

Most natural-forming calcites precipitate at isotopic equilibrium

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Short Report

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Abstract

Based on thermodynamic equilibrium isotope fractionation theory, this letter reasonably understands the clumping ^{13}C - ^{18}O (Δ_{47}), as well as carbon and oxygen isotope fractionation in calcites with extremely slow-growing rates from Devils Hole and Laghetto Basso (Corchia Cave) at atomic level with solid physical precipitation models and quantum-mechanical backgrounds. It is found that most calcites in nature precipitate in at equilibrium.

Main

The fundamental thermodynamic theory of isotope fractionation is firstly studied by Urey in 1947¹, who indicates that carbon and oxygen isotope fractionation could be used as geo-thermometers. M. Daëron et al. study $^{18}\alpha_{\text{cc/w}}$ and clumped isotopes (Δ_{47}) vs. temperature in calcites with extremely slow-growing rates from Devils Hole and Laghetto Basso (Corchia Cave) and conclude that “most Earth-surface calcites precipitate out of isotopic equilibrium”². However, I point out that both Δ_{47} and oxygen isotope fractionation are at equilibrium in nature, based on cutting-edge quantum calculation results. Therefore, the conclusion that isotope fractionation in natural-forming calcite is at disequilibrium is not justified.

To explain M. Daëron et al.’s experiments I use polynomial of equilibrium Δ_{47} fractionation factor in pure calcite from *ab initio* theoretical calculations³. The theoretical results reasonably reproduce Δ_{47} values in calcitic, as well as aragonitic, samples collected by Ghosh et al. (2006) from all over the world with extremely high accuracy (at 10^{-5} level or smaller)^{3,4,5}. Similarly, data from M. Daëron et al.’s paper agree with my theoretical line very well (Fig. 1), within necessary precision (~ 10 ppm) (Supplemental Table 1) between different experimental laboratories^{2,4}. Slow-growing calcites from Devils Hole Laghetto Basso are very close to the theoretical line within 0.0038 and 0.0090 per mil, respectively. The maximum difference between theoretical line and experimental data is 0.0178 per mil at 20.3°C. Such derivations further consist with the magnitude of influence of metal cations on Δ_{47} (also at 10^{-5} level or smaller)^{3,5}. This indicates that all ^{13}C - ^{18}O clumped signatures of calcites in M. Daëron et al.’s paper are theoretically at equilibrium fractionation states.

Besides, my equilibrium results also indicate obvious variation of oxygen isotope fractionation between metal-calcite and pure calcite: $\Delta(^{18}/^{16}\text{O}) = 1000 * \ln(\text{RPFR}_{(\text{Metal ion})}/\text{RPFR}_{\text{pure}})$ s are -0.1 (Mg^{2+}), -1.8 (Fe^{2+}) and 0.1 (Zn^{2+}) at 25°C⁵. The variation range agree with 1~2 ‰ change of oxygen isotope in calcite given by M. Daëron et al. This agreement between theory and experiments indicates that oxygen isotope ratios ($\delta^{18}\text{O}$) in calcite change at equilibrium in nature, at least, due to the existence of metal cations.

Finally, I address that my calculations are based on thermodynamic equilibrium isotope fractionation theory^{1,6,7}, with solid physical precipitation models^{8,9,10,11} and quantum-mechanical backgrounds¹², and that they can be used to reasonably understand carbon and oxygen, as well as their clumping ^{13}C - ^{18}O (Δ_{47})⁴, isotope fractionation in calcite and other carbonates at atomic level. Based on the analysis

above and conclusions in my previous papers^{3,4,5}, I suggest that most calcites in nature precipitate in an equilibrium state.

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Declarations

Author contributions

Y.J. designed the project, drawn the figures, and wrote the paper.

Competing financial interests: declared none.

Figures

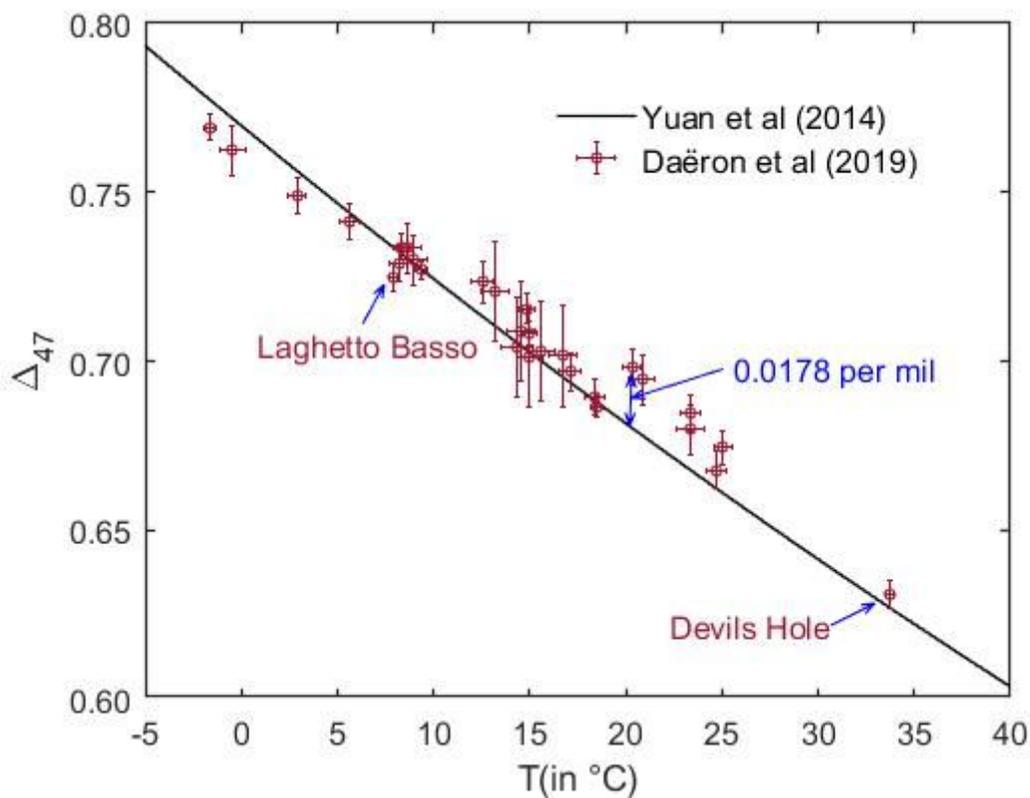


Figure 1

Quantum theoretical line³ (black solid) and M. Daëron et al (2019)'s values² (purple circle, with one sigma error) of clumped isotopes in carbonates (Δ_{47}) as a function of crystallization temperature T . Slow-growing calcites from Devils Hole Laghetto Basso are very close to the theoretical line within 0.0038 and 0.0090 per mil, respectively. The maximum difference between theoretical line and experimental data is 0.0178 per mil at 20.3°C.