on instrumental development at LIPhy, and the second half working on applications at LSCE. Needless to say, this schedule was wildly optimistic, and Tim spent most of his time at LIPhy, where he achieved impressive progress on the instrumental front despite having little prior background in laser physics. At the end of his PhD, our VCOF-CRDS instrument was capable of measuring  $\Delta^{17}\text{O}$  with a precision of 10 ppm (1SE) in 10 minutes, in a stable continuous flow of pure  $\text{CO}_2$  at 20 mbar<sup>[38]</sup>. Having thus established that we could achieve the required instrumental precision, I tried very hard to secure additional funding for Tim to continue working on this project at LSCE. Unfortunately, my attempts failed completely and Tim moved on to a lucrative engineering position at AP2E, a private company developing spectroscopic gas analyzers.



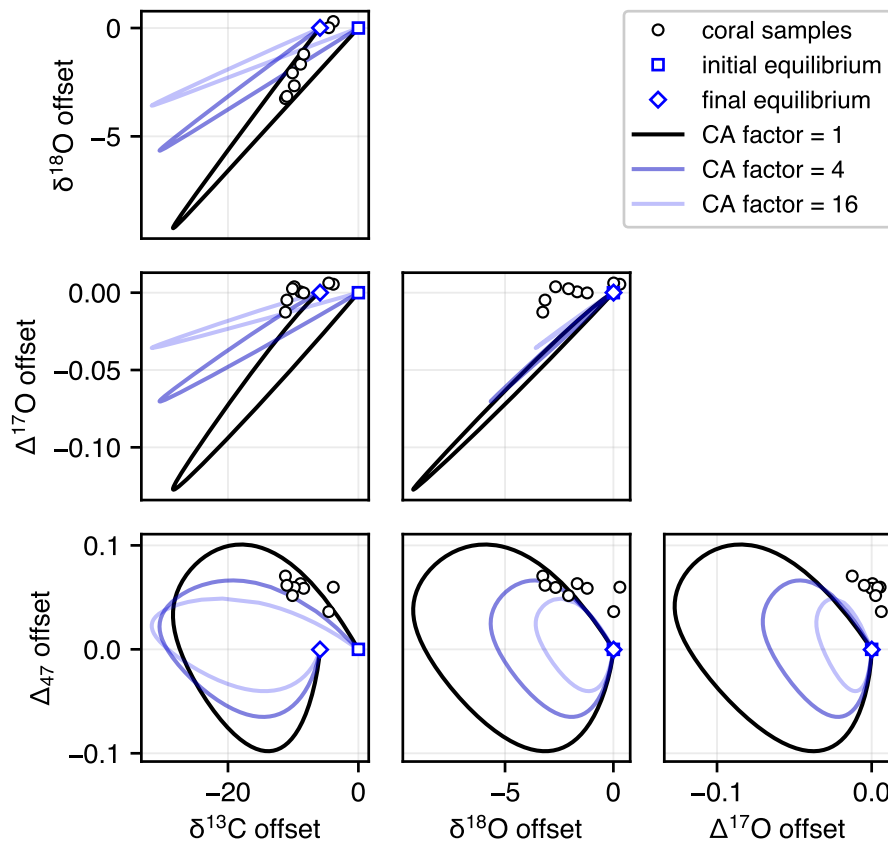
**Figure 1.3 — Allan variance plot of a  $\Delta^{17}\text{O}$  measurement in a continuous flow of pure  $\text{CO}_2$ .** Plot from Tim Stoltmann’s PhD results [38], showing the Allan standard deviation of a typical  $\Delta^{17}\text{O}$  measurement using VCOF-CRDS. In blue, the uncorrected data set. In orange, the same data with a temperature gradient correction applied.

[38] Stoltmann *et al.* (2017).  
[10.1021/acs.analchem.7b02853](https://doi.org/10.1021/acs.analchem.7b02853)





Since 2021, I am a co-advisor, with Claire Rollion-Bard and Sébastien Nomade, to **Marie Pesnin**, a graduate student with a background in biology and biogeochemistry. Marie’s PhD project, funded by CEA, aims to study biocalcification processes in various species known to precipitate carbonate with isotopic compositions far from thermodynamic equilibrium (e.g., corals, coccoliths...). Our proposed approach is to combine different types of isotopic tracers on the carbonate phase, such as  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measured by classical IRMS,  $\Delta^{17}\text{O}$  measured by VCOF-CRDS,  $\Delta_{47}$  and  $\Delta_{48}$  potentially measured by IRMS and/or VCOF-CRDS, and to determine how these tracers covary with respect to expected “equilibrium” compositions. Because different processes are expected to produce distinct covariations in this 5-dimensional composition space, these observations should act as a fingerprint of the chemical processes at play in each species (fig. 1.5). Marie’s thesis defense is scheduled around the end of 2024.



**Figure 1.5 — Comparison between observed and predicted isotopic disequilibrium in coral aragonite.** Work-in-progress plots from the work of Marie Pesnin. Predictions curves are from the *isoDIC* model of Guo [39], ported to Python (cf appendix A.2.7). Observations are IRMS measurements of  $\Delta_{47}$ ,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  combined with VCOF-CRDS measurements of  $\Delta^{17}\text{O}$ ,  $\delta^{13}\text{C}$ , and  $\delta^{18}\text{O}$  (both techniques yield indistinguishable  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values). Blue-colored models include the effects of carbonic anhydrase with different levels of activity.

[39] Guo (2020). [10.1016/j.gca.2019.07.055](https://doi.org/10.1016/j.gca.2019.07.055)



## 2 Past and present research

Here I provide context for the two primary “arcs” of my research activity since I arrived at LSCE. The first one covers how I was involved, in one way or the other, in the sustained methodological advances of  $\Delta_{47}$  measurements over the past 15 years. In my opinion, the first-order problems with calcite  $\Delta_{47}$  metrology and thermometry have now all been effectively solved. Many problems remain open, including metrological and calibration issues with mineralogies other than calcite, predictive models of isotopic disequilibrium in biogenic and inorganic carbonates, or solid-state reordering kinetics and processes. However, in its now mature state, I am hopeful that the scientific discourse will soon be much more about questions of interpretation, driven by field-specific knowledge (e.g., foraminifer ecology, or climate modeling), than by methodological debates.

The second arc corresponds to my (presumptuous?) project to develop a new method of laser spectroscopy dedicated to high-precision, high-sensitivity measurements of isotopologues in  $\text{CO}_2$  and other simple molecular gases. This project is now over 10 years old, and we are finally making the first (quasi-)routine measurements of  $\Delta^{17}\text{O}$  on pure  $\text{CO}_2$  with state-of-the-art precision and accuracy. In the years to come I expect we will be reaping the benefits of this long-term effort, with many exciting potential applications for me and other researchers.

### 2.1 Metrology and interpretation of clumped isotopes in carbonates

#### 2.1.1 What are clumped isotopes, in the simplest terms?

As my students can attest, I never grow tired of reminding them that they should be able to explain what they do “in terms that a clever ten-year-old would understand”. I am fond of this turn of phrase because children in particular tend to be more ignorant than stupid, a statement that applies also to most adults. In other words it’s a healthy exercise to try and explain something

you know very well in terms understandable to the widest audience possible (see also: [ELI5](#)). The following paragraphs are my attempt at explaining clumped-isotope thermometry in very simple terms, copied verbatim from a comment I once wrote when the popular science website [Ars Technica](#) reported on a clumped-isotope study<sup>[40]</sup> revisiting Cenozoic deep ocean temperatures:



Here is how clumped isotope thermometry works in carbonates. These minerals are made of metal ions and carbonate groups. Each carbonate group is made of one carbon atom and three oxygen atoms. Most of these carbon atoms are carbon-12 ( $^{12}\text{C}$ ), but a few of them are carbon-13 ( $^{13}\text{C}$ ). Most of the oxygen atoms are oxygen-16 ( $^{16}\text{O}$ ), but a few of them are oxygen-18 ( $^{18}\text{O}$ ). As a result, most carbonate groups are made of one  $^{12}\text{C}$  and three  $^{16}\text{O}$ , but a few of them have  $^{13}\text{C}$  instead of  $^{12}\text{C}$ ; some others have one  $^{18}\text{O}$  instead of one  $^{16}\text{O}$ ; some (very few) others have both one  $^{13}\text{C}$  and one  $^{18}\text{O}$ , and these are called “doubly substituted”. Knowing the abundance of  $^{13}\text{C}$  and  $^{18}\text{O}$  in a given mineral, we can compute the abundance of doubly substituted carbonate groups expected for a completely random distribution of the carbon and oxygen isotopes among carbonate groups.

For fundamental thermodynamic reasons, carbonate minerals favor “clumping”  $^{13}\text{C}$  and  $^{18}\text{O}$  together, meaning that most natural carbonates have slightly more doubly substituted groups than expected for a completely random distribution. This statistical “excess” is small (close to zero, i.e. quasi-random) in minerals formed at high temperatures (e.g., marble), and greater (but still pretty small) in minerals formed at lower temperatures (e.g., foraminifer shells).

It’s technically difficult but still feasible to measure these isotopic abundances with a good enough precision that we can estimate the formation temperature of carbonate minerals with a precision of 1-2 °C. This kind of analysis is technically more challenging and requires much larger amounts of carbonate material than traditional oxygen-18 thermometry\*. Both techniques are thus complementary and equally useful for investigating past climates.

Because all carbon and oxygen isotopes mentioned above are stable (as opposed, for instance, to  $^{14}\text{C}$ ), the clumped isotope excess is potentially preserved at geologic time scales (at least hundreds of millions of years). But for older samples, it is often quite challenging to obtain enough well-preserved material, because various natural processes are likely to modify the clumped isotope signal over long time scales.

\* Admittedly, I lost the ten-years-olds at “oxygen-18 thermometry”.

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[40] Meckler *et al.* (2022). [10.1126/science.abk0604](https://doi.org/10.1126/science.abk0604)

### 2.1.2 How do you measure $\Delta_{47}$ values?

Measuring  $\Delta_{47}$  in carbonate samples is quite simple in its principle. React the sample with anhydrous phosphoric acid to produce  $\text{CO}_2$ , with each carbonate group ( $\text{CO}_3^{2-}$ ) losing one oxygen atom in the process. Isolate and purify this  $\text{CO}_2$ , then inject it in a dual-inlet gas-source mass spectrometer configured to detect masses/charge ratios ( $m/z$ ) from 44 to 49, corresponding to all stable isotopologues of  $\text{CO}_2$ , from the lightest ( $^{16}\text{O}^{12}\text{C}^{16}\text{O}$ ) to the heaviest ( $^{18}\text{O}^{13}\text{C}^{18}\text{O}$ ).

Carefully measure the relative intensities of the six ion beams, assumed to vary linearly with the total number of isotopologues for each  $m/z$  value. In dual-inlet IRMS, these relative abundances are expressed as delta-values, noted  $\delta_{45}$  to  $\delta_{49}$ , relative to a “working gas”, i.e. an arbitrarily selected tank of  $\text{CO}_2$  whose composition is assumed to be known and constant through time. Starting from the postulated composition ( $\delta^{13}\text{C}_{\text{VPDB}}$ ,  $\delta^{18}\text{O}_{\text{VSMOW}}$ ) of this working gas and the “known” isotope abundance ratios in VPDB and VSMOW (plus an additional parameter,  $\lambda_{17}$  which we will conveniently ignore until section 2.1.4), we compute the molar fraction of each isotopologue in the working gas. Summing these working gas molar fractions according to their molecular mass yields working gas “isobar ratios”, noted  $R_{45}^{\text{wg}}$  to  $R_{49}^{\text{wg}}$ . Combining these working gas isobar ratios with the ( $\delta_{45} \dots \delta_{49}$ ) delta-values yields isobar ratios for the unknown analyte. From there, one may compute the analyte’s ( $\delta^{13}\text{C}_{\text{VPDB}}$ ,  $\delta^{18}\text{O}_{\text{VSMOW}}$ ) composition based on its  $R_{45}$  and  $R_{46}$  values (for historical reasons, this step is named as an “oxygen-17 correction”, see section section 2.1.4 below).

