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Triple oxygen isotope fractionation of carbonate during carbonate precipitation

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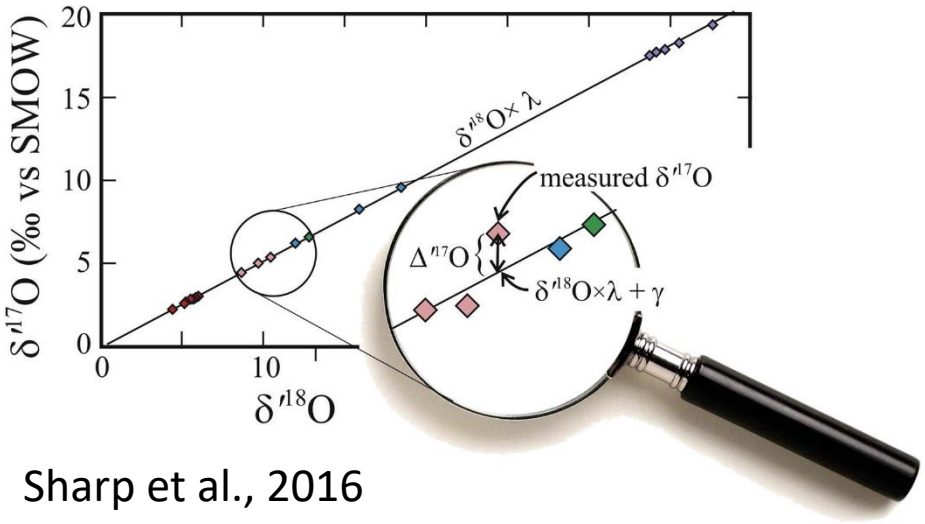
Introduction

	^{16}O	^{17}O	^{18}O
Mass	15.995	16.999	17.999
Abundance	99.76%	0.04%	0.20%

$$\delta^i O = \left(\frac{R^i_{sample}}{R^i_{standard}} - 1 \right) X1000\ ‰$$

R represents the ratio between the heavier and the lighter isotopes and the i represents ^{17}O or ^{18}O



Sharp et al., 2016

$$\Delta'^{17}O = \delta'^{17}O - \lambda_{ref} * \delta'^{18}O$$

- ^{17}O excess in water, is a potential proxy to independently constrain some aspects of paleoclimate studies such as the precipitation source variation.

