

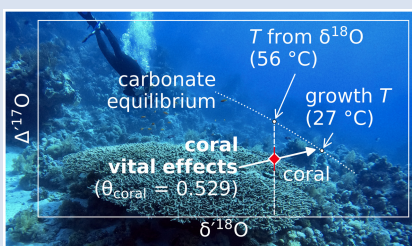
Correcting for vital effects in coral carbonate using triple oxygen isotopes

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Abstract



Carbonate oxygen isotopes ($^{18}\text{O}/^{16}\text{O}$) are a valuable tool for estimating palaeotemperatures, but their accuracy can be limited by so called vital effects that influence the isotope composition of biomineralised hard parts. In this study, we analysed the triple oxygen isotope composition ($^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$) of cold- and warm-water corals to demonstrate how such data can be used to identify and correct for vital effects. We found that the observed slopes in triple oxygen isotope space between the measured and expected equilibrium compositions are mainly controlled by CO_2 absorption, although there is a possibility of additional isotope fractionation effects from processes such as CO_2 (aq) diffusion through the cell membrane. We corrected these effects using an empirical vital effect slope and obtained accurate coral growth temperatures. The precision of reconstructed temperatures, considering the measurement error only, is ± 5 °C.

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Introduction

Classic oxygen isotope thermometry typically assumes that respective carbonates form in thermodynamic equilibrium with the ambient seawater, and thus, the carbonates' isotope composition only depends on temperature (T) and the composition of the ambient water. In biogenic carbonates, however, vital effects exert additional control on the magnitude of the total fractionation. Vital effects are a combination of kinetic and metabolic effects that influence the isotope composition of many biogenic minerals, including coral carbonate. While coral carbonate serves as a valuable high resolution climate archive, interpreting their isotopic code remains challenging due to the complexity of their biomineralisation mechanism.

It has long been noticed that most modern coral carbonate comprises much lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ than expected from equilibrium (Weber and Woodhead, 1972; McConnaughey, 1989a; Smith *et al.*, 2000; Adkins *et al.*, 2003). Temperature estimates from equilibrium $\delta^{18}\text{O}$ - T calibration curves indicate higher T (by >10 °C) compared to actual growth T . Although species-specific $\delta^{18}\text{O}$ - T calibrations can partly account for vital effects (Weber and Woodhead, 1972; Smith *et al.*, 2000), the reconstructed temperatures can remain inaccurate (Marali *et al.*, 2013). Likewise, coral growth T determined using clumped isotope thermometry (Δ_{47}) is also

biased by >10 °C, but towards lower T (Thiagarajan *et al.*, 2011; Saenger *et al.*, 2012). Accurate coral thermometry will only become feasible if the isotopic bias is accounted for (e.g., Davies *et al.*, 2022).

Dual clumped isotope thermometry (Δ_{47} and Δ_{48}) is a new approach currently explored to extract quantitative temperature information from carbonate samples affected by kinetic effects (Bajnai *et al.*, 2020). For coral carbonates, Davies *et al.* (2022) show systematic deviations from clumped isotope equilibrium along slopes characteristic of the underlying kinetic mechanisms. Apparent temperatures are corrected by back-extrapolating to the equilibrium line, providing accurate growth temperature reconstructions with a precision better than ± 3 °C (1 s.e.). Here, we propose a similar concept for attaining accurate carbonate growth temperatures but using triple oxygen isotopes.

Triple oxygen isotope analyses involve the simultaneous analysis of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$. Most Earth surface processes result in mass-dependent fractionation, which leads to a nearly perfect correlation between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values with a slope of approximately 0.5. The mass-dependent fractionation between two phases is described by Equation 1, where θ represents the triple oxygen isotope exponent characteristic of the process and temperature, and α is the equilibrium isotope fractionation factor:

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$$\theta_{A/B} = \frac{\ln(\alpha_{A/B}^{17})}{\ln(\alpha_{A/B}^{18})} \quad \text{Eq. 1}$$

Because the θ values of mass-dependent processes vary within a small range, the $\Delta^{17}\text{O}$ notation (in ppm) is used to visualise differences between them:

$$\Delta^{17}\text{O} = \left[10^3 \cdot \ln\left(\frac{\delta^{17}\text{O}}{1000} + 1\right) - \lambda_{\text{RL}} \times 10^3 \cdot \ln\left(\frac{\delta^{18}\text{O}}{1000} + 1\right) \right] \times 10^3 \quad \text{Eq. 2}$$

Here, we chose 0.528 for λ_{RL} (Luz and Barkan, 2010). The logarithmic transformation of the δ -values in Equation 2 is commonly abbreviated as δ' . All oxygen isotope values in this study are reported on the VSMOW (Vienna Standard Mean Ocean Water) scale.