Up to this point, we have been closely following the classical dual-inlet approach to measure the “bulk composition” ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ) of  $\text{CO}_2$ . Going further, we may use the newly determined “bulk composition” of the analyte to predict what its isobar ratios ( $R_{45} \dots R_{49}$ ) would be under the assumption of a purely random (“stochastic”) distribution of isotopes. These stochastic ratios are noted ( $R_{45}^* \dots R_{49}^*$ ), and they are the last missing piece of information to compute the clumped-isotope anomalies:

$$\Delta_{47} \equiv 1 - \frac{R_{47}}{R_{47}^*} \quad \Delta_{48} \equiv 1 - \frac{R_{48}}{R_{48}^*} \quad \Delta_{49} \equiv 1 - \frac{R_{49}}{R_{49}^*} \quad (2.1)$$

### 2.1.3 From “raw” measurements to “true” $\Delta_{47}$ : standardization models

The computations summarized above might be scary the first time students encounter it, but I insist that they are, at heart, a fairly linear sequence of simple calculations, easily automated in software. But things become murkier when we start probing the assumptions we made along the way. For one thing, when computing ( $R_{45}^{\text{wg}} \dots R_{49}^{\text{wg}}$ ), it is traditional to postulate that the working gas isotopes are stochastically distributed ( $\Delta_{47}^{\text{wg}} = \Delta_{48}^{\text{wg}} = \Delta_{49}^{\text{wg}} = 0$ ), which is very unlikely. To correct this (knowingly) wrong assumption, John Eiler’s group originally designed a procedure to produce stochastic  $\text{CO}_2$  by heating a sealed aliquot at 1000 °C. Analyzing such “heated gases” allowed correcting for the non-stochasticity of the working gas, with the relationship linking the apparent/measured  $\Delta_{47}^{\text{raw}}$  value of an analyte to its true value  $\Delta_{47}^{\text{true}}$  being:

$$\Delta_{47}^{\text{raw}} = \Delta_{47}^{\text{true}} + c \quad \text{with} \quad c = -\Delta_{47}^{\text{wg}} \quad (2.2)$$

Another problem appeared later, as the mass spectrometer used for these early measurements got older (or so I am told, since this happened before my involvement). The  $\Delta_{47}^{\text{raw}}$  values of heated gases started drifting with time, always following an affine relationship with  $\delta_{47}$ . Years later, it was established that this was caused by small errors in the electrical backgrounds subtracted from each Faraday collector's output<sup>[41, 42]</sup>. But even before this insight, a pragmatic solution was to add another correction term based on the observed “heated gas slope” ( $b$ ) at any given time, constrained by analyzing heated CO<sub>2</sub> with different bulk compositions:

$$\Delta_{47}^{\text{raw}} = \Delta_{47}^{\text{true}} + b \cdot \delta_{47} + c \quad (2.3)$$

Later still, circa 2008, it became apparent that one or more processes, most likely involving dissociation-recombination of molecules in the gas source, were compressing  $\Delta_{47}^{\text{raw}}$  values relative to  $\Delta_{47}^{\text{true}}$ . This led to adding yet another correction term:

$$\Delta_{47}^{\text{raw}} = a \cdot \Delta_{47}^{\text{true}} + b \cdot \delta_{47} + c \quad (2.4)$$

In practice,  $a$  may be constrained by analyzing CO<sub>2</sub> equilibrated at low temperature (e.g., 25 °C), whose  $\Delta_{47}^{\text{true}}$  values are known *a priori* from theoretical models, along with heated gases. The introduction of this final correction term was a critical requirement to reliably compare measurements across groups, or even compare old analyses to new ones within a single laboratory, and led to the definition of the Carbon Dioxide Equilibrium Scale (CDES), the first metrological scale for  $\Delta_{47}$ <sup>[43]</sup>.

Applying the corrections of eqs (2.2–2.4) has one inescapable consequence: estimating the correction parameters ( $a, b, c$ ) based on “known” reference materials (such as heated and equilibrated CO<sub>2</sub>) can be highly sensitive to how you select the reference material analyses to consider. Your final results may change considerably if you decide to correct analyses based on a year's worth of standards instead of a week's worth, for example, or depending on your criteria to exclude problematic outliers. Of course this is true for most geochemical measurements, but compared to other isotopic or elemental tracers, carbonate clumped isotopes stand out in that analytical uncertainties remain large relative to the typical range of  $\Delta_{47}$  values in natural samples. As a result,  $\Delta_{47}$  applications call for robust models of analytical error propagation, comparable in scope and sophistication to the error models used by geochronologists<sup>[44]</sup>. In 2021, I published an article proposing that the corrections of eq. (2.4) could be expressed in general terms as a least-squares optimization problem, and solved using well-established mathematical approaches allowing for rigorous error propagation<sup>[25]</sup>. In this paper, I estimated that these typically ignored

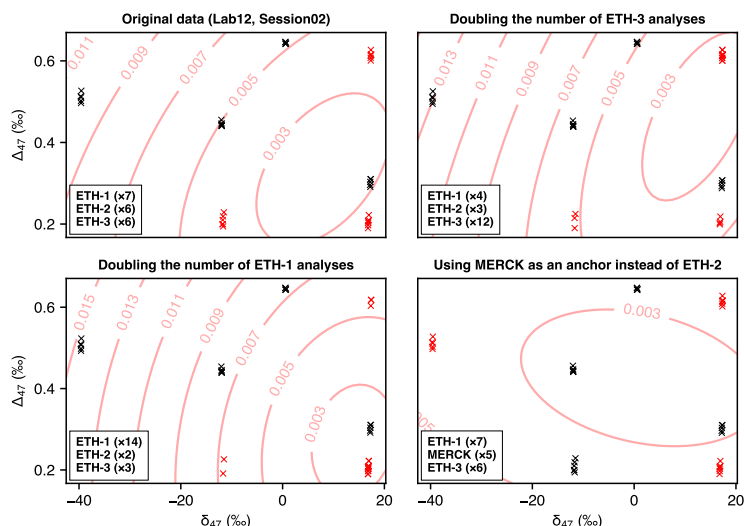
[41] He *et al.* (2012). [10.1002/rcm.6436](https://doi.org/10.1002/rcm.6436)

[42] Bernasconi *et al.* (2013). [10.1002/rcm.6490](https://doi.org/10.1002/rcm.6490)

[43] Dennis *et al.* (2011). [10.1016/j.gca.2011.09.025](https://doi.org/10.1016/j.gca.2011.09.025)

[44] Vermeesch (2018). [10.1016/j.gsfc.2018.04.001](https://doi.org/10.1016/j.gsfc.2018.04.001)

[25] Daëron (2021). [10.1029/2020gc009592](https://doi.org/10.1029/2020gc009592)



**Figure 2.1 —** Plots illustrating how the number of reference material analyses and the compositional distribution of unknowns and standards alike affect  $\Delta_{47}$  standardization errors. Figure from *Daëron* [25]. Red contours characterize the component of analytical error due to the standardization itself, which is independent from and added quadratically to the measurement uncertainties affecting  $\Delta_{47}^{\text{raw}}$ .

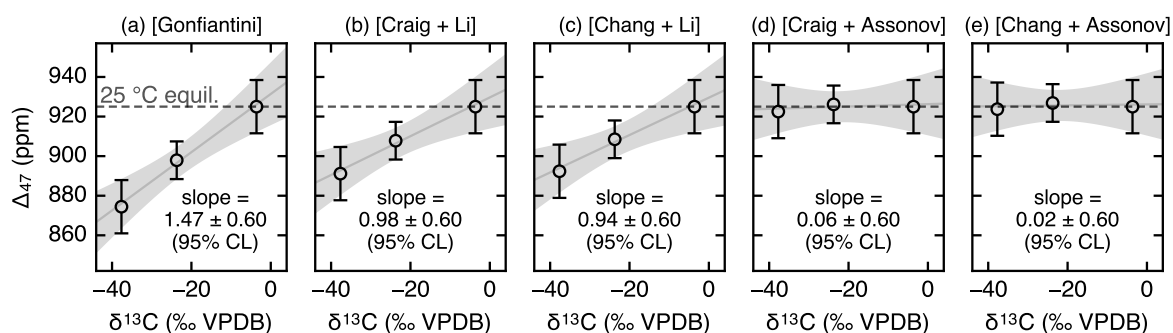
standardization errors could be as great (or greater, in the case of exotic bulk compositions) as traditionally reported  $\Delta_{47}$  uncertainties.

Knowing full well that most of my colleagues were not looking forward to invert covariance matrices by themselves, I released, along with the article, an open-source library (**D47crunch**) implementing my standardization models, and a web application allowing anyone with a browser to apply them to their own analytical data (**ClumpyCrunch**). These software tools are currently used by several other research groups, and feedback from some of them has led to new releases of D47crunch extending its ability to process  $\Delta_{48}$  and  $\Delta_{49}$  as well as  $\Delta_{47}$ . More importantly, eminent colleagues from the University of Washington were recently kind enough to send an email to express their appreciation of the D47crunch library, along with promises of future “frothy beverages”. I believe this firmly establishes D47crunch as my most successful scientific contribution to date.

#### 2.1.4 From “raw” measurements to “true” $\Delta_{47}$ : oxygen-17 correction issues

Another assumption hidden in section 2.1.2 is that we know the true isotope abundance ratios in VPDB and VSMOW. It was recognized early on that the choice of oxygen-17 correction parameters would have an influence on  $\Delta_{47}^{\text{raw}}$  values, but it seemed at the time that this effect would act equally on both unknown and standard analyses, and thus be corrected by subsequent standardization corrections<sup>[45]</sup>. As it turned out, at the 5<sup>th</sup> International Clumped Isotope Workshop of 2016, Andy Schauer (University of Washington) presented new evidence that equilibrated gases with very different  $\delta^{13}\text{C}$  values unexpectedly displayed different  $\Delta_{47}$  signatures. The ensuing discussion mainly focused on the practicality of introducing yet another correction factor, but Gerry Olack and/or Albert Colman (University of Chicago) also pointed out that this could result from a poor choice of oxygen-17 correction parameters. Later that same year, within a few months of each other, both our group and Andy Schauer’s published independent yet convergent

[45] Affek & Eiler (2006). [10.1016/j.gca.2005.08.021](https://doi.org/10.1016/j.gca.2005.08.021)



**Figure 2.2 — Results of an experiment arguing for the use of new oxygen-17 correction parameters.** Figure from *Daëron et al.* [19]. Three CO<sub>2</sub> samples equilibrated at 25 °C, expected to have indistinguishable  $\Delta_{47}$  values despite different  $\delta^{13}\text{C}$  values, were analyzed at LSCE. The five panels show the results of processing the corresponding raw data ( $\delta_{45} \dots \delta_{49}$ ) using five different sets of oxygen-17 parameters.

articles<sup>[19, 20]</sup> demonstrating that the effects of oxygen-17 correction on  $\Delta_{47}^{\text{raw}}$  are only partially corrected for by the standardization approach of eq. (2.4). Crucially, the resulting bias can vary subtly yet systematically between labs, depending on the relative bulk compositions of unknown and standard samples. In the end, both of our papers advocated for the use of the same updated set of oxygen-17 correction parameters, causing virtually all clumped-isotope laboratories to switch to the new parameters shortly thereafter.

Several of us were initially hopeful that oxygen-17 correction issues were the root cause for the large discrepancies between  $\Delta_{47}$  calibrations from different labs (fig. 1.1), and that switching to updated oxygen-17 parameters would neatly solve the problem. After an initial phase of more-or-less-acknowledged competition during which three different groups started independently compiling raw data sets of past calibration studies, we ended up collaborating, ultimately resulting in a community-wide publication which found that unified reprocessing with the new parameters substantially reduced inter-laboratory discrepancies without eliminating them<sup>[21]</sup>.

### 2.1.5 Establishment of a carbonate $\Delta_{47}$ metrological scale

During the 6<sup>th</sup> International Clumped Isotope Workshop of 2017, co-organized in Paris by IPGP and LSCE, several of us pushed hard for setting up an inter-laboratory comparison exercise with  $\Delta_{47}$  standardization based no longer on heated and equilibrated gases, as in the CDES, but on carbonate reference materials exclusively, as initially proposed by Stefano Bernasconi’s group at ETH Zürich<sup>[46]</sup>. Along with Magali Bonifacie (IPGP), Kristin Bergmann (MIT), Nele Meckler (Univ. of Bergen), and Stefano Bernasconi, I co-organized the resulting InterCarb exercise, in which seven carbonate reference materials (including two IAEA standards) were analyzed in 22 laboratories. I was additionally in charge of the InterCarb data processing.

[19] Daëron *et al.* (2016).