Introduction

Measured from sample

Constant value of 0.528

Well constrained

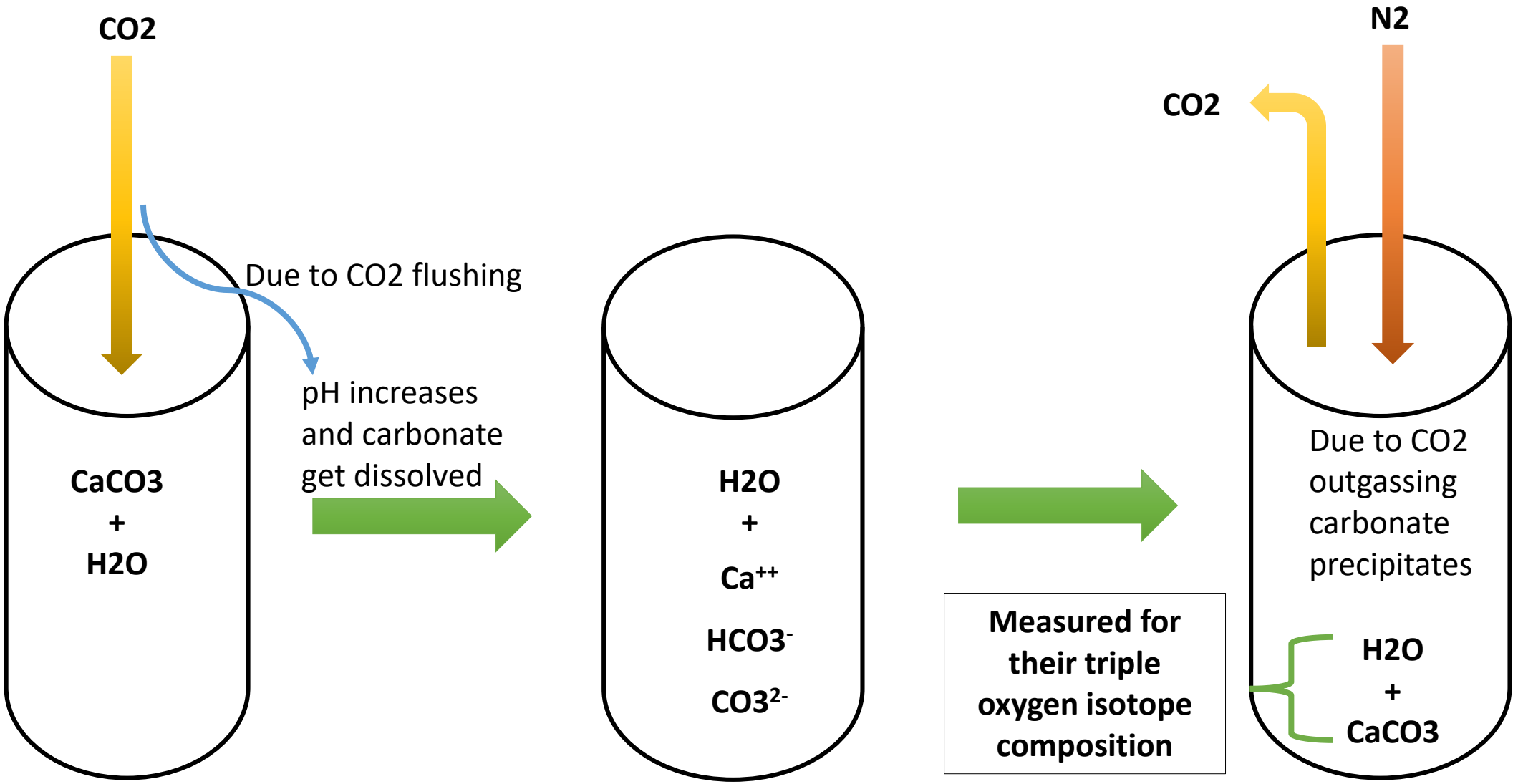
$$\Delta'^{17}O_{water} = \Delta'^{17}O_{carbonate} - 10^3 * (\theta - \lambda_{ref}) * 1000 \ln \alpha^{18}$$

$$\theta = \frac{\delta'^{17}_{Carbonate} - \delta'^{17}_{Water}}{\delta'^{18}_{Carbonate} - \delta'^{18}_{Water}}$$

- Published $\theta_{\text{carbonate-water}}$ ranges between 0.5242 and 0.5256
- The discrepancy is of 0.0014
- This can leads to an offset of 42 permeg in Δ'17O value