Carbonates forming in thermodynamic equilibrium must fall on the equilibrium curve in $\Delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ space. Kinetic processes simultaneously drive $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ away from this curve. The slope (or θ) of any given kinetic process is a physical constant. Yet, apparent slopes may result from a combination of processes (Guo and Zhou, 2019; Wostbrock *et al.*, 2020a; Herwartz, 2021; Bajnai *et al.*, 2024). Constraining an empirical slope for the vital effects in corals and using it for back-extrapolation to the equilibrium curve makes accurate paleotemperature reconstructions feasible. In addition, the kinetic slope in triple oxygen isotope space can help in the mechanistic understanding of the underlying vital effects.

Coral Triple Oxygen Isotope Analyses

We analysed the triple oxygen isotope composition of 17 modern scleractinian (aragonitic) corals, representing four cold-water and five warm-water species. We retrieved seawater temperature and $\delta^{18}\text{O}_{\text{sw}}$ for each sample from a global gridded database (Breitkreuz *et al.*, 2018), using the interpolation method outlined in Daëron and Gray (2023). For some samples, *in situ* measured T and $\delta^{18}\text{O}_{\text{sw}}$ values were also available, which we used to assess the accuracy of the database estimates. The database and *in situ* measured values showed close agreement, typically within ± 1 °C and ± 0.2 ‰ (Fig. S-1). We regarded these average differences as indicative of the precision of the database and additionally factored in the interpolation error (on average ± 1 °C and ± 0.2 ‰) to obtain the final uncertainty of the database's seawater T and $\delta^{18}\text{O}$ estimates. We used the database values and their uncertainties to calculate the expected equilibrium $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values. Seawater $\Delta^{17}\text{O}$ values were not directly measured but universally assumed to be $\Delta^{17}\text{O}_{\text{sw}} = -11 \pm 6$ ppm, which covers most modern seawater data (Luz and Barkan, 2010; Lin *et al.*, 2021). Information on the samples is summarised in Tables S-1 and S-3.

The triple oxygen isotope analyses were conducted at the University of Göttingen using a tuneable infrared laser direct absorption spectrometer (TILDAS), detailed in Bajnai *et al.* (2023). The CO_2 analyte gas was derived from acid digestion at 25 °C. Carbonate-derived CO_2 data were normalised relative to two in-house standards: heavy CO_2 and light CO_2 measured alongside the samples, as detailed in Bajnai *et al.* (2024) (Figs. S-2, S-3). Briefly, the triple oxygen isotope composition of these two reference gases was determined relative to NBS-18 and IAEA-603 measurements and the values reported by Wostbrock *et al.* (2020b). A 25 °C acid fractionation factor was applied to the CO_2 data to calculate the isotope composition of the coral aragonite (*i.e.* $^{18}\alpha_{25^\circ\text{C-acid-CO}_2/\text{aragonite}} = 1.01063$ (Kim *et al.*, 2007) and $\theta_{25^\circ\text{C-acid-CO}_2/\text{carbonate}} = 0.523$ (Wostbrock *et al.*, 2020b)).

In our final dataset, we included the warm-water coral data point reported by Passey *et al.* (2014) (sample JBC03, *Porites porites*). To normalise this data point to our carbonate reference frame, we followed the steps outlined in Huth *et al.* (2022). Specifically, we applied empirical fractionation factors to the reported O_2/CaCO_3 values to account for fractionations induced by acid digestion and fluorination ($^{18}\alpha_{\text{empirical}} = 1.00812$ and $\theta_{\text{empirical}} = 0.5234$). Additionally, to account for the difference in the acid fractionation factors between aragonite and calcite, we shifted the corrected $\delta^{18}\text{O}$ value by 0.41 ‰ (Kim *et al.*, 2007). The respective seawater temperature and $\delta^{18}\text{O}_{\text{sw}}$ values were determined in the same manner as for our samples.

Results

The results of the triple oxygen isotope analyses are presented in Tables S-2 and S-3 and shown in Figure 1a. The long-term repeatability of the $\Delta^{17}\text{O}$ measurements of the heavy CO_2 and light CO_2 reference gases was 8–12 ppm. For the coral samples, the standard deviation of 2 to 7 replicate analyses was generally ± 5 ppm for $\Delta^{17}\text{O}$, while for $\delta^{18}\text{O}$ it was ± 0.1 ‰.

Discussion

Seeing through vital effects. We chose the theoretical aragonite calibration of Guo and Zhou (2019) as representative of thermodynamic equilibrium. In triple oxygen isotope space, all cold- and warm-water corals fall below their respective equilibrium lines (Figs. 1, 2). These offsets indicate that these corals did not form carbonate in equilibrium with seawater. Thus, respective $\delta^{18}\text{O}$ -temperature estimates are inaccurate (Fig. 3a) and attaining true T requires a correction for vital effects.