[10.1016/j.chemgeo.2016.08.014](https://doi.org/10.1016/j.chemgeo.2016.08.014)

[20] Schauer *et al.* (2016). [10.1002/rcm.7743](https://doi.org/10.1002/rcm.7743)

[21] Petersen *et al.* (2019). [10.1029/2018gc008127](https://doi.org/10.1029/2018gc008127)

[46] Meckler *et al.* (2014). [10.1002/rcm.6949](https://doi.org/10.1002/rcm.6949)

The resulting community-wide publication<sup>[22]</sup> concluded that standardizing  $\Delta_{47}$  measurements using carbonate reference materials exclusively yielded inter-laboratory scatter which was congruent (neither smaller nor greater) than expected from fully propagated analytical uncertainties based on the error propagation models discussed above (section 2.1.3). By contrast, using gas standards exclusively, as done in the CDES, led to larger scatter than could be reasonably expected from analytical error models, most likely because gas-based standardization failed to correct for inter-laboratory differences in the effects of the phosphoric acid reaction used to convert carbonates into  $\text{CO}_2$ . The article also established a new  $\Delta_{47}$  metrological scale, the InterCarb-CDES, or I-CDES, designed to closely approximate CDES scaling, but with metrological “anchors” being three internationally distributed calcite reference materials. The entire anonymized raw data and InterCarb processing code was open-sourced and archived<sup>[47]</sup>.

### 2.1.6 Using a novel least-squares formulation to reconcile $\Delta_{47}$ calibrations

Published shortly after the establishment of the I-CDES scale, two independent calibration studies that I was peripherally involved in, based on re-analyzed and newly-analyzed carbonates of various types, yielded apparently consistent I-CDES  $\Delta_{47}$  values as a function of temperature<sup>[23, 48]</sup>. Subjectively, I was inclined (in other words, biased) to trust that these results supported the hypothesis that the I-CDES scale may fully solve our long-standing calibration problem. Being well aware of my own bias, I wanted to test this hypothesis in a mathematically rigorous way, by reprocessing as many existing calibration data as possible in the I-CDES scale and subjecting the resulting data set to proper statistical tests.

Doing so, however, first required solving a very specific mathematical problem. Calibrating the carbonate  $\Delta_{47}$  thermometer is equivalent to fitting a regression model to  $(x, y)$  data, with potentially large uncertainties in both  $x$  and  $y$  values (formation temperature and  $\Delta_{47}$ , respectively). In such cases, one would naturally use something like York regression<sup>[49]</sup>, a least-squares method accounting for uncertainties in both dimensions. But analytical errors in  $\Delta_{47}$  data from the same calibration study are likely to be correlated due to the typical magnitude of standardization uncertainties<sup>[25]</sup>, which cannot be accounted for using York regression. Dealing with such correlated errors is the purview of so-called “generalized” least-squares methods, but they, in turn, are not designed to handle uncertainties in the  $x$  dimension. More generally, and somewhat surprisingly, none of the current commonly-used flavors of least-squares regression take into account the full set of possible covariances between all observed  $(x, y)$  values.

In a paper currently in review, I propose an original approach to perform “truly generalized” least-squares regression, properly taking into account arbitrarily complex covariance matrices between all  $x$  and all  $y$  values. The original version of the manuscript first described this “Omnivariant Least-Squares Regression” (OGLS) method, then used it to test for statistically

[22] Bernasconi *et al.* (2021). [10.1029/2020GC009588](https://doi.org/10.1029/2020GC009588)

[47] Daëron (2021). [10.5281/zenodo.4314448](https://doi.org/10.5281/zenodo.4314448)

[23] Anderson *et al.* (2021). [10.1029/2020gl092069](https://doi.org/10.1029/2020gl092069)

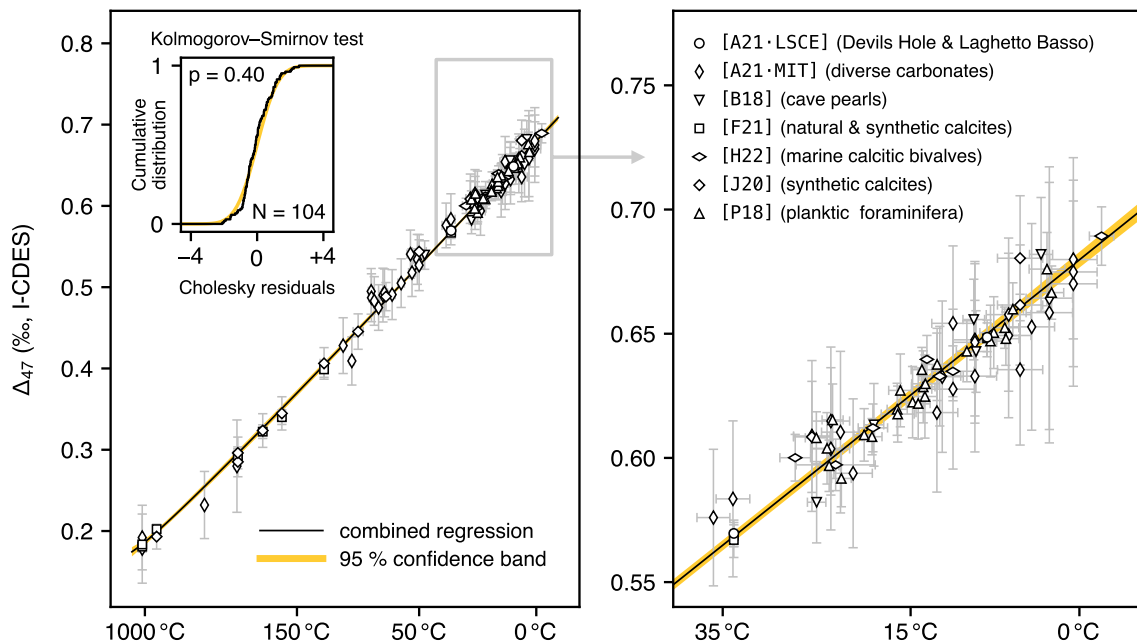
[48] Fiebig *et al.* (2021). [10.1016/j.gca.2021.07.012](https://doi.org/10.1016/j.gca.2021.07.012)

[49] York *et al.* (2004). [10.1119/1.1632486](https://doi.org/10.1119/1.1632486)

[25] Daëron (2021). [10.1029/2020gc009592](https://doi.org/10.1029/2020gc009592)

significant discrepancies between various reprocessed I-CDES calibration data sets. A week before submission, however, I crossed paths with Pieter Vermeesch (University College London), a prominent geochronologist well-versed in such regression issues, and we realized that we had both been working for years on this same problem, independently reaching equivalent solutions despite the use of different mathematical formulations. We decided that the best course of action was to combine our findings into a single manuscript explicitly addressing the separate problems that initially motivated our work, and promptly did so<sup>[24]</sup>.

Regarding the  $\Delta_{47}$  calibration problem, I am now able to conclude, based on OGLS-adapted goodness-of-fit estimates and quantitative statistical tests, that all calibration data sets (re)processed in the I-CDES metrological scale so far are in statistical agreement with each other, and that a single quadratic calibration function provides a good fit to the whole data set ( $N = 104$ ). In my opinion this finding, if it holds true, marks another milestone in the progress of clumped-isotope thermometry. Today, I would go so far as to claim that we now have constraints on equilibrium  $\Delta_{47}$  values which are accurate and precise enough for the vast majority of known applications, including virtually all paleo-environmental reconstructions (fig. 2.3).



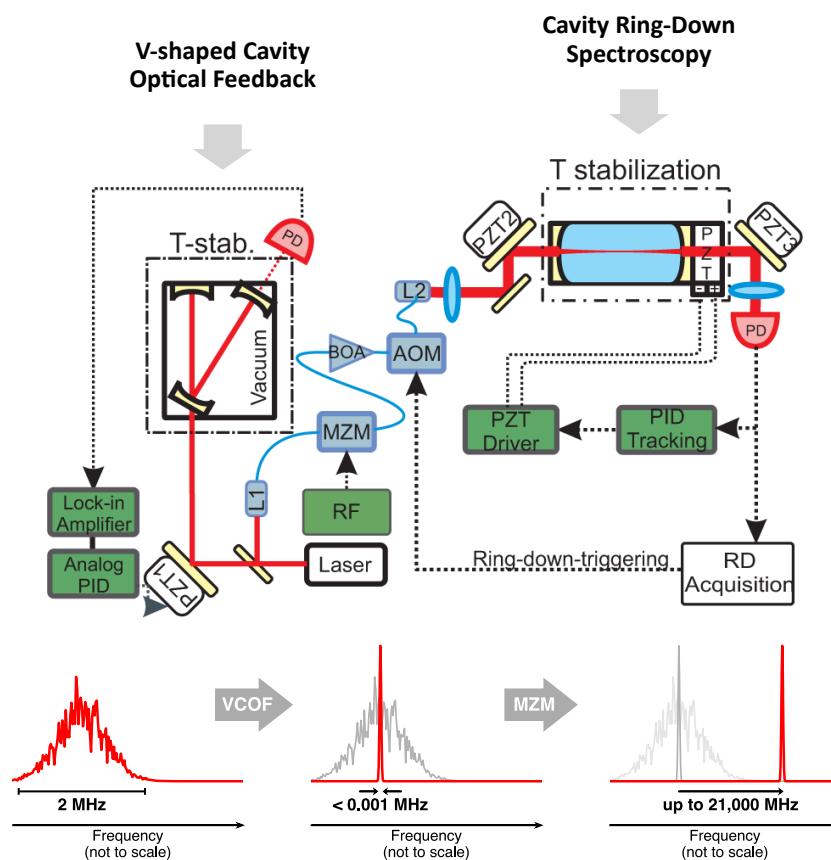
**Figure 2.3 — Combined  $\Delta_{47}$  calibration plot using OGLS regression.** Modified from *Daëron & Vermeesch* [24]. A second-degree polynomial regression yields a good fit to the whole data set combining all samples ( $N = 104$ ) from 7 distinct prior studies. Cholesky residuals are statistically indistinguishable from the expected Gaussian distribution.

[24] Daëron & Vermeesch (2023). (in press).  
[10.31223/x5k394](https://doi.org/10.31223/x5k394)



## 2.2 Spectroscopic measurements of CO<sub>2</sub> isotopologues using VCOF-CRDS

Laser spectroscopy in geochemistry is primarily known for its ability to acquire data in the field, more or less continuously. From the start, our own goal was instead to design a lab instrument competitive with state-of-the-art IRMS under controlled conditions. The project started from the ground level, with very basic questions. First, can we gain the technical capacity to make spectroscopic measurements with the sensitivity and precision required for isopic anomalies ( $\Delta^{17}\text{O}$ ,  $\Delta_{47}$ ,  $\Delta_{48}$ ) in pure CO<sub>2</sub> under perfect/ideal experimental conditions? This first stage roughly corresponds to the period of Tim Stoltmann's PhD. Secondly, how close can we get to these perfect/ideal conditions, taking into account real-world requirements and limitations of our work, e.g., keeping sample size reasonably small? We started working on these issues in the “dark years” following the end of Tim's PhD. Being severely understaffed, we mostly characterized the technical problems to solve, but real progress had to wait until the arrival of Justin Chaillot, whose engineering experience proved invaluable. At the end of Justin's PhD, a year ago, we were mostly able to manipulate samples in a reproducible way, and to correct for slow, subtle instrumental drift through the use of a working gas. We also started to investigate sample preparation protocols, and these investigations are still ongoing.



**Figure 2.4 — Schematic of a VCOF-CRDS instrument.** Modified from *Stoltmann et al.* [38]. Section 2.2.1 provides a simple description of the principles behind VCOF-CRDS.

Below, I summarize the key stages in this decade-long effort, but I must emphasize again that these results would never have been possible without the involvement of these two graduate student and my LiPhy colleagues, primarily Samir Kassi but also Erik Kerstel, Daniele Romanini, Alain Campargue and others.

### 2.2.1 V-Cavity Optical Feedback Cavity Ring-Down Spectroscopy (VCOF-CRDS)

In line with my insistence that we should strive to be understood by a curious ten-year-old, here is how I would describe the principle of VCOF-CRDS:



Start with a regular infrared laser diode. Optically lock it to an ultra-stable V-shaped cavity whose dimensions are virtually constant and whose mirrors are ultra-reflective. This causes the laser source to emit light at a very stable, very narrow frequency band. Shift the frequency (i.e. wavelength) of this light by a precisely defined arbitrary offset using an electro-optic device. Using this system, we can generate a beam of very fine, very stable, arbitrarily tunable infrared light, which we inject into a second cavity filled with pure CO<sub>2</sub>. By slightly adjusting the length of that cavity, we make it resonant with the incoming wavelength and then determine the sample's absorption at this wavelength by measuring the ring-down time constant. Then we repeat this measurement by shifting the same laser source to a different frequency or by switching to another laser diode.