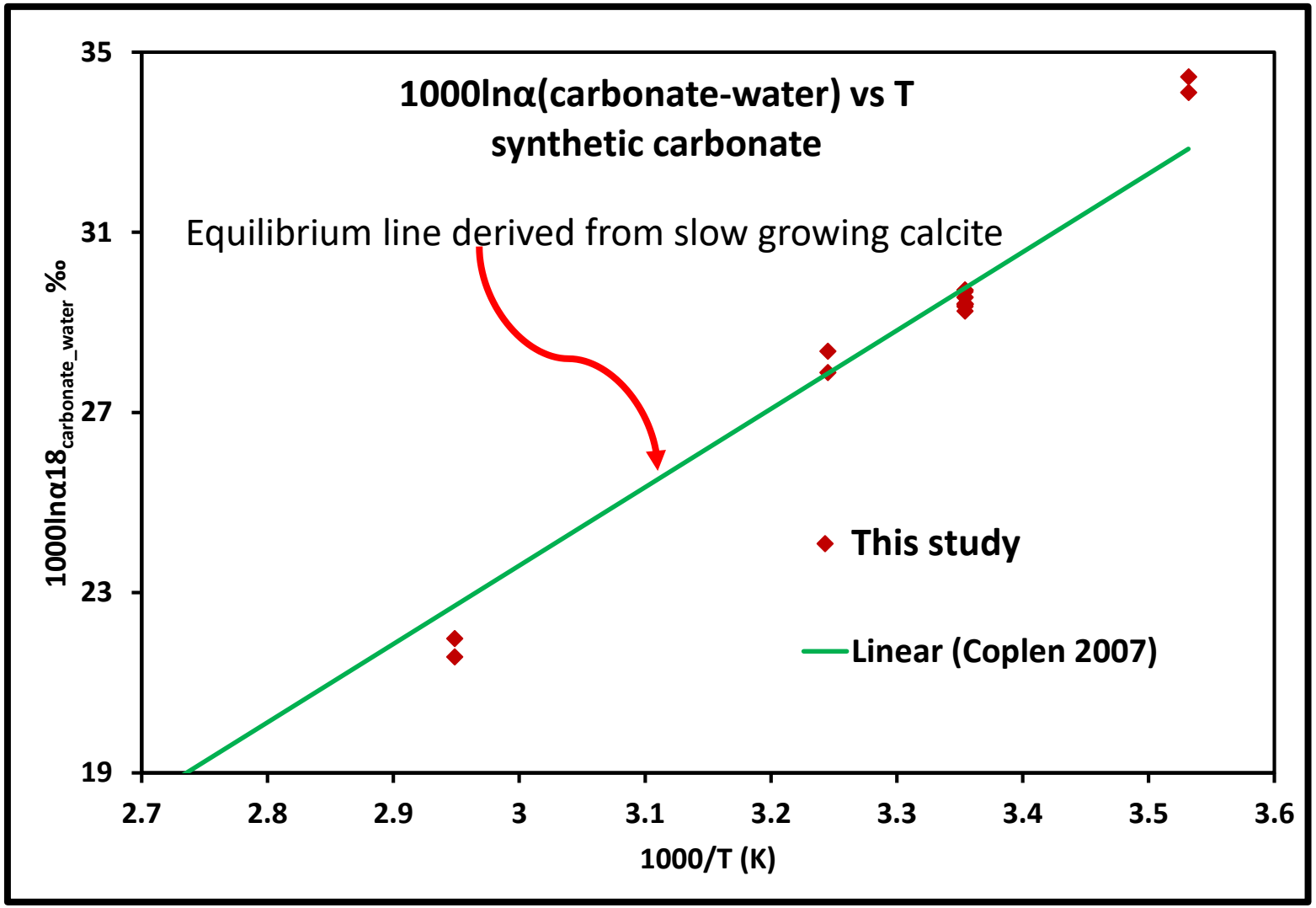
- The triple oxygen isotope exponent θ must be known a priori and precisely