For each coral, we calculated the effective vital effect slope (θ_{coral}) in triple oxygen isotope space, by connecting the measured and the expected equilibrium values (Fig. 1). The θ_{coral} values ranged between 0.527 and 0.531, with a mean of 0.529 and a standard deviation of ± 0.001 ppm. To evaluate the accuracy of each θ_{coral} estimate, we used Monte Carlo error propagation, considering measurement errors and growth parameter uncertainties. The error of the individual θ_{coral} values was approximately ± 0.002 .

There was no resolvable difference in the vital effect slopes between species or among cold- and warm-water corals (Fig. S-5). In contrast, in dual clumped isotope space, cold- and warm-water corals exhibit distinct kinetic trajectories, explained by differences in the calcification parameters, such as the carbonic anhydrase activity, growth temperature, and the pH of the calcifying fluid (Davies *et al.*, 2022). Variations in these calcification parameters have a smaller impact on the kinetic slope in triple oxygen isotope space because the offset in $\delta^{18}\text{O}$ is an order of magnitude larger than in $\Delta^{17}\text{O}$ (Figs. 1b, S-4). The vital effect slopes are, thus, primarily driven by the kinetic fractionation exerting the largest effect while species-specific variations in calcification parameters appear to be less important.

To calculate growth temperatures corrected for vital effects, we back-extrapolated individual data points to their respective equilibrium line using unique vital effect slopes ($T_{\Delta^{17}\text{O}}$; Figs. 2, 3b, S-6). Rather than employing the previously established mean θ_{coral} , we calculated a distinct slope for each coral, derived from the data of all other corals except the one under analysis, thereby avoiding circularity in our calculations (Table S-3). The unique slopes were indistinguishable from the mean θ_{coral} of 0.529 within ± 0.001 . The reconstructed $T_{\Delta^{17}\text{O}}$ match the respective database T generally within ± 3 °C (Fig. 3b). Considering the uncertainty of the isotope analyses

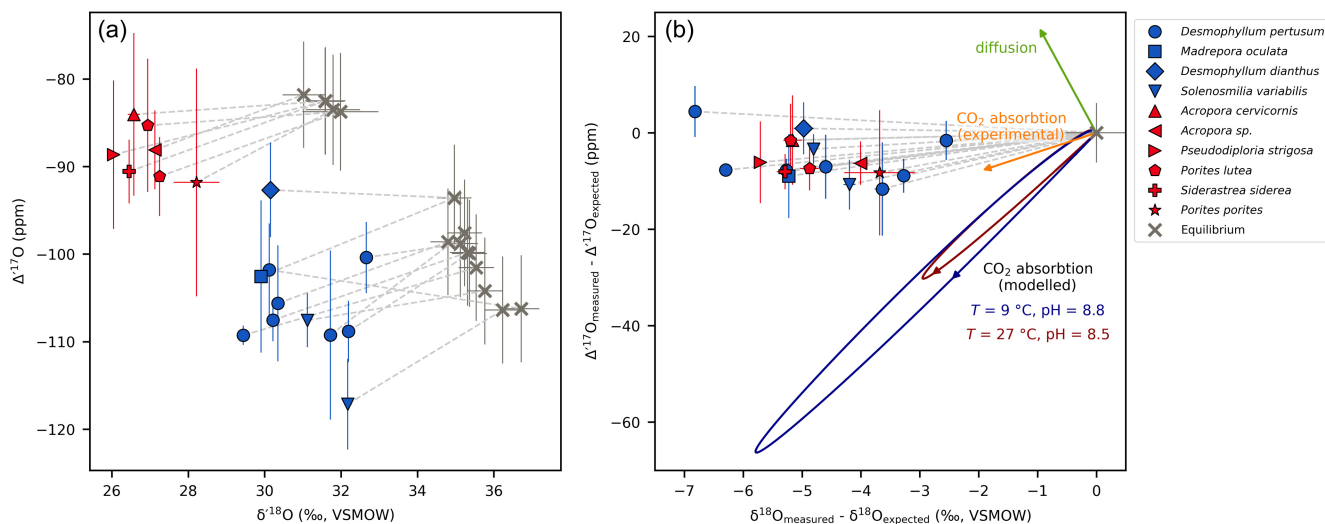


Figure 1 Triple oxygen isotope data for cold- and warm-water corals presented (a) in $\Delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ space and (b) as an offset plot. The expected equilibrium positions for each sample (grey crosses) are based on respective seawater $\delta^{18}\text{O}$ and T estimates. The dashed grey lines represent the effective vital effect slopes, moving away from the coral carbonate from equilibrium. The CO₂ absorption loops are made using the isoDIC model, simulating conditions resembling the internal calcification environment of cold- and warm-water corals (see Figure S-4 for details). The experimental CO₂ absorption vector considers a slope of 0.532, as discussed in the text. The *P. porites* sample is from Passey et al. (2014).