Using this method, we can very precisely measure weak absorptions for any number of arbitrarily-chosen, precisely sampled frequencies. These measurements, combined with state-of-the-art spectroscopic models, are used to constrain the abundance of each isotopologue of interest.

The key design insight of VCOF-CRDS is that, by using two different cells, one to lock the laser frequency and the other to perform ring-downs (cf fig.2.4), an extreme mechanical stability of the first cell will translate into an equivalent spectral stability of the laser beam. The main challenge at this early stage of the work was thus to design a V-shaped cavity with ultra-stable mechanical properties. Several generations of V-cavities were designed and tested at LiPhy. Other LiPhy students greatly contributed to this long-term effort, including Johannes Burkart and Mathieu Casado (whose PhD grant was funded by Amaelle Landais's ERC, and who now has a CNRS position at LSCE).

The second challenge was to implement a system capable of precisely and continuously shifting the ultra-stable frequency of the V-locked laser beam by an arbitrary spectral offset. By doing so, we gained the ability to precisely target, within the range of a given laser diode, any arbitrary combination of frequencies, providing optimal conditions to target the absorption peaks for all isotopologues of interest.

While working on these optical issues, we chose to remain in optimal “sampling” conditions, by making all measurements in a continuous flow of pure CO<sub>2</sub> at a stabilized pressure, thus avoiding any fractionation/adsorption/reaction effects on the analyte. In 2017, we published an article describing these developments<sup>[38]</sup>, in which we were able to demonstrate our ability to measure  $\Delta^{17}\text{O}$  anomalies in CO<sub>2</sub> with an instrumental precision of 10 ppm within 10 minutes (fig. 1.3). Reaching that milestone meant that we were now limited by our ability to manipulate and store CO<sub>2</sub> aliquots for the duration of the measurement.

### 2.2.2 Static analyses of small CO<sub>2</sub> aliquots

It is often said that geochemical analyses are only as good as their sample treatment protocols. Transitioning from continuous flow analyses to small, finite aliquots of CO<sub>2</sub> required (a) calling on my own geochemical experience with manipulating small amounts of CO<sub>2</sub> in a reproducible manner, avoiding or minimizing isotopic fractionations, and (b) solving new spectroscopic problems. For example, we were long confounded by our failure to recognize that CO<sub>2</sub> analytes were briefly in contact with a hot solenoid when moving through a proportional valve used to regulate the flow of gas into the CRDS cavity. The current in the solenoid varied as a function of the valve’s opening, probably leading to a variable balance between viscous and diffusive flow. Combined with variability in the width of the passage through the valve, this seemed to fractionate our analytes in unacceptable ways. To solve this problem, we replaced the inlet valve with calibrated-diameter orifices, greatly improving the reproducibility of our measurements.

We also had to battle adsorption and desorption effects: immediately after injecting pure CO<sub>2</sub> into the CRDS cell, water starts desorbing from the cell wall, while CO<sub>2</sub> starts being adsorbed. As a result, pCO<sub>2</sub> decreases over several minutes after sample introduction, while the total pressure in the cell may overall decrease or increase, depending on the amount of desorbing water. This presents a spectroscopic challenge, because cavity ring-downs take some time (several ms) and we target different wavelengths in sequence, so that a complete spectral scan may require several seconds or tens of seconds. If, over this time scale, the abundance of each isotopologue varies substantially, spectroscopic absorption models will not be able to reproduce the observed spectrum because they are designed to make predictions for a fixed gas composition. To overcome this problem, we decided to dramatically reduce the spectral resolution of our acquisitions, sampling only the tops and baselines of a few absorption peaks (instead of attempting to fit a high-resolution spectrum, as was done before). This “parking” approach allowed us to rapidly switch between all isotopologues, closely tracking the pressure changes over the duration of one analysis.

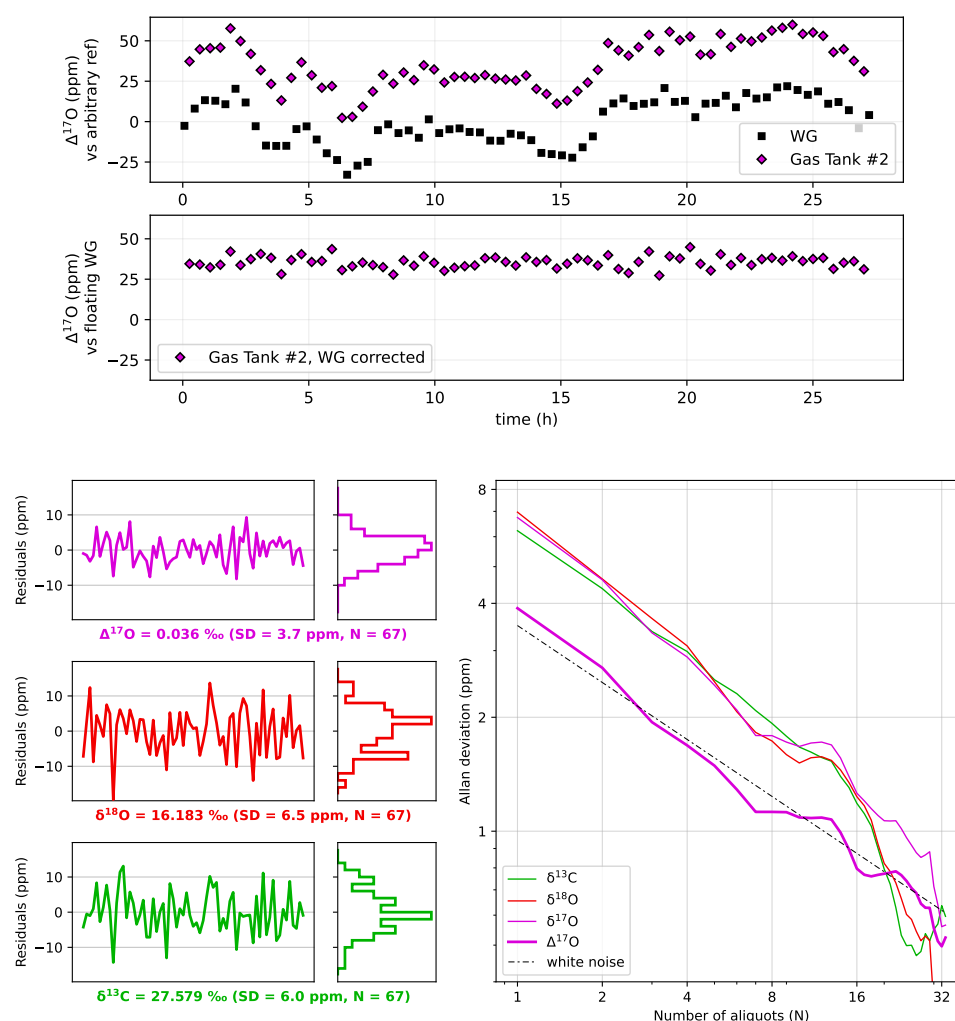
Of course, we also had to write our own data processing pipelines, from ring-down acquisition and fitting to the final standardization steps. We went through several iterations of these pipelines over the years, preferentially using open-source tools. Today, we have a reasonably mature stack

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[38] Stoltmann *et al.* (2017).  
[10.1021/acs.analchem.7b02853](https://doi.org/10.1021/acs.analchem.7b02853)

of Labview and Python codes which not only generates high-quality data, but also attempts to make the whole process as reproducible as possible, which we have found to be critical in development stages, when analytical procedures are continuously evolving.

Figure 2.5 illustrates the outcome of these improvements. Because transient pressure variations, limiting precision in a continuous-flow analysis, are virtually eliminated in a static sample, we achieve substantially better precision than the 10 ppm demonstrated by *Stoltmann et al.*<sup>[38]</sup>.



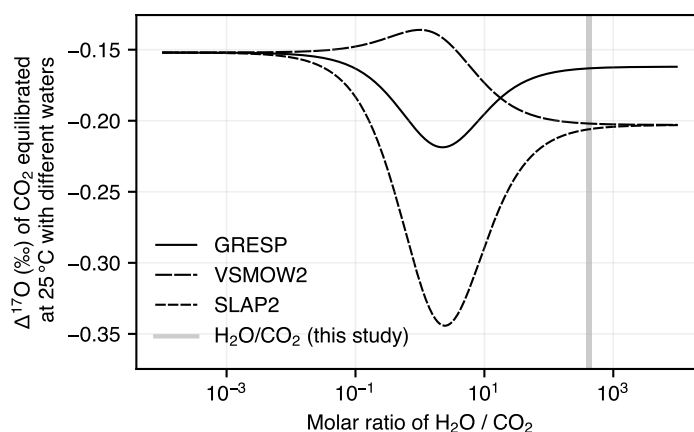
**Figure 2.5 — Allan variance plot of repeated  $\Delta^{17}\text{O}$  analyses of  $\text{CO}_2$  aliquots from a single tank.** Thanks to the working-gas corrections illustrated in the top panel, the instrumental repeatability of our measurements is around 6-7 ppm for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  and  $\sim 4$  ppm for  $\Delta^{17}\text{O}$ .

[38] Stoltmann *et al.* (2017).  
[10.1021/acs.analchem.7b02853](https://doi.org/10.1021/acs.analchem.7b02853)

### 2.2.3 Analytical protocols and metrological issues

Once you have a instrument capable of precise measurements, you still need to test whether your analytical repeatability is on the same order as your instrumental precision, or, in other words, whether you are limited by short-term instrumental precision, long-term instrumental stability, and/or the experimental repeatability of everything that happens before the instrumental measurement. You also need to check the validity/accuracy of the numbers you are getting, by making observations that you are able to predict independently.

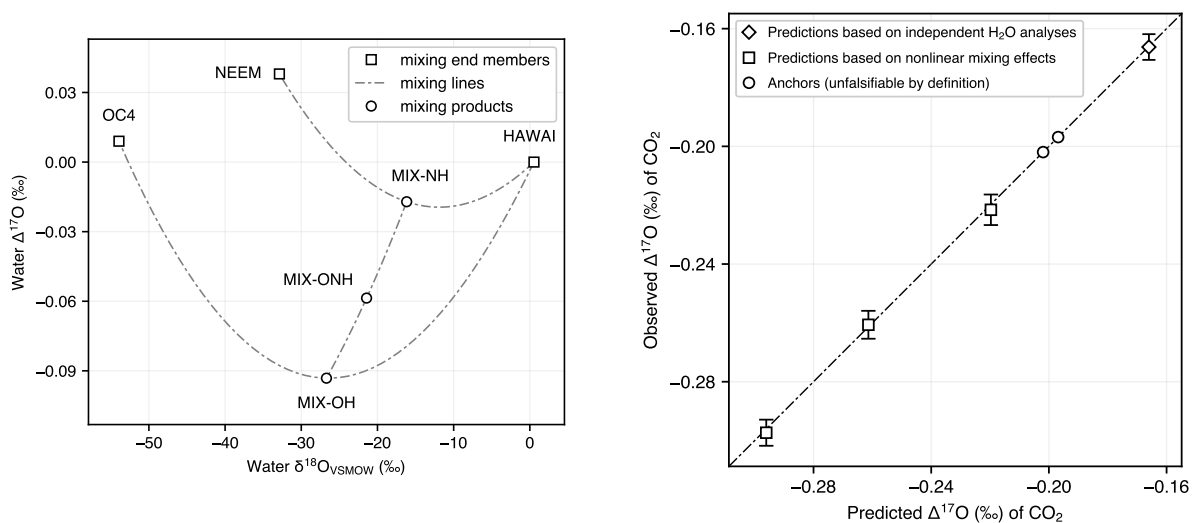
In terms of sample preparation, we are mostly interested in the triple oxygen isotopes composition of carbonates (which may be converted to  $\text{CO}_2$  by acid reaction) and water (which may be isotopically equilibrated with  $\text{CO}_2$ ). For carbonate samples, the jury is still out as to whether we can detect differences in the repeatability of calcite samples reacted manually (by a human operator) at  $25^\circ\text{C}$  versus  $90^\circ\text{C}$ . We are however, in the process of building an automated line for acid reactions, which, in my prior experience, may further improve  $\Delta^{17}\text{O}$  repeatability. For now, we are happy to work with external repeatabilities of  $\sim 6$  ppm (1SD) for calcite reference materials reacted at  $90^\circ\text{C}$ . For water samples, we developed a modified equilibration protocol whereby water and  $\text{CO}_2$  in a large but finite molar ratio of 200:1 to 500:1 are sealed in a glass ampule and left to equilibrate for a week at  $25^\circ\text{C}$ . In the case of an infinite  $\text{H}_2\text{O}/\text{CO}_2$  ratio, the triple-oxygen composition of the equilibrated  $\text{CO}_2$  would depend only on the water's composition. In the case of a finite ratio, non-linear mixing effects may shift  $\Delta^{17}\text{O}$  of the equilibrated  $\text{CO}_2$  by several ppm, with the sign of this effect depending primarily on the relative  $\delta^{18}\text{O}$  values of the initial water and  $\text{CO}_2$ , and to a second order also on their relative  $\Delta^{17}\text{O}$  values (fig. 2.6). These small offsets may not truly matter in the case of some (but not all) natural samples, but are too large to ignore in many other cases, such as when using water reference materials to standardize  $\Delta^{17}\text{O}$  measurements.