Preparation of synthetic carbonate



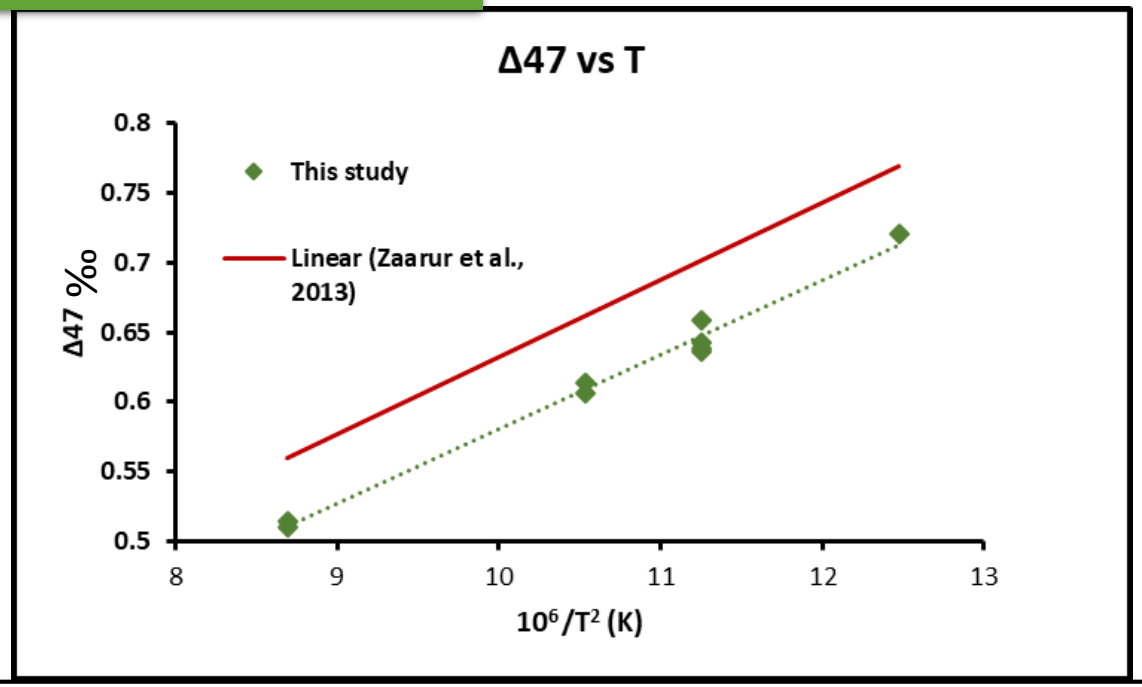
Results and Discussion

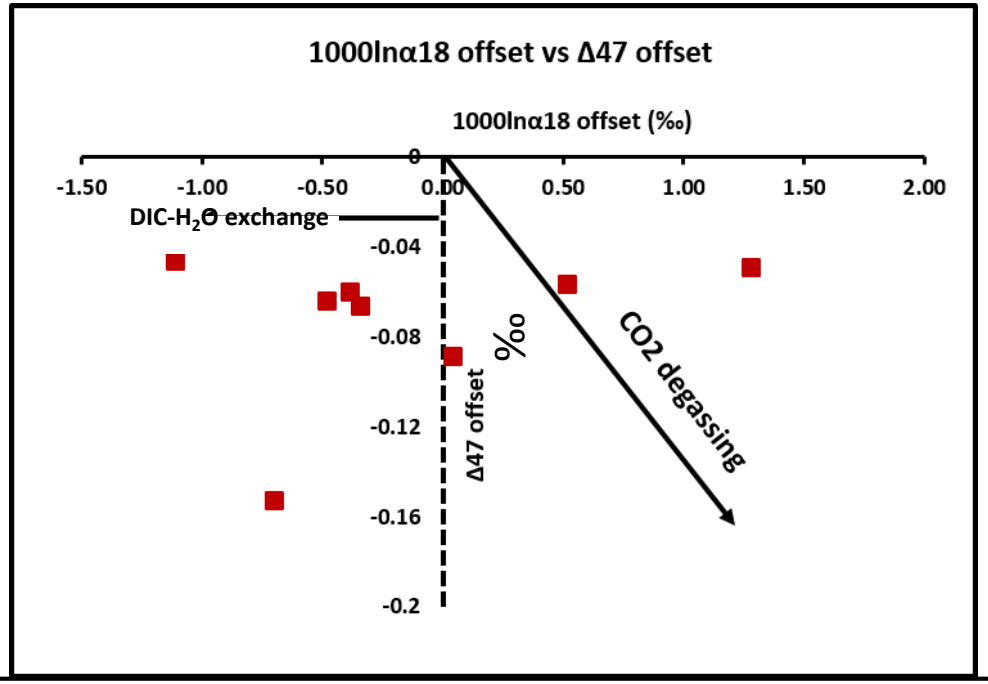
$$1000\ln\alpha 18_{carbonate\_water} = \delta'^{18}O_{carbonate} - \delta'^{18}O_{water}$$



- The data points falling on the equilibrium line was precipitated in equilibrium with the water
- The data points deviate from the equilibrium line did not attain the equilibrium
- The data points falling below the equilibrium line incorporated kinetic isotope effect during $HCO3^-$ - H2O exchange
- The data points falling above the equilibrium line incorporated kinetic isotope effect during CO2 degassing from the system