and the seawater parameters, the accuracy of $T_{\Delta^{17}\text{O}}$ is much larger, ca. $\pm 10^\circ\text{C}$. Sensitivity analyses show that every 1 ppm decrease in $\Delta^{17}\text{O}$ errors corresponds to an approximately 1°C reduction in the $T_{\Delta^{17}\text{O}}$ errors. Therefore, the ± 6 ppm uncertainty in the seawater $\Delta^{17}\text{O}$ alone already accounts for an uncertainty over $\pm 5^\circ\text{C}$. Currently, only limited data exist for the triple oxygen

isotope composition of seawater (Luz and Barkan, 2010; Lin et al., 2021). The inherent uncertainty of global variations in seawater $\Delta^{17}\text{O}$ is reduced when focusing on individual locations and effectively cancels out when reconstructing relative temperature shifts. Disregarding the uncertainty in seawater $\Delta^{17}\text{O}$ improves the accuracy of $T_{\Delta^{17}\text{O}}$ to $\pm 5^\circ\text{C}$.

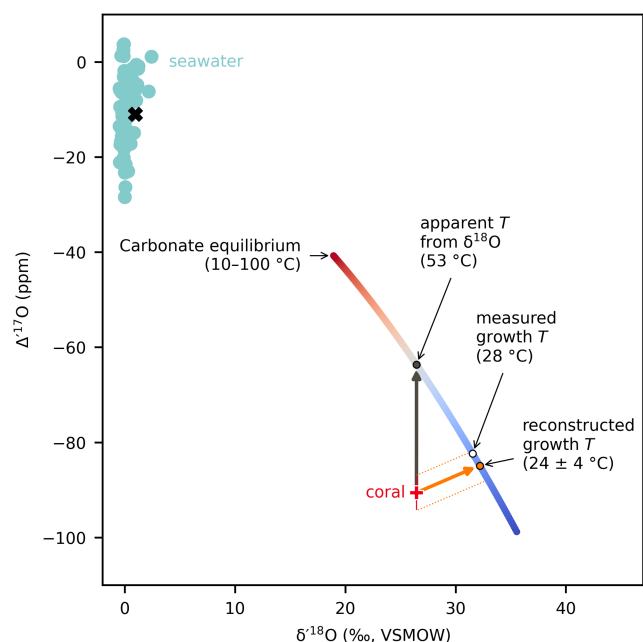


Figure 2 The concept of correcting vital effects using triple oxygen isotopes demonstrated on a warm-water coral (*Siderastrea siderea*; SK-SA5, red cross). The $\delta^{18}\text{O}$ of the coral yields an apparent temperature estimate, which is too warm (grey arrow and circle). A back-extrapolation to the equilibrium curve yields a corrected temperature estimate (orange arrow and circle) that is indistinguishable from the actual coral growth temperature (white circle). Error propagation considers the measurement error but not the error of the seawater isotope composition (see text).

Similar to Wostbrock et al. (2020a), who explain how to ‘see through’ diagenesis using triple oxygen isotopes, the correction scheme outlined above allows us to see through vital effects. Importantly, a consistent but not necessarily “correct” reference frame is required for reconstructing growth temperatures. That is, the choice of equilibrium calibration does not significantly affect the $T_{\Delta^{17}\text{O}}$ estimates because the empirical slope obtained for a particular equilibrium curve is later used to back-extrapolate to the same curve, resulting in identical $T_{\Delta^{17}\text{O}}$ estimates. The lack of variability in the θ_{coral} between species means that triple oxygen isotopes can be well suited for correcting vital effects in extinct organisms. This is not limited by the uncertainties in past seawater $\Delta^{17}\text{O}$ values because it was modelled to change only within ± 10 ppm during the Phanerozoic (Guo et al., 2022).

Looking at vital effects. Coral calcification models aim to reproduce observed $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ covariations in carbonates and mainly consider: 1) CO₂ absorption leading to disequilibrium between H₂O and DIC in the calcifying fluid; 2) isotope effects at the mineral water interface; and 3) CO₂ (aq) diffusion across the cell membranes. Besides the diffusive flux of CO₂ (aq) through the lipid membrane, carbon is also sourced directly from seawater. The calcifying fluid is not perfectly isolated from seawater but isolated enough to significantly up-regulate pH via the enzyme Ca-ATPase that pumps Ca²⁺ into and H⁺ out of the calcifying fluid (Rollion-Bard et al., 2003). Another prominent enzyme, carbonic anhydrase, accelerates CO₂ (aq)–HCO₃[–] interconversion. Respective enzyme activities moderate both the carbonate precipitation rates and the isotope exchange rates. Biomineralisation models focusing on isotope effects reproduce the observed $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ covariations (McConnaughey, 1989b; Adkins et al., 2003; Chen et al., 2018). Davies et al. (2022) compare dual clumped isotope data of corals with a respective theoretical CO₂ absorption model and show that certain mechanisms (e.g., DIC speciation