**Figure 2.6 — Predicted final  $\Delta^{17}\text{O}$  composition of  $\text{CO}_2$  equilibrated at  $25^\circ\text{C}$  with three international water reference materials.** Figure from *Chaillot et al.* (in prep.). The equilibrated  $\Delta^{17}\text{O}$  value depends mostly on the initial isotopic composition of the water, but is potentially offset by several ppm due to nonlinear mixing effects.

In the upcoming VCOF-CRDS publications, we also describe a modified version of the least-squares standardization models I developed for clumped isotopes, with an additional twist designed to account for the strong covariation in  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  observations, in spite of the fact that, mathematically speaking,  $\delta^{17}\text{O}$  standardization corrections and  $\delta^{18}\text{O}$  standardization corrections are computed from completely separate sets of values, yielding final, standardized values of  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  which are mathematically independent, considerably overestimating final analytical uncertainties in  $\Delta^{17}\text{O}$ .

Finally, in what I consider to be the culminating experiment of a decade-long effort, we tested our ability, provided with samples covering a very wide range of independently-predicted  $\Delta^{17}\text{O}$  values, to measure these values with an accuracy comparable to our claimed analytical precision. To do so, we took advantage of the fact that we are able to compute nonlinear mixing effects with almost perfect accuracy, even for mixing end-members whose  $\Delta^{17}\text{O}$  are not perfectly known. We started out with three local water standards of known triple-oxygen composition, from Amaëlle Landais' group, which are more or less equivalent to the international reference materials VSMOW2, SLAP2 and GRESP. By mixing these standards in varying proportions, we generate water samples with oxygen-17 excess values (relative to VSMOW, with  $\lambda = 0.528$ ) ranging from  $-0.09\text{‰}$  to  $+0.04\text{‰}$  (fig. 2.7). We then equilibrated these water samples with small aliquots of the same  $\text{CO}_2$ , recollected the  $\text{CO}_2$  afterwards and analyzed it, treating  $\text{CO}_2$  equilibrated with our pseudo-VSMOW2 and our pseudo-SLAP2 as standards, and all the other samples as unknowns. The analytical repeatability in this experiment ( $\text{SD} = 4.6\text{ ppm}$  on  $\Delta^{17}\text{O}$ ) is indistinguishable from the purely instrumental precision shown in fig. 2.5. More importantly, the final, standardized results are virtually indistinguishable from our theoretical predictions ( $\text{RMSE} = 1.2\text{ ppm}$ , fig. 2.7), despite the fact that we cover a very wide range of  $\Delta^{17}\text{O}$  values exceeding the typical variability in most natural samples.



**Figure 2.7 — Results demonstrating the quasi-perfect linearity of our VCOF-CRDS measurements of  $\Delta^{17}\text{O}$  in  $\text{CO}_2$ .** Plots from a manuscript in preparation by *Chailiot et al.* Above: triple-oxygen compositions of the water end-members and water mixtures we prepared for this experiment. Right panel: comparison of the measured versus predicted  $\Delta^{17}\text{O}$  values for  $\text{CO}_2$  samples equilibrated with these waters. The agreement is excellent, with RMSE on the order of 1 ppm.

“Dire que dans quelques minutes, ou bien nous marcherons sur le sol de la Lune, ou bien nous serons tous morts. C’est merveilleux!...”

(*On a marché sur la Lune*, 1954)

## 3 Prospects and projects

### 3.1 One ring-down to rule them all: redefining state-of-the-art measurements of isotopic anomalies in CO<sub>2</sub>

So far, all of my spectroscopy projects have been advertised as aiming for  $\Delta^{17}\text{O}$  measurements. This strategic decision was because  $^{16}\text{O}^{12}\text{C}^{17}\text{O}$  are more abundant, thus less difficult to precisely analyze, than multiply-substituted isotopologues, but also because  $\Delta^{17}\text{O}$  analyses using IRMS require converting CO<sub>2</sub> to some other phase (usually O<sub>2</sub>) to overcome isobaric interference between  $^{16}\text{O}^{12}\text{C}^{17}\text{O}$  and the much more abundant  $^{16}\text{O}^{13}\text{C}^{16}\text{O}$ . This CO<sub>2</sub>-to-O<sub>2</sub> conversion step is chemically challenging, work-intensive, potentially dangerous, and potentially fractionates analytes in poorly understood ways<sup>[50]</sup>.

The latest VCOF-CDRS instruments have now demonstrated our ability to perform rapid, painless analyses of  $\Delta^{17}\text{O}$  in 30–40  $\mu\text{mol}$  aliquots of CO<sub>2</sub> with state-of-the-art precision (better than 10 ppm). A natural next step, currently underway, is to go for the doubly-substituted isotopes  $^{16}\text{O}^{13}\text{C}^{18}\text{O}$  and  $^{18}\text{O}^{12}\text{C}^{18}\text{O}$  (abbreviated as 638 and 828, respectively). Our motivation is threefold:

(1) As mentioned in section 2.1.3,  $\Delta_{47}$  standardization corrections are necessary to correct for various instrumental non-linearities which vary slowly through time. These corrections introduce a non-negligible amount of analytical uncertainty<sup>[25]</sup>, which can only be minimized by continuously analyzing many reference materials. The design choices of VCOF-CRDS, by using CRDS in a relatively weakly absorbing spectral region, favor instrumental stability and metrological linearity over sensitivity. We are expecting these choices to pay off by reducing, perhaps dramatically, the magnitude of instrumental corrections we need to apply on a daily basis. Here I must acknowledge that Aerodyne Research has already demonstrated their ability

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[50] Wostbrock *et al.* (2020).  
[10.1016/j.chemgeo.2019.119432](https://doi.org/10.1016/j.chemgeo.2019.119432)

[25] Daëron (2021). [10.1029/2020gc009592](https://doi.org/10.1029/2020gc009592)

to measure  $\Delta_{638}$  (functionally equivalent to  $\Delta_{47}$ ) with acceptable precision. However, possibly because of very different design choices, they still observe metrological non-linearities on par with those in IRMS methods (see for instance fig.2 of Yanay *et al.*<sup>[51]</sup>). I believe we may soon be in a position to improve on that.

(2) Dual-inlet measurements of  $\Delta_{47}$  and  $\Delta_{48}$  are currently limited by counting statistics. In other words, assuming that the probability of ionizing a molecule in the source is a random process following a Poisson distribution, detecting  $n$  ions allows us to estimate the corresponding average ion beam current with a relative precision of  $n^{-1/2}$ . Given the typical ion currents corresponding to  $m/z$  values of 48, it is extremely challenging for IRMS to measure  $\Delta_{48}$  with a better precision than 25-30 ppm in a few hours<sup>[52]</sup>. VCOF-CRDS measurements have a completely different set of constraints and limitations, and the technique is at a stage where the number of improvement ideas exceeds the time available to test them. A few years from now, laser spectroscopy might thus become the go-to technique for “dual” clumped-isotope applications.

(3) In dual-inlet IRMS, Faraday cups simultaneously acquire data for all isotopologues. Molecular absorption spectroscopy, by contrast, samples different wavelengths, and thus different isotopologues, in sequence. This means that we may arbitrarily decide how to apportion measurement time spent on each isotopologue. This decision happens entirely at the software level: we could theoretically have subsequent analyses target different isotopic anomalies without making any material modifications to the instrument. The unmatched versatility of VCOF-CRDS offers a way to aim either for the most precise determination of a specific tracer (e.g.,  $\Delta^{17}\text{O}$ , or  $\Delta_{638}$ , or even  $\delta^{13}\text{C}$  in very small samples), or for simultaneous measurements of all isotopologues ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ ,  $\Delta_{638}$ ,  $\Delta_{828}$ ).

Finally, it would be near-sighted to consider VCOF-CRDS only in terms of what one or two groups will do, looking at one or two molecules; this technique opens up a very broad range of spectroscopic and geochemical applications. I know that my LIPhy colleagues are working hard on the former. Regarding geochemistry, I believe it is critical to foster the emergence of an informal community of researchers invested in VCOF-CRDS developments and applications, perhaps through regular workshops, or through large-scale national or international networks and/or projects. Whatever shape this networking takes, it is critical that us geochemists become drivers, rather than consumers, of today’s spectroscopic revolution, which will require us to learn new skills, comparable to but distinct from our traditional IRMS expertise. Future developments that could aim for include for example quadruple sulfur isotopes, clumped isotopes in methane, real-time field measurements of isotopic anomalies so far restricted to laboratory analyses, sending miniaturized VCOF-CRDS instruments to lower Earth orbit or to the Martian surface...

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[51] Yanay *et al.* (2022). [10.1126/sciadv.abq0611](https://doi.org/10.1126/sciadv.abq0611)

[52] Fiebig *et al.* (2019). [10.1016/j.chemgeo.2019.05.019](https://doi.org/10.1016/j.chemgeo.2019.05.019)



## 3.2 Hydrothermal carbonates associated with seafloor alteration, agents and archives of the oxygen and carbon cycles

Although an HDR memoir is not expected to be exhaustive, it may appear strange that the Earth-science applications that ultimately motivate my work have so far remained conspicuously in the background. This is partly due to the fact that methodological and instrumental developments take time (particularly so when more than half of our time is eaten up by seemingly unnecessary friction in the French research system). An other factor is that Earth science, more so than others, works by combining different kinds of expertise, and that very few of us are able to become experts in five different highly specialized fields. As a result, my applicative work so far has been in collaboration with other researchers, touching on a diversity of topics including speleothem records of glacial cycles<sup>[14]</sup>, paleoceanographic reconstructions using foraminifera<sup>[28, 30]</sup> and bivalves<sup>[32, 33]</sup>, and hydrothermal carbonates associated with seafloor alteration<sup>[35]</sup>. This last topic is one that I hope to study much more extensively in the coming years, for reasons I elaborate below.

### 3.2.1 Context and implications to the carbon and oxygen cycles

Much of what we know about Phanerozoic climates (0–540 Ma) is based on the oxygen-18 composition of marine biogenic carbonates, reflecting some combination of seawater  $^{18}\text{O}/^{16}\text{O}$  ratios and temperatures through time, potentially modified by diagenetic alteration. For certain ice-free periods (e.g., the mid-Cretaceous), one may assume seawater  $\delta^{18}\text{O}_{\text{VSMOW}}$  values of around  $-1\text{‰}$  and interpret the carbonate  $\delta^{18}\text{O}$  values in terms of paleo-temperatures, but on longer time scales the carbonate  $\delta^{18}\text{O}$  record displays a clear trend, increasing by 8–10 ‰ from the Cambrian to the present (fig. 3.1). Despite decades of research there is an ongoing, vigorous controversy<sup>[53]</sup> regarding whether this trend primarily reflects progressive  $^{18}\text{O}$  enrichment of the ocean, progressive cooling of the ocean from as high as  $\sim 50^\circ\text{C}$  in the Cambrian, and/or pervasive diagenetic alteration of the carbonate record.