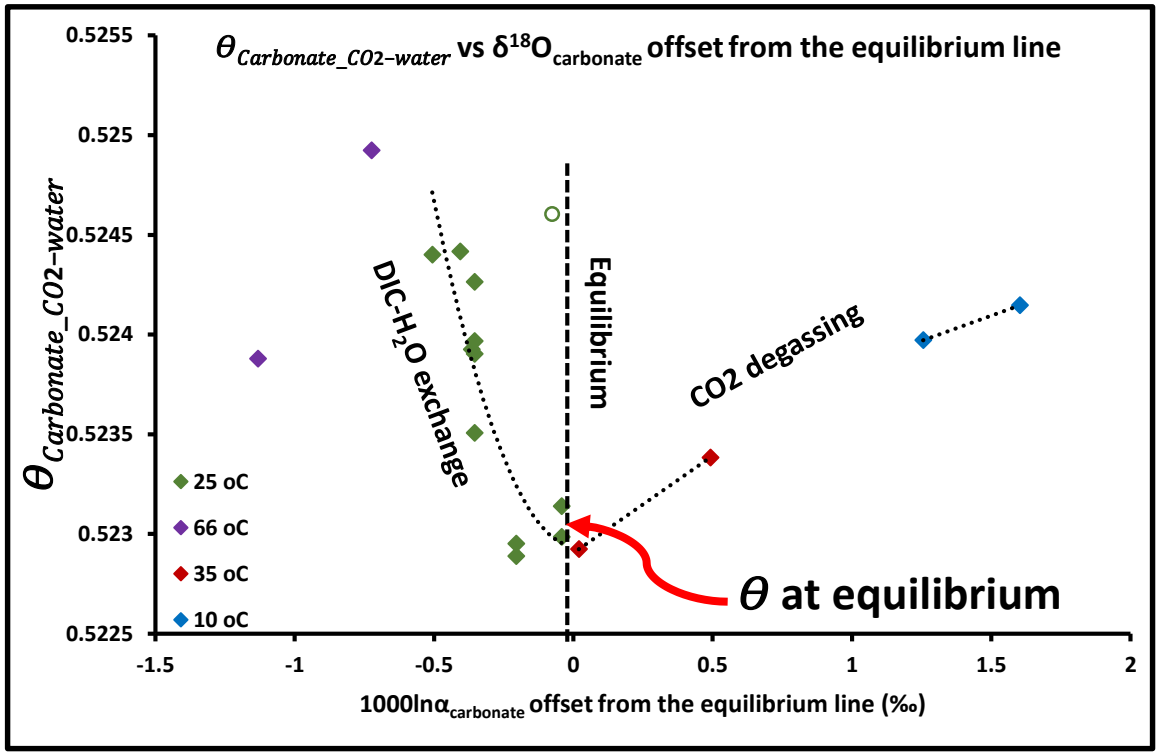
Results and Discussion



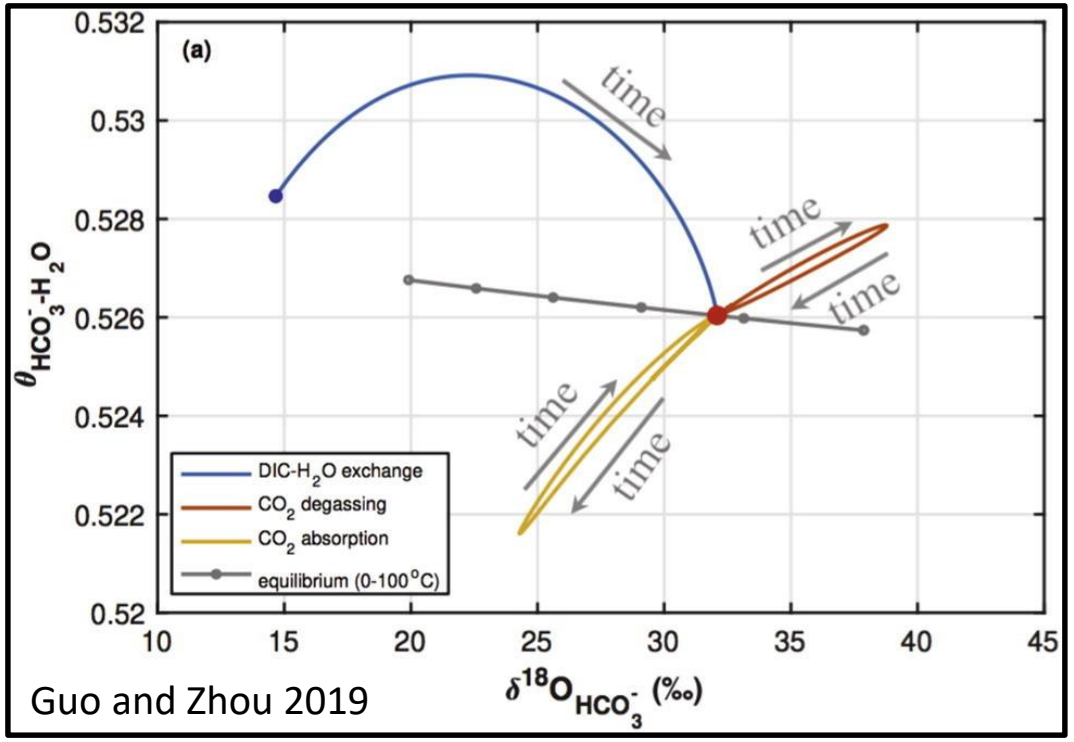


- All of our obtained Δ47 values are lower than the prediction of Zaarur et al., 2013 indicating clumped isotope disequilibrium
- The clumped isotope disequilibrium caused by the faster growth rate and/or CO2 degassing results in lowering of the Δ47 values (Klug et al., 2014)
- When we plot our data in 1000lnα18 offset vs Δ47 offset space we find that samples precipitated at 10 ◦C and 35 ◦C falls in the CO2 degassing regime while the rest of the samples fall in the DIC-H2O exchange disequilibrium region
- This observation further supports our observed disequilibrium in 1000lnα18.

Results and Discussion



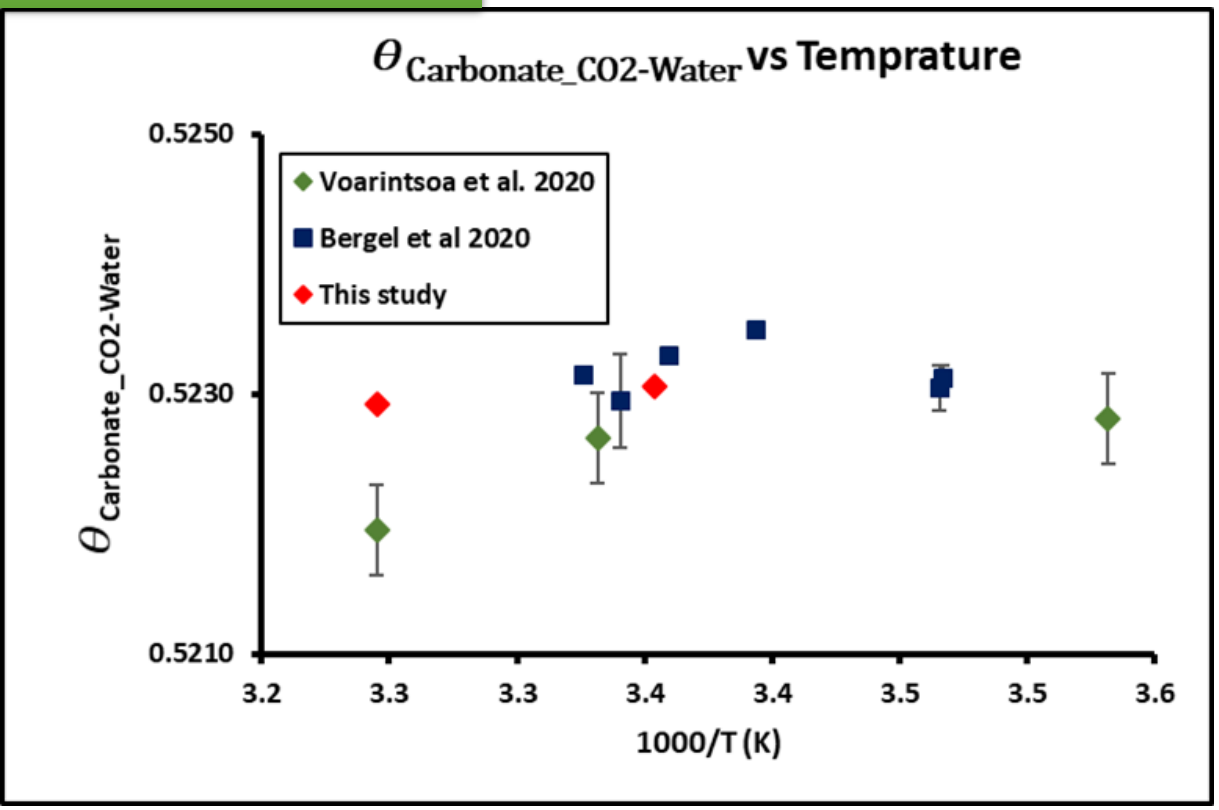
This study



Theoretical prediction

- Majority of our samples incorporated kinetic isotope effect
- The equilibrium $\theta_{\text{carbonate\_CO2-water}}$ is 0.523
- Our observed effect of disequilibrium on θ value is in good agreement to the theoretical prediction of Guo and Zhou 2019

Results and Discussion



From our data, we find that the $\theta_{Carbonate\_CO2\text{-}water}$ value remains fairly constant between 25 ◦C and 35 ◦C

Conclusions

- The θ value in carbonate water system is sensitive to the disequilibrium effect
- The equilibrium $\theta_{carbonate\_CO2\text{-}water}$ value for carbonate water system is 0.523
- The equilibrium $\theta_{carbonate\_CO2\text{-}water}$ remain fairly constant between 25 °C and 35 °C

Thank You