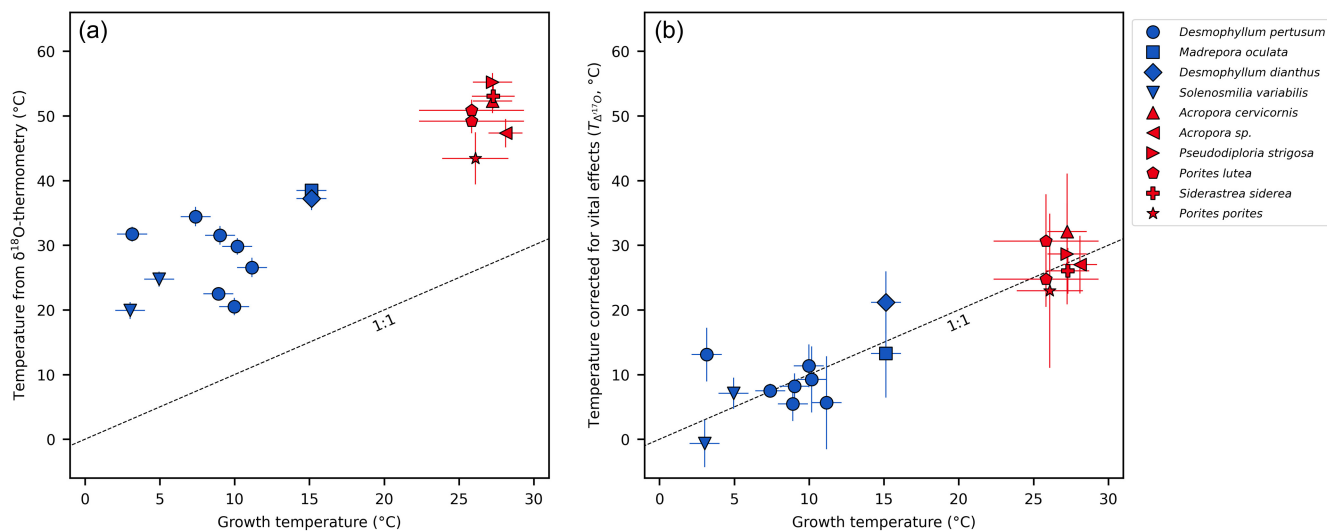


Figure 3 Apparent growth temperatures reconstructed from isotope thermometry compared to actual growth temperatures. (a) Temperature estimates from classical $\delta^{18}\text{O}$ thermometry are too warm compared to the actual growth temperatures. (b) Temperatures corrected for vital effects using $\Delta^{17}\text{O}$ match the actual growth temperatures within error. The *P. porites* sample is from Passey *et al.* (2014).

effects — the classic pH effect) are inconsistent with observed dual clumped isotope fractionation trends. Although contributions from kinetic isotope fractionation at the carbonate–water interface cannot be excluded (Watson, 2004; Watkins *et al.*, 2014), the almost perfect fit of the theoretical model with analytical results led these authors to suggest that CO_2 absorption is the main mechanism inducing kinetic effects. Guo and Zhou (2019) also attribute the offset from the expected equilibrium in the warm water coral data of Passey *et al.* (2014) to CO_2 absorption kinetics. The CO_2 absorption mechanism is a classic candidate for vital effects in biogenic carbonates (McConnaughey, 1989a, 1989b; Adkins *et al.*, 2003; Thiagarajan *et al.*, 2011; Saenger *et al.*, 2012; Chen *et al.*, 2018; Guo and Zhou, 2019; Davies *et al.*, 2023), providing a starting point for comparing theoretical and empirical triple oxygen isotope slope values.

The choice of equilibrium calibration affects the θ_{coral} values and, consequently, how these slopes are interpreted with respect to vital effects. The mean θ_{coral} value obtained using the Guo and Zhou (2019) aragonite equilibrium calibration is 0.529 ± 0.001 (within a range of 0.527 to 0.531), reflecting the net effect of several superimposed processes. Using other calibrations affects the mean θ_{coral} estimates but does not affect the main conclusions drawn here (see Supplementary Information). Although a consistently used reference frame has no impact on the reconstructed $T_{\Delta^{17}\text{O}}$, only the correct reference frame will provide accurate empirical triple oxygen isotope slope values required to interpret the biomineralisation mechanisms correctly.