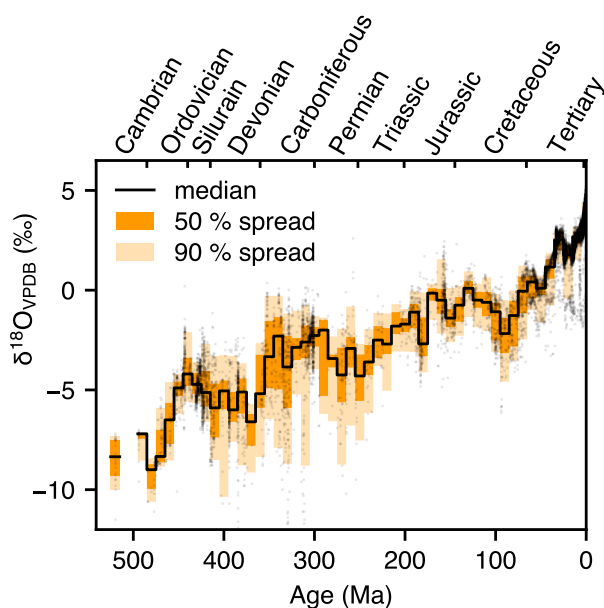
This issue has far-reaching implications, because (a) oceanic temperatures are one of the primary factors constraining our understanding of the Earth’s climate history; (b) large changes in  $\delta^{18}\text{O}$  of the ocean (on longer time scales than glacial cycles, which only account for 1–2 ‰) require significant variation in the isotopic fluxes associated with continental weathering and hydrothermal alteration of oceanic crust; (c) our paleo-biologic understanding of key periods such as the Cambrian explosion might need to account for much warmer conditions than previously assumed; (d) oxygen-isotope exchange between seafloor lavas and seawater is directly linked to the major element exchanges responsible for alkalinity production — thus  $\text{CO}_2$  consumption —

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- [14] Wainer *et al.* (2011).  
[10.1016/j.quascirev.2010.07.004](https://doi.org/10.1016/j.quascirev.2010.07.004)  
[28] Peral *et al.* (2020).  
[10.1016/j.palaeo.2020.109603](https://doi.org/10.1016/j.palaeo.2020.109603)  
[30] Daëron & Gray (2023). [10.1029/2023PA004660](https://doi.org/10.1029/2023PA004660)  
[32] Briard *et al.* (2020).  
[10.1016/j.palaeo.2019.109582](https://doi.org/10.1016/j.palaeo.2019.109582)

- [33] Letulle *et al.* (2022). [10.5194/cp-18-435-2022](https://doi.org/10.5194/cp-18-435-2022)  
[35] Coogan *et al.* (2019).  
[10.1016/j.epsl.2018.12.014](https://doi.org/10.1016/j.epsl.2018.12.014)  
[53] Veizer & Prokoph (2015).  
[10.1016/j.earscirev.2015.03.008](https://doi.org/10.1016/j.earscirev.2015.03.008)

and both are sensitive to bottom water temperatures<sup>[35]</sup>. This means that the oxygen-isotope composition of seawater is linked to the long-term carbon fluxes and climate in ways that are only partially understood.

Past efforts to reconstruct the isotopic composition of ancient seawater have been based on the study of altered oceanic crust<sup>[54]</sup>, marine bio-carbonates<sup>[53, 55]</sup>, cherts<sup>[56, 57]</sup>, kerogens<sup>[58]</sup>, and marine iron oxides<sup>[59]</sup>. In theory, it should be possible to solve this controversy by using  $\Delta_{47}$  thermometry to constrain both the crystallization temperatures of well-chosen carbonate samples, and, simultaneously, the oxygen-18 composition of the water in which they formed. Past attempts do so have generally been hindered by pervasive, cryptic diagenetic alteration<sup>[60–62]</sup>. On one hand, although clumped-isotope signatures are known to be susceptible to closed-system isotopic reordering at elevated temperatures, and thus potentially more easily altered than oxygen-18 signatures, this may be used as a more sensitive indicator of cryptic diagenesis<sup>[63]</sup>. On the other hand, it has been argued that pristine biogenic calcite is particularly vulnerable to isotopic reordering through early intra- and inter-crystalline annealing<sup>[53]</sup>, potentially making most of the “old” biogenic bio-carbonate record unsuitable for clumped-isotope thermometry. *Ryb & Eiler*<sup>[60]</sup> tried to circumvent this issue by analyzing  $\Delta_{47}$  in Phanerozoic dolostones (dolomite being more resistant than calcite to isotopic reordering). They found no evidence for large  $^{18}\text{O}$  depletion in Phanerozoic seawater, but their samples are largely mineralized in carbonate



**Figure 3.1 — Phanerozoic record of marine carbonate  $\delta^{18}\text{O}$**  (including foraminifera, bivalves, brachiopods, belemnites, conodonts) based on a compilation by J. Veizer

([https://mysite.science.uottawa.ca/jveizer/isotope\\_data](https://mysite.science.uottawa.ca/jveizer/isotope_data)).

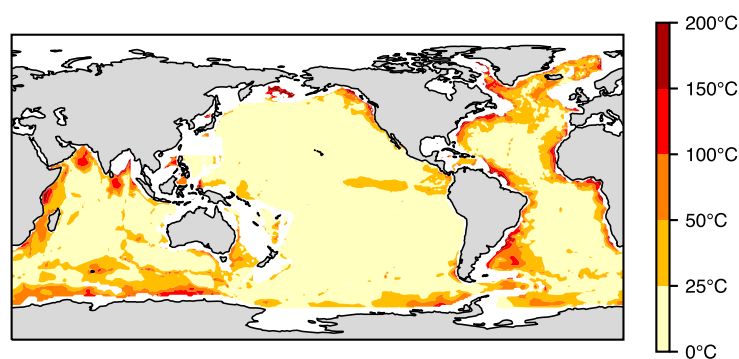
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- [35] Coogan *et al.* (2019). [10.1016/j.epsl.2018.12.014](https://doi.org/10.1016/j.epsl.2018.12.014)
  - [54] Muehlenbachs (1986)
  - [55] Jaffrès *et al.* (2007). [10.1016/j.earscirev.2007.04.002](https://doi.org/10.1016/j.earscirev.2007.04.002)
  - [53] Veizer & Prokoph (2015). [10.1016/j.earscirev.2015.03.008](https://doi.org/10.1016/j.earscirev.2015.03.008)
  - [56] Karhu & Epstein (1986). [10.1016/0016-7037\(86\)90136-5](https://doi.org/10.1016/0016-7037(86)90136-5)
  - [57] Robert & Chaussidon (2006). [10.1038/nature05239](https://doi.org/10.1038/nature05239)
  - [58] Tartèse *et al.* (2016). [10.7185/geochemlet.1706](https://doi.org/10.7185/geochemlet.1706)
  - [59] Galili *et al.* (2019). [10.1126/science.aaw9247](https://doi.org/10.1126/science.aaw9247)
  - [60] Ryb & Eiler (2018). [10.1073/pnas.1719681115](https://doi.org/10.1073/pnas.1719681115)
  - [61] Bergmann *et al.* (2018). [10.2110/jsr.2018.51](https://doi.org/10.2110/jsr.2018.51)
  - [62] Henkes *et al.* (2018). [10.1016/j.epsl.2018.02.001](https://doi.org/10.1016/j.epsl.2018.02.001)
  - [63] Cummins *et al.* (2014). [10.1016/j.gca.2014.05.024](https://doi.org/10.1016/j.gca.2014.05.024)

platform sequences through sediment/rock reaction with diagenetically modified seawater, which complicates interpretations. Other studies targeting fossil biocarbonates<sup>[61, 62]</sup> reached similar conclusions, but required careful screening for post-burial alteration, and the resulting seawater reconstructions still suffer from large scatter on the order of several per mil.

Recent studies by *Sengupta & Pack* and *Wostbrock et al.* highlight how triple oxygen isotopes may help with these issues, because seawater  $\delta^{18}\text{O}$  variations reflecting changes in the balance of high-temperature versus low-temperature alteration of the crust should be strongly correlated with changes in seawater  $\Delta^{17}\text{O}$ <sup>[64]</sup>. What's more, diagenetic recrystallization (as opposed to closed-state, diffusional reordering) is expected to produce large negative  $^{17}\text{O}$  anomalies due to the non-linear mixing properties of  $\Delta^{17}\text{O}$ <sup>[65]</sup>.

### 3.2.2 Objectives, strategy and proof-of-concept results

In collaboration with Laurence Coogan (University of Victoria) and others, I propose that we could shed light on the long-term evolution of seawater temperature and composition by studying the triple-oxygen-isotope and clumped-isotope composition of calcites formed by low-temperature alteration of the upper oceanic crust, in off-axis hydrothermal systems where bottom seawater circulates rapidly through aquifers within a permeable layer of basaltic lava overlain by sediments<sup>[66]</sup>. Such aquifers offer a priori optimal conditions for the chemical and isotopic preservation of clumped-isotope signatures, as calcium ions are continuously leached from the crust, minimizing  $\text{CaCO}_3$  dissolution, and because, over most of the global ocean, estimated water temperatures in well-mixed off-axis aquifers are generally expected to be only up to 10-20 °C warmer than bottom waters (fig. 3.2), preserving original  $\Delta_{47}$  values from the effects of solid-state isotopic reordering.



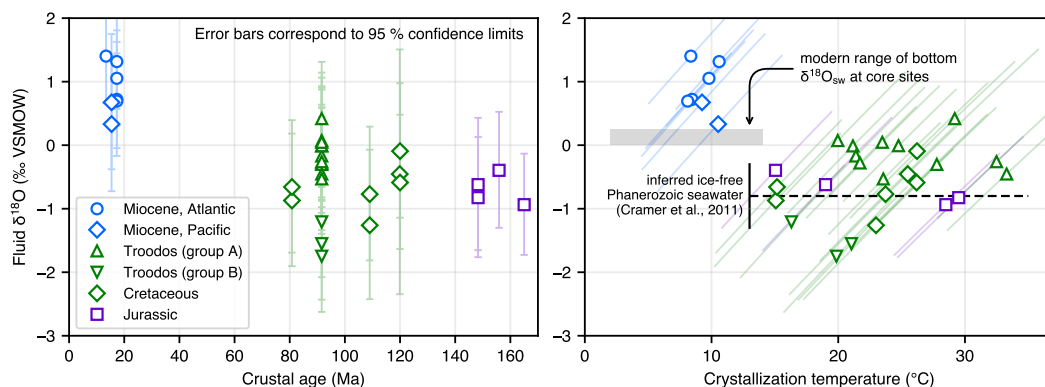
**Figure 3.2 — Model temperature for well-mixed crustal aquifers.** Based on total marine sediment thickness, and crust-age-derived heat flow estimates [66]. The vast majority of such aquifers remain much cooler than 100 °C, above which solid-state reordering starts affecting clumped-isotope signatures.

[64] Sengupta & Pack (2018).  
[10.1016/j.chemgeo.2018.07.012](https://doi.org/10.1016/j.chemgeo.2018.07.012)  
 [65] Wostbrock *et al.* (2020).  
[10.1016/j.gca.2020.07.045](https://doi.org/10.1016/j.gca.2020.07.045)

[66] Coogan & Gillis (2018).  
[10.1146/annurev-earth-082517-010027](https://doi.org/10.1146/annurev-earth-082517-010027)

We thus propose to collect hydrothermal carbonates from the upper lava section of oceanic crust, sampled from carefully selected DSDP/ODP crustal cores and ophiolite regions offering the best prospects for long-term clumped-isotope preservation. Some of the oldest samples will doubtlessly have been affected by solid-state reordering, but we may still use  $\Delta^{17}\text{O}$  as a paleothermometer, under certain assumptions<sup>[65]</sup>. In cases with no clear evidence of solid-state reordering, triple-oxygen-isotope thermometry (based on calcite-water isotopic equilibrium, which we are currently in the process of recalibrating using slow-precipitated natural calcites and high-temperature experiments) and  $\Delta_{47}$  thermometry are expected to yield the same temperature estimates, providing useful redundancy to support our interpretations.

We have already been (slowly) exploring these ideas for the past few years, and we now have a sizable proof-of-concept data set extending back 170 Ma (fig. 3.3). I have also had good contacts with potential collaborators beyond Laurence Coogan, including Christophe Pécuyer (IPREM, U/Pb dating of carbonates) and David Zakharov (Western Michigan University, triple oxygen isotopes of silicates). If I ever finally manage to dedicate a large chunk of my professional time to Earth-science applications, this is the topic that I would most want to contribute to.



**Figure 3.3 — Proof-of-concept results (128 analyses).** Most of the Troodos samples are from *Coogan et al.* [35]; all other samples unpublished. Jurassic and Cretaceous carbonates yields fluid  $\delta^{18}\text{O}$  indistinguishable from an expected “ice-free” seawater composition of  $-0.8\text{‰}$  [67], while samples from Miocene crust formed as expected from cooler and  $^{18}\text{O}$ -enriched waters. Pacific water compositions for the Miocene are close to modern ocean average, while Atlantic waters appear more  $^{18}\text{O}$ -enriched, perhaps reflecting an influx of evaporatively fractionated proto-Mediterranean water.

