



Remaining uncertainties in carbonate specific Δ_{47} acid fractionations and advantages of analyzing mineral specific standards

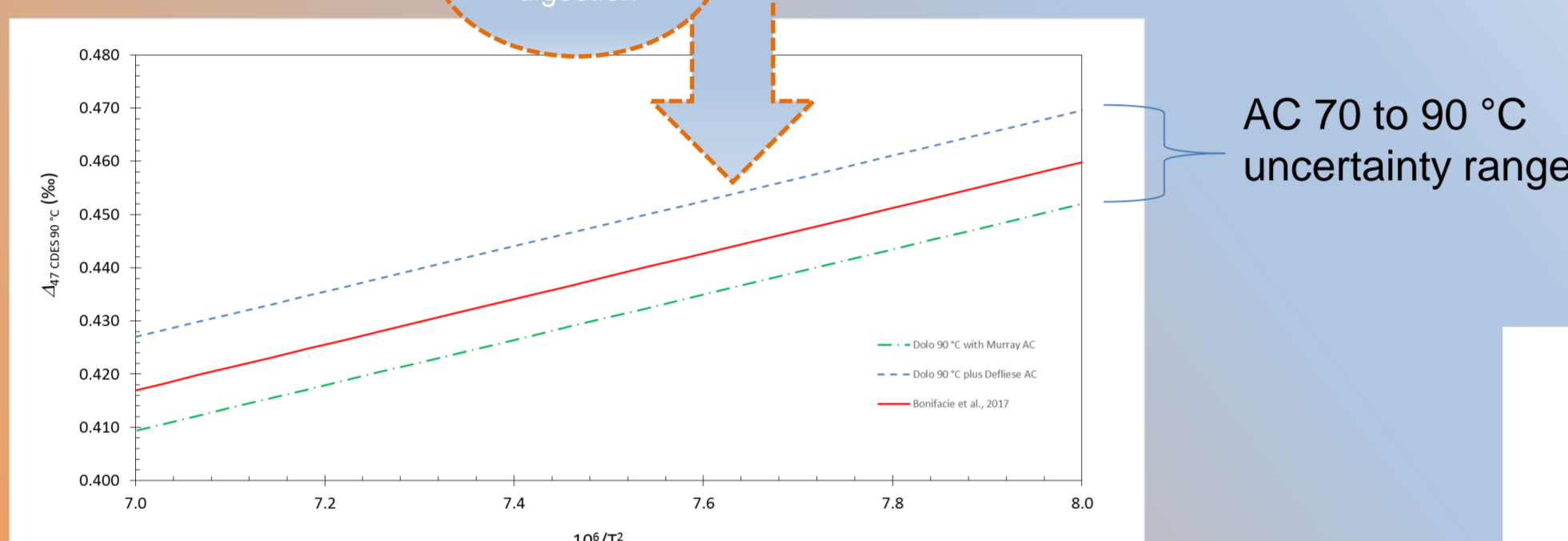