Guo and Zhou (2019) presented theoretical slopes for CO_2 absorption ($\theta_{\text{absorption}} = 0.538$ to 0.541 at pH between 8.4 and 9, respectively), which differ significantly from our observed $\theta_{\text{coral}} = 0.529 \pm 0.001$. Assuming that normalisation issues are insignificant, this discrepancy implies that vital effects in corals are not dominated by CO_2 absorption. Shallower slopes hint towards considerable proportions of CO_2 (aq) diffusion, which follows much shallower slopes (*i.e.* $\theta_{\text{diffusion}} = 0.506$; Herwartz, 2021). Diffusion has been suggested to be an important contributor to the vital effects in brachiopods (Davies *et al.*, 2023). The theoretical $\theta_{\text{absorption}}$ range of 0.538 to 0.541 could imply that 34–39 % of the total vital effect is induced by diffusion. An alternative explanation for the observed discrepancy between the

observed vital effect slopes and CO_2 absorption in triple oxygen isotope space is that the theoretical CO_2 absorption slopes are inaccurate.

The slope for the hydroxylation reaction ($\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$) hinges on the triple oxygen isotope compositions of the reacting OH^- and CO_2 (aq). The model of Guo and Zhou (2019) considers parameters derived from experimental fractionation factors, which are inconsistent with the most recent theoretical models. Experimental work by Bajnai *et al.* (2024) recently constrained the $\Delta^{17}\text{O}$ values of the two reacting species in CO_2 absorption and yielded consistent results with theory. Accordingly, these authors' revised estimates for hydroxylation and hydration in seawater are $\theta_{\text{hydroxylation}} \approx 0.532$ and $\theta_{\text{hydration}} \approx 0.531$ (Fig. S-7). The corrected estimate for the CO_2 absorption slope at pH 8 is 0.532, which is more consistent with the observed empirical slopes but still allows for some superimposed diffusion of up to 19 % of the total vital effect.

From a triple oxygen isotope perspective, it is not possible to distinguish between the diffusion of CO_2 (aq) through the membrane and diffusion happening at the mineral–water interface. It is worth pointing out that surface effects are not necessarily related to diffusion (Watson, 2004; Watkins *et al.*, 2014). The θ values for other processes, such as entrapment or the inheritance of isotope signals from amorphous calcium carbonate precursors, are presently unknown and may significantly contribute to coral vital effects without necessarily affecting the observed slope.

Outlook. Robust estimates for the slopes in triple oxygen isotope space for all potentially relevant kinetic processes will allow the evaluation of coral calcification models and corroborate the theoretical triple oxygen isotope framework. Theoretical approaches can calculate full thermodynamic equilibrium (*e.g.*, Guo and Zhou, 2019), but their confirmation using natural samples remains challenging. This is at least partly related to the diverse suite of methods applied for carbonate $\Delta^{17}\text{O}$ analyses (Passey *et al.*, 2014; Bergel *et al.*, 2020; Wostbrock *et al.*, 2020a, 2020b; Huth *et al.*, 2022). One way to test equilibrium calibrations is to check if experimental data referenced to them reproduce theoretical θ_{KIE} calculations. Also, compared to equilibrium models, kinetic isotope models work with far more parameters. In turn, kinetic models provide information on parameters such

as precipitation rates and pH, while equilibrium models “only” provide temperature information. The concept of seeing through vital effects aims to reconstruct equilibrium conditions and, consequently, palaeotemperatures. However, triple oxygen isotopes also allow us to look at vital effects and help constrain calcification parameters beyond temperature. By combining triple oxygen isotopes with other isotope systems, such as carbon isotopes and dual clumped isotopes, along with elemental concentrations, it becomes possible to constrain the numerous variables in kinetic models.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2430>.