[65] Wostbrock *et al.* (2020).  
[10.1016/j.gca.2020.07.045](https://doi.org/10.1016/j.gca.2020.07.045)

[67] Cramer *et al.* (2011). [10.1029/2011jc007255](https://doi.org/10.1029/2011jc007255)

# Concluding notes

## **Becoming a well-balanced geochemist: harder than it looks?**

In retrospect, I have to recognize that I severely overestimated, back in the day, my ability to lead the way both in the methodology and in the applications of clumped-isotope geochemistry. Today, I try to warn students that, faced with clear limitations in the methods they wish to apply in their own research, they will likely have to make a pragmatic choice between solving the underlying methodological problem (which could require ten years) and working within its confines for the time being (with perhaps better short-term publication prospects). My own focus on “hard” methodology would probably have been ill-advised without the luxury of a permanent CNRS position.

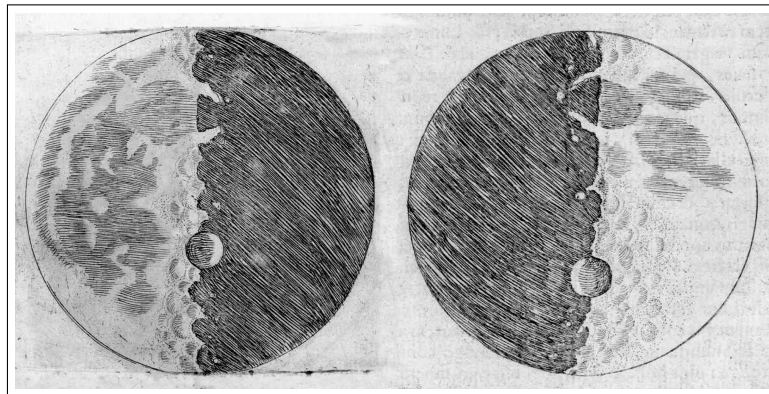
Taking a step back, I would argue that most of our published research output falls into three distinct categories: (a) description and implementation of a general tool/approach, not specific to a particular region/context, providing methods potentially applicable in various geologic settings; (b) new information about a specific site or case study, adding incrementally to a large body of geologic information which other/future geologists may draw on to study both “local” and more general issues; (c) new interpretations/insights about general topics, fueling the long-term, collective exchange of ideas regarding the interpretation of geologic evidence.

It seems obvious how “good” research usually rests on the combination of these three categories. What is less obvious, at least to me, is how these different “work packages” are best distributed among individual researchers. On one hand, my intuitive belief is that having some experience in these three dimensions, and being able to switch from one mode of thinking to another, are crucial qualities of a well-rounded geoscientist. On the other hand, there are only so many hours in the day, and there are many examples of excellent researchers who are highly specialized in one dimension or another. The work division may even vary from one specialty to the other, e.g., when comparing geochronologists and stable isotope geochemists. Whatever the case, one of my primary goals in the years to come is to achieve a satisfying balance between instruments/methods, applications, and so-called “big” questions.

## Observation versus motivation: a tale of two Italians

I would like to conclude this memoir by considering a point of contention regarding how we think and talk about our research, presenting it predominantly in terms of either *solving problems* or *observing the world*.

As illustration, I will invoke two famous Italians who both profoundly changed the worldview of their times. The first one is Christopher Columbus, who persistently lobbied various funding bodies of his day, aiming to establish a western sea passage to the East Indies with strong, self-evident economic motivations. His proposal was successful, and his accomplishments led to a number of great and/or terrible things, almost all entirely orthogonal to his originally stated goals. The second one is Galileo Galilei, who, after several instrumental development projects including a thermoscope, and a hydrostatic balance, designed a new kind of refracting telescope inspired from a recent Dutch patent application. His critical achievement was that instead of using it as intended, to observe distant ships or troops, he pointed it to the skies and discovered mountains on the Moon and satellites around Jupiter, which remain among the most momentous observations in the history of human knowledge.



*Moon drawings from 1610.  
Galileo's prior background in painting and drawing  
proved critical to communicating his findings.*

One often gets the impression that our modern funding bodies want us all to be Columbus: target a problem, fund a plan, publish and/or profit. In many cases, our professional career will greatly benefit from an ability to “storytell” our work in these terms. We should, however, remain suspicious of this narrative.

There is a recurring motif with many new geochemical proxies: a new tracer (or the novel interpretation of an existing tracer) appears, and is soon featured in a high-impact article; shortly thereafter, more fastidious methodological studies show that some of the assumptions in earlier publication should be revisited. Leaving aside the issue of whether or not this is just the system working as expected, this back-and-forth between proxy applications and limitations is

too often framed in terms of “how useful/reliable is my proxy for my objectives”. It may be more interesting to ask instead how new evidence changes the “perimeter of usefulness” for this proxy. Granted, paleoaltimetry based on  $\Delta_{47}$  thermometry of pedogenic carbonates turned out to be more challenging than we once hoped for. However, in this case, bad news for the study of orogenesis is good news for that of pedogenesis; ultimately, we can learn a lot about the timing and mechanisms of soil processes using clumped isotopes.

Over the years, I have often encountered examples of this “glass half-empty / glass half-full” dialectic. For instance, the realization that, in most geologic settings, clumped-isotope signatures are slowly reset at the scale of hundred million years is a disappointment to those interested in the Precambrian but a boon to those studying erosion and/or diagenesis. The fact that corals precipitate carbonate with  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$ ,  $\Delta_{47}$ ,  $\Delta_{48}$  signatures strongly out of isotopic equilibrium may dishearten paleoceanographers but provides an excellent opportunity to fingerprint the calcification processes at play in different types of corals (fig.1.5). Instead of working from objectives, we might be better off carefully surveying the *terra incognita* before us and trying to understand its rules before we decide what our observations will be useful for.

Ultimately, I am thus a strong believer that science is best served by following Galileo, looking at the world with new eyes and trying to make sense of what we observe. Contrary to popular representation, we do not engage in research to cure cancer or to reverse climate change or to feed the world. It seems much more likely that we are motivated instead by a primal human need to describe and explain the world in which we exist. Deep down, we study stable isotopes for the same reason we paint cave walls, create myths, and speculate about the origin of life: because it pleases us, nothing more and nothing less.

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## Appendix:

# Scientific production

### A.1 Complete list of peer-reviewed publications

- (1) **M. Daëron** & W. R. Gray. Revisiting oxygen-18 and clumped isotopes in planktic and benthic foraminifera. *Paleoceanography and Paleoclimatology* (2023). [10.1029/2023pa004660](#).
- (2) **M. Daëron** & P. Vermeesch. Omnivariant Generalized Least Squares regression: theory, geochronological applications, and making the case for reconciled  $\Delta_{47}$  calibrations. *Chemical Geology* (2023).
- (3) J. Viallon, T. Choteau, E. Flores, F. Idrees, P. Moussay, R. I. Wielgosz, Z. Loh, C. Allison, L. Huang, A. Chivelscu, F. Camin, B. Krajnc, N. Ogrinc, A. de Lima Fioravante, M. Fasciotti, T. V. C. Monteiro, B. C. Garrido, E. C. P. Rego, W. Wollinger, C. R. Augusto, S. Michel, J. S. Lee, J. K. Lim, **M. Daëron**, S. Kass, H. Moossen, L. Hai, Z. Zhou, A. Srivastava, T. Shimosaka, E. Mussel Webber, R. Hill-Pearce, P. Brewer, M. Chartrand, O. Rienitz, V. Ebert, L. Flierl, J. Braden-Behrens, J. Nwaboh, A. Emad, A. Simsek, & I. Chubchenko. Final report of CCQM-P204, comparison on CO<sub>2</sub> isotope ratios in pure CO<sub>2</sub>. *Metrologia* 60:(1A) (2023), pp. 08026. [10.1088/0026-1394/60/1a/08026](#).
- (4) M. Casado, T. Stoltmann, A. Landais, N. Jobert, **M. Daëron**, F. Prié, & S. Kass. High stability in near-infrared spectroscopy: part 1, adapting clock techniques to optical feedback. *Applied Physics B* 128:(3) (2022). [10.1007/s00340-022-07774-2](#). [citations: 4].
- (5) J. Chaillot, S. Dasari, H. Fleurbaey, **M. Daëron**, J. Savarino, & S. Kass. High-precision laser spectroscopy of H<sub>2</sub>S for simultaneous probing of multiple-sulfur isotopes. *Environmental Science: Advances* (2022). [10.1039/d2va00104g](#). [citations: 1].
- (6) D. Huyghe, **M. Daëron**, M. de Rafelis, D. Blamart, M. Sébilo, Y.-M. Paulet, & F. Lartaud. Clumped isotopes in modern marine bivalves. *Geochimica et Cosmochimica Acta* 316 (2022), pp. 41–58. [10.1016/j.gca.2021.09.019](#). [citations: 13].
- (7) T. Letulle, G. Suan, **M. Daëron**, M. Rogov, C. Lécuyer, A. Vinçon-Laugier, B. Reynard, G. Montagnac, O. Lutikov, & J. Schlögl. Clumped isotope evidence for Early Jurassic extreme polar warmth and high climate sensitivity. *Climate of the Past* 18:(3) (2022), pp. 435–448. [10.5194/cp-18-435-2022](#). [citations: 3].
- (8) A. Moulin, L. Benedetti, L. Vidal, J. Hage-Hassan, A. Elias, J. Van der Woerd, I. Schimmelpfennig, **M. Daëron**, & P. Tapponnier. LGM glaciers in the SE Mediterranean? First evidence from glacial landforms and <sup>36</sup>Cl dating on Mount Lebanon. *Quaternary Science Reviews* 285 (2022), pp. 107502. [10.1016/j.quascirev.2022.107502](#). [citations: 4].
- (9) M. Peral, F. Bassinot, **M. Daëron**, D. Blamart, J. Bonnin, F. Jorissen, C. Kissel, E. Michel, C. Waelbroeck, H. Rebaubier, & W. R. Gray. On the combination of the planktonic foraminiferal Mg/Ca, clumped ( $\Delta_{47}$ ) and conventional ( $\delta^{18}\text{O}$ ) stable isotope paleothermometers in palaeoceanographic studies. *Geochimica et Cosmochimica Acta* 339 (2022), pp. 22–34. [10.1016/j.gca.2022.10.030](#). [citations: 2].
- (10) N. T. Anderson, J. R. Kelson, S. Kele, **M. Daëron**, M. Bonifacie, J. Horita, T. J. Mackey, C. M. John, T. Kluge, P. Petschnig, A. B. Jost, K. W. Huntington, S. M. Bernasconi, & K. D. Bergmann. A Unified Clumped Isotope Thermometer Calibration (0.5–1,100 °C) Using Carbonate-Based Standardization. *Geophysical Research Letters* 48:(7) (2021). [10.1029/2020gl092069](#). [citations: 76].



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- (13) J. Fiebig, **M. Daëron**, M. Bernecker, W. Guo, G. Schneider, R. Boch, S. M. Bernasconi, J. Jautzy, & M. Dietzel. Calibration of the dual clumped isotope thermometer for carbonates. *Geochimica et Cosmochimica Acta* 312 (2021), pp. 235–256. [10.1016/j.gca.2021.07.012](#). [citations: 24].
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- (18) **M. Daëron**, R. N. Drysdale, M. Peral, D. Huyghe, D. Blamart, T. B. Coplen, F. Lartaud, & G. Zanchetta. Most Earth-surface calcites precipitate out of isotopic equilibrium. *Nature Communications* 10(1) (2019), pp. 429. [10.1038/s41467-019-08336-5](#). [citations: 118].
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*All reference numbers below this point correspond to the above bibliography.*

## A.2 Software libraries and Web applications

### A.2.1 D47crunch

**Code:** <https://github.com/mdaeron/D47crunch>

**PyPI:** <https://pypi.org/project/D47crunch>

**DOI:** [10.5281/zenodo.4314550](https://doi.org/10.5281/zenodo.4314550)

D47crunch is a fairly mature Python library for processing and standardizing carbonate clumped-isotope analyses, from low-level data out of a dual-inlet mass spectrometer to final, “absolute”  $\Delta_{47}$ ,  $\Delta_{48}$  and  $\Delta_{49}$  values with fully propagated analytical error estimates based on the error models I designed for this purpose [12]. To date, D47crunch is used by several well-established groups including K. Huntington’s (University of Washington) and J. Fiebig’s (Goethe-Universität Frankfurt). Miguel Bernecker (also from GUF) recently contributed some code implementing  $\Delta_{49}$  processing, and has been using D47crunch as the underlying engine for their in-lab data processing web application. Also comes with a built-in command-line interface to process basic  $\Delta_{47}$  data sets.

### A.2.2 ClumpyCrunch

**Code:** <https://github.com/mdaeron/clumpycrunch>

**App:** <https://clumpycrunch.pythonanywhere.com/>

ClumpyCrunch is a web application enabling people to use D47crunch without any coding skill requirements. It is less customizable than D47crunch but is suitable for routine clumped-isotope analyses. It is currently (or was, until very recently) used by Magali Bonifacie (IPGP), Uri Ryb (Hebrew University, Jerusalem), and some among the Caltech group. There are likely other users I don’t know about.

### A.2.3 ogls

**Code:** <https://github.com/mdaeron/ogls>

**PyPI:** <https://pypi.org/project/ogls>

**DOI:** [10.5281/zenodo.8357230](https://doi.org/10.5281/zenodo.8357230)

A Python library implementing OGLS regression (see section 2.1.6). Supports arbitrary functions, with additional support for polynomial functions and polynomial functions of inverse absolute temperature.

### A.2.4 D47calib

**Code:** <https://github.com/mdaeron/D47calib>

**PyPI:** <https://pypi.org/project/D47calib>

**DOI:** [10.5281/zenodo.8357232](https://doi.org/10.5281/zenodo.8357232)

A Python library using OGLS regression in the context of  $\Delta_{47}$  calibrations, with built-in support for the calibrations reprocessed by *Daëron & Vermeesch* (in review, see section 2.1.6). Comes with a built-in command-line interface to perform batch conversions between  $\Delta_{47}$  and temperature.

#### A.2.5 `pyp1`

**Code:** <https://github.com/mdaeron/pyp1>

PyPL (Python Prep Line) is an open source, open hardware, Python-first automation system. Originally designed for processing geochemical samples in our clumped-isotope lab, but the system is flexible enough to fit many other needs. PyPL will potentially soon be also deployed in the new lumped-isotope lab of Alexis Licht at CEREGE.

#### A.2.6 `co2irms` / `carbonatix`

**Code:** <https://github.com/mdaeron/co2irms> – <https://github.com/mdaeron/carbonatix>

`co2irms` is a small Python library providing computations relevant to IRMS measurements of carbon dioxide, such as oxygen-17 corrections. It is intended for people who don't care about multiply-substituted isotopologues or oxygen-17 excess.

`carbonatix` is a web application to process IRMS measurements of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  in carbonate samples. It uses `co2irms` under the hood, as well as original standardization procedures designed to handle unacknowledged complexities arising from the non-trivial relationship between  $(\delta^{13}\text{C}, \delta^{18}\text{O})$  and  $(\delta_{45}, \delta_{46})$ . This is a work in progress, that will hopefully soon be refined and deployed in the Paleoceanography group at LSCE.

#### A.2.7 `isoDIC.py`

A Python re-implementation of Weifu Guo's `isoDIC` model, originally written for Matlab. Because of Weifu's original choice of license, I have not yet made this code public, but friendly negotiation is underway.

#### A.2.8 `cornerplots`

**Code:** <https://github.com/mdaeron/cornerplots>

**PyPI:** <https://pypi.org/project/cornerplots>

Simple library to create corner plots in `matplotlib`. Corner plots provide a simple way to visualize multidimensional data, with each dimension plotted against every other dimension. The main goal is to let the user specify data and/or model predictions in arbitrary subsets of the multi-dimensional space and let the code take care of where to plot these values. Originated as a simple way to explore `isoDIC.py` outputs.



### A.2.9 `lmfit-fullcovar`

**Code:** <https://github.com/mdaeron/lmfit-fullcovar>

Small Python library extending the output of `lmfit`, a well-known library for non-linear least-squares minimization and curve fitting. `lmfit-fullcovar` computes the full variance-covariance matrix for all fitted parameters along with the corresponding standard errors and correlation matrix.

### A.2.10 `micropython-zacwire`

**Code:** <https://github.com/mdaeron/micropython-zacwire>

MicroPython implementation of the ZACwire protocol used in **TSic 506F** temperature sensors, which have excellent accuracy ( $\pm 0.1$  °C). Useful for monitoring of PID applications.

## A.3 Reproducible code repositories

Whenever possible, I recommend that scientific articles should point to a publicly-accessible code and data repository allowing anyone to fully reproduce the results of the study, from the “raw” input data to the final published figures.

### A.3.1 `isoForam`

**Code:** <https://github.com/mdaeron/isoForam>

**DOI:** [10.5281/zenodo.4314550](https://doi.org/10.5281/zenodo.4314550)

**Article:** *Daëron & Gray* [1].

### A.3.2 `D47_error_propagation`

**Code:** [https://github.com/mdaeron/D47\\_error\\_propagation](https://github.com/mdaeron/D47_error_propagation)

**DOI:** [10.5281/zenodo.4314593](https://doi.org/10.5281/zenodo.4314593)

**Article:** *Daëron* [12].

### A.3.3 `InterCarb`

**Code:** <https://github.com/mdaeron/InterCarb>

**DOI:** [10.5281/zenodo.4314448](https://doi.org/10.5281/zenodo.4314448)

**Article:** *Bernasconi, Daëron, Bergmann, Bonifacie, Meckler et al.* [11].

# B

## Appendix: Selected works

All articles that I co-authored are available at <https://daeron.fr/biblio>. The five papers reprinted here cover what I believe are my most substantial scientific contributions to date.



*Absolute isotopic abundance ratios and the accuracy of  $\Delta_{47}$  measurements.*  
M. Daëron, D. Blamart, M. Peral & H. Affek (2016)  
Chemical Geology



*Direct, precise measurements of isotopologue abundance ratios in  $\text{CO}_2$  using molecular absorption spectroscopy: application to  $\Delta^{17}\text{O}$ .*  
T. Stoltmann, M. Casado, M. Daëron, A. Landais & S. Kassi (2017)  
Analytical Chemistry



*Full propagation of analytical uncertainties in  $\Delta_{47}$  measurements.*  
M. Daëron (2021)  
Geochemistry, Geophysics, Geosystems



*InterCarb: A community effort to improve inter-laboratory standardization of the carbonate clumped isotope thermometer using carbonate standards.*  
S. Bernasconi, M. Daëron, K. Bergmann, M. Bonifacie, A. Meckler, and 56 other co-authors (2021)  
Geochemistry, Geophysics, Geosystems



*Omnivariant Generalized Least Squares regression: theory, geochronological applications, and making the case for reconciled  $\Delta_{47}$  calibrations.*  
M. Daëron & P. Vermeesch  
(in press at Chemical Geology)

# Curriculum vitæ

November 2023

Mathieu DAËRON, 47 years old, three children

## Education :

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**1996-1999:** Ecole Polytechnique (majors: experimental sciences and quantum physics)

**1999-2000:** DEA de géophysique interne, Institut de Physique du Globe de Paris (IPGP)

**2000-2005:** PhD (Géophysique Interne) at IPGP, entitled “Rôle, cinématique et comportement sismique à long terme de la faille de Yammouneh, principale branche décrochante du coude transpressif libanais (faille du Levant)”, supervised by P. Tapponnier

## Work experience:

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**2005-2006 :** Post-doctoral fellow at the Caltech (California Institute of Technology). Focus on neotectonics of the fore-land basins of the Tien Shan continental mountain range, in collaboration with J.-P. Avouac.

**2006-2007 :** Post-doctoral fellow at Caltech. Focus on characterizing the clumped-isotope composition of pedogenic carbonates and speleothems, in collaboration with J. Eiler.

**2007-2008 :** Post-doctoral fellow at LSCE (Laboratoire des Sciences du Climat et de l'Environnement). Focus on paleo-climate applications of clumped isotopes in carbonates, in collaboration with D. Genty and D. Blamart.

**2008-2023 :** Chargé de recherches CNRS at LSCE.

## Scientific societies and research networks:

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- Réseau Isotopie Stables (RéGEF)
- Société Française des Isotopes
- European Association of Geochemistry (on and off)
- American Geophysical Union (on and off)

## Management and administrative duties:

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- **2015-2019 :** Member of the prospective committee on the establishment of RéGEF (Réseau Géochimique et Expérimental Français)
- **2019-2023 :** Co-animator, with F. Fourel, of the Stable Isotopes network within RéGEF
- **2013-2023 :** Scientific, technical and administrative manager of the clumped-isotope facility at LSCE

## Teaching:

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- **2010-2012 :** Taught a single-session, yearly Master 2 course on climate-applied paleothermometry at the Orsay university
- **2012-2013 :** Taught a single-session, yearly course speleothem studies at Ecole Nationale Supérieure de Géologie de Nancy
- **2015 :** Taught a single-session Master 2 course on climate-applied paleothermometry at the Orsay university

### Selected funding sources:

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- **2010-2011** : 20 k€ LEFE/INSU – Absolute Temperature Records from Clumped Isotopes Obtained Using Speleothems (ATROCIOUS)
- **2011** : 240 k€ R2DS funding from Région Ile-de-France + internal CEA support + INSU Mi-lourds, for establishing a state-of-the-art  $\Delta_{47}$  facility at LSCE.
- **2012-2013** : 79 k€ LEFE/INSU – Cavity Ring-Down Spectrometric Measurements of Triple Oxygen Isotopes in CO<sub>2</sub>
- **2013-2017** : 200 k€ ANR-JCJC – Laser Instrument for Triple Oxygen Spectrometry (LITOS)
- **2015**: First-tier competitive PhD funding from CEA (“Investigating the Mid-Pleistocene Transition using clumped isotopes in foraminera”).
- **2021**: 19 k€ Défi ISOTOP, MITI CNRS – iCO<sub>2</sub>-LASER
- **2021**: First-tier competitive PhD funding from CEA (“Study of isotopic disequilibrium in bio-carbonates using new isotopic tracers measured by VCOF-CRDS”).
- **2021-2023** : 220 k€ SESAME, Région Ile-de-France – Isotopic geogemistry using VCOF-CRDS
- **2023-2024** : DIM PAMIR, Région Ile-de-France – post-doctoral grant (PaléoLASER)

### Selected invited presentations and lectures:

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- **2010**: “Clumped isotopes in speleothems”. First International Workshop on Clumped Isotopes (Seattle, WA)
- **2010**: “Principles, methods and applications of “clumped isotope” geochemistry”. Fifth International Symposium on Isotopomers (Amsterdam, Netherlands).
- **2011**: “Clumped-isotope thermometry of speleothems: understanding and correcting for large kinetic fractionation induced by CO<sub>2</sub> degassing”. Benelux Association of Stable Isotope Scientists meeting (Brugge, Belgium).
- **2013**: “Clumped isotopes in speleothems”. Invited presentation at CRPG.
- **2016**: “Absolute isotopic abundance ratios and the accuracy of  $\Delta_{47}$  measurements”. Invited presentation at Imperial College London.
- **2019**: “Treize ans de clumping isotopique dans les carbonates : de l'âge ingrat à l'âge adulte ?”. Invited presentation at CRPG.
- **2020**: “How I Learned to Stop Worrying and Embrace Isotopic Disequilibrium in Carbonate Minerals”. Invited speaker, AGU Fall Meeting.
- **2021**: “Traitement des incertitudes dans les mesures isotopiques (entre autres) par spectroscopie laser (entre autres)”. Invited course, Journées Laser de la Société Française des Isotopes.
- **2023**: “Clumped isotopes all grown up — How I stopped worrying about  $\Delta_{47}$  calibrations”. Invited presentation at CEREGE.

### Organization of scientific meetings:

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- **2011**: Co-convenor of the session entitled “Stable isotopes as a tool in (paleo-)climate studies” at the EGU meeting (Vienna)
- **2013**: Co-convenor of the session entitled “Deviant Isotopologues: theory, processes and measurements of clumped isotopes and position-specific fractionations” at the Goldschmidt conference (Florence)
- **2014**: Member of the scientific committee for the 4<sup>th</sup> International Workshop on Clumped Isotopes (Zürich)
- **2016**: Member of the scientific committee for the 5<sup>th</sup> International Clumped Isotope Workshop (St Petersburg, FL)
- **2017**: Co-organizer of the 6<sup>th</sup> International Clumped Isotope Workshop (Paris)