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References

- ADKINS, J.F., BOYLE, E.A., CURRY, W.B., LUTRINGER, A. (2003) Stable isotopes in deep-sea corals and a new mechanism for “vital effects.” *Geochimica et Cosmochimica Acta* 67, 1129–1143. [https://doi.org/10.1016/s0016-7037\(02\)01203-6](https://doi.org/10.1016/s0016-7037(02)01203-6)
- BAJNAI, D., CAO, X., KLIPSCH, S., PACK, A., HERWARTZ, D. (2024) Triple oxygen isotope systematics of CO₂ hydroxylation. *Chemical Geology* 654, 122059. <https://doi.org/10.1016/j.chemgeo.2024.122059>
- BAJNAI, D., GUO, W., SPÖTL, C., COPLEN, T.B., METHNER, K., LÖFFLER, N., KRŠNIK, E., GISCHLER, E., HANSEN, M., HENKEL, D., PRICE, G.D., RADDATZ, J., SCHOLZ, D., FIEBIG, J. (2020) Dual clumped isotope thermometry resolves kinetic biases in carbonate formation temperatures. *Nature Communications* 11, 4005. <https://doi.org/10.1038/s41467-020-17501-0>
- BAJNAI, D., PACK, A., ARDUIN RODE, F., SEEFELD, M., SURMA, J., DI ROCCO, T. (2023) A dual inlet system for laser spectroscopy of triple oxygen isotopes in carbonate-derived and air CO₂. *Geochemistry, Geophysics, Geosystems* 24, e2023GC010976. <https://doi.org/10.1029/2023GC010976>
- BERGEL, S.J., BARKAN, E., STEIN, M., AFFEK, H.P. (2020) Carbonate ¹⁷O_{excess} as a paleo-hydrology proxy: Triple oxygen isotope fractionation between H₂O and biogenic aragonite, derived from freshwater mollusks. *Geochimica et Cosmochimica Acta* 275, 36–47. <https://doi.org/10.1016/j.gca.2020.02.005>
- BREITKREUZ, C., PAUL, A., KURAHASHI-NAKAMURA, T., LOSCH, M., SCHULZ, M. (2018) A dynamical reconstruction of the global monthly mean oxygen isotopic composition of seawater. *Journal of Geophysical Research: Oceans* 123, 7206–7219. <https://doi.org/10.1029/2018JC014300>
- CHEN, S., GAGNON, A.C., ADKINS, J.F. (2018) Carbonic anhydrase, coral calcification and a new model of stable isotope vital effects. *Geochimica et Cosmochimica Acta* 236, 179–197. <https://doi.org/10.1016/j.gca.2018.02.032>
- DAÉRON, M., GRAY, W.R. (2023) Revisiting oxygen-18 and clumped isotopes in planktic and benthic foraminifera. *Paleoceanography and Paleoclimatology* 38, e2023PA004660. <https://doi.org/10.1029/2023PA004660>
- DAVIES, A.J., BRAND, U., TAGLIAVENTO, M., BITNER, M.A., BAJNAI, D., STAUDIGEL, P., BERNECKER, M., FIEBIG, J. (2023) Isotopic disequilibrium in brachiopods disentangled with dual clumped isotope thermometry. *Geochimica et Cosmochimica Acta* 359, 135–147. <https://doi.org/10.1016/j.gca.2023.08.005>
- DAVIES, A.J., GUO, W., BERNECKER, M., TAGLIAVENTO, M., RADDATZ, J., GISCHLER, E., FLÖGEL, S., FIEBIG, J. (2022) Dual clumped isotope thermometry of coral carbonate. *Geochimica et Cosmochimica Acta* 338, 66–78. <https://doi.org/10.1016/j.gca.2022.10.015>
- GUO, M., WOSTBROCK, J.A.G., PLANAVSKY, N.J., KORENAGA, J. (2022) Reconstructing seawater δ¹⁸O and Δ¹⁷O values with solid Earth system evolution. *Earth and Planetary Science Letters* 592, 117637. <https://doi.org/10.1016/j.epsl.2022.117637>
- GUO, W., ZHOU, C. (2019) Triple oxygen isotope fractionation in the DIC-H₂O-CO₂ system: A numerical framework and its implications. *Geochimica et Cosmochimica Acta* 246, 541–564. <https://doi.org/10.1016/j.gca.2018.11.018>
- HERWARTZ, D. (2021) Triple oxygen isotope variations in Earth’s crust. *Reviews in Mineralogy and Geochemistry* 86, 291–322. <https://doi.org/10.2138/rmg.2021.86.09>
- HUTH, T.E., PASSEY, B.H., COLE, J.E., LACHNIET, M.S., MCGEE, D., DENNISTON, R.F., TRUEBE, S., LEVIN, N.E. (2022) A framework for triple oxygen isotopes in speleothem paleoclimatology. *Geochimica et Cosmochimica Acta* 319, 191–219. <https://doi.org/10.1016/j.gca.2021.11.002>
- KIM, S.-T., MUCCI, A., TAYLOR, B.E. (2007) Phosphoric acid fractionation factors for calcite and aragonite between 25 and 75 °C: Revisited. *Chemical Geology* 246, 135–146. <https://doi.org/10.1016/j.chemgeo.2007.08.005>
- LIN, Y., WU, N., TA, K., LANDAIS, A., PENG, X. (2021) Triple oxygen isotopic compositions of ocean water from the Mariana Trench. *ACS Earth and Space Chemistry* 5, 3087–3096. <https://doi.org/10.1021/acsearthspacechem.1c00187>
- LUZ, B., BARKAN, E. (2010) Variations of ¹⁷O/¹⁶O and ¹⁸O/¹⁶O in meteoric waters. *Geochimica et Cosmochimica Acta* 74, 6276–6286. <https://doi.org/10.1016/j.gca.2010.08.016>
- MARALI, S., WISSHAK, M., LÓPEZ CORREA, M., FREIWARD, A. (2013) Skeletal microstructure and stable isotope signature of three bathyal solitary cold-water corals from the Azores. *Palaeogeography, Palaeoclimatology, Palaeoecology* 373, 25–38. <https://doi.org/10.1016/j.palaeo.2012.06.017>
- MCCONNAUGHEY, T. (1989a) ¹³C and ¹⁸O isotopic disequilibrium in biological carbonates: I. Patterns. *Geochimica et Cosmochimica Acta* 53, 151–162. [https://doi.org/10.1016/0016-7037\(89\)90282-2](https://doi.org/10.1016/0016-7037(89)90282-2)
- MCCONNAUGHEY, T. (1989b) ¹³C and ¹⁸O isotopic disequilibrium in biological carbonates: II. *In vitro* simulation of kinetic isotope effects. *Geochimica et Cosmochimica Acta* 53, 163–171. [https://doi.org/10.1016/0016-7037\(89\)90283-4](https://doi.org/10.1016/0016-7037(89)90283-4)
- PASSEY, B.H., HU, H., JI, H., MONTANARI, S., LI, S., HENKES, G.A., LEVIN, N.E. (2014) Triple oxygen isotopes in biogenic and sedimentary carbonates. *Geochimica et Cosmochimica Acta* 141, 1–25. <https://doi.org/10.1016/j.gca.2014.06.006>
- ROLLION-BARD, C., CHAUSSIDON, M., FRANCE-LANORD, C. (2003) pH control on oxygen isotopic composition of symbiotic corals. *Earth and Planetary Science Letters* 215, 275–288. [https://doi.org/10.1016/S0012-821X\(03\)00391-1](https://doi.org/10.1016/S0012-821X(03)00391-1)
- SAENGER, C., AFFEK, H.P., FELIS, T., THIAGARAJAN, N., LOUGH, J.M., HOLCOMB, M. (2012) Carbonate clumped isotope variability in shallow water corals: Temperature dependence and growth-related vital effects. *Geochimica et Cosmochimica Acta* 99, 224–242. <https://doi.org/10.1016/j.gca.2012.09.035>
- SMITH, J.E., SCHWARZ, H.P., RISK, M.J., MCCONNAUGHEY, T.A., KELLER, N. (2000) Paleotemperatures from deep-sea corals: Overcoming “vital effects.” *Palaios* 15, 25–32. [https://doi.org/10.1669/0883-1351\(2000\)015<0025:pfdsco>2.0.co;2](https://doi.org/10.1669/0883-1351(2000)015<0025:pfdsco>2.0.co;2)
- THIAGARAJAN, N., ADKINS, J., EILER, J. (2011) Carbonate clumped isotope thermometry of deep-sea corals and implications for vital effects. *Geochimica et Cosmochimica Acta* 75, 4416–4425. <https://doi.org/10.1016/j.gca.2011.05.004>
- WATKINS, J.M., HUNT, J.D., RYERSON, F.J., DEPAOLO, D.J. (2014) The influence of temperature, pH, and growth rate on the δ¹⁸O composition of inorganically precipitated calcite. *Earth and Planetary Science Letters* 404, 332–343. <https://doi.org/10.1016/j.epsl.2014.07.036>

- WATSON, E.B. (2004) A conceptual model for near-surface kinetic controls on the trace-element and stable isotope composition of abiogenic calcite crystals. *Geochimica et Cosmochimica Acta* 68, 1473–1488. <https://doi.org/10.1016/j.gca.2003.10.003>
- WEBER, J.N., WOODHEAD, P.M.J. (1972) Temperature dependence of oxygen-18 concentration in reef coral carbonates. *Journal of Geophysical Research* 77, 463–473. <https://doi.org/10.1029/JC077i003p00463>
- WOSTBROCK, J.A.G., BRAND, U., COPLEN, T.B., SWART, P.K., CARLSON, S.J., BREARLEY, A.J., SHARP, Z.D. (2020a) Calibration of carbonate-water triple oxygen isotope fractionation: Seeing through diagenesis in ancient carbonates. *Geochimica et Cosmochimica Acta* 288, 369–388. <https://doi.org/10.1016/j.gca.2020.07.045>
- WOSTBROCK, J.A.G., CANO, E.J., SHARP, Z.D. (2020b) An internally consistent triple oxygen isotope calibration of standards for silicates, carbonates and air relative to VSMOW2 and SLAP2. *Chemical Geology* 533, 119432. <https://doi.org/10.1016/j.chemgeo.2019.119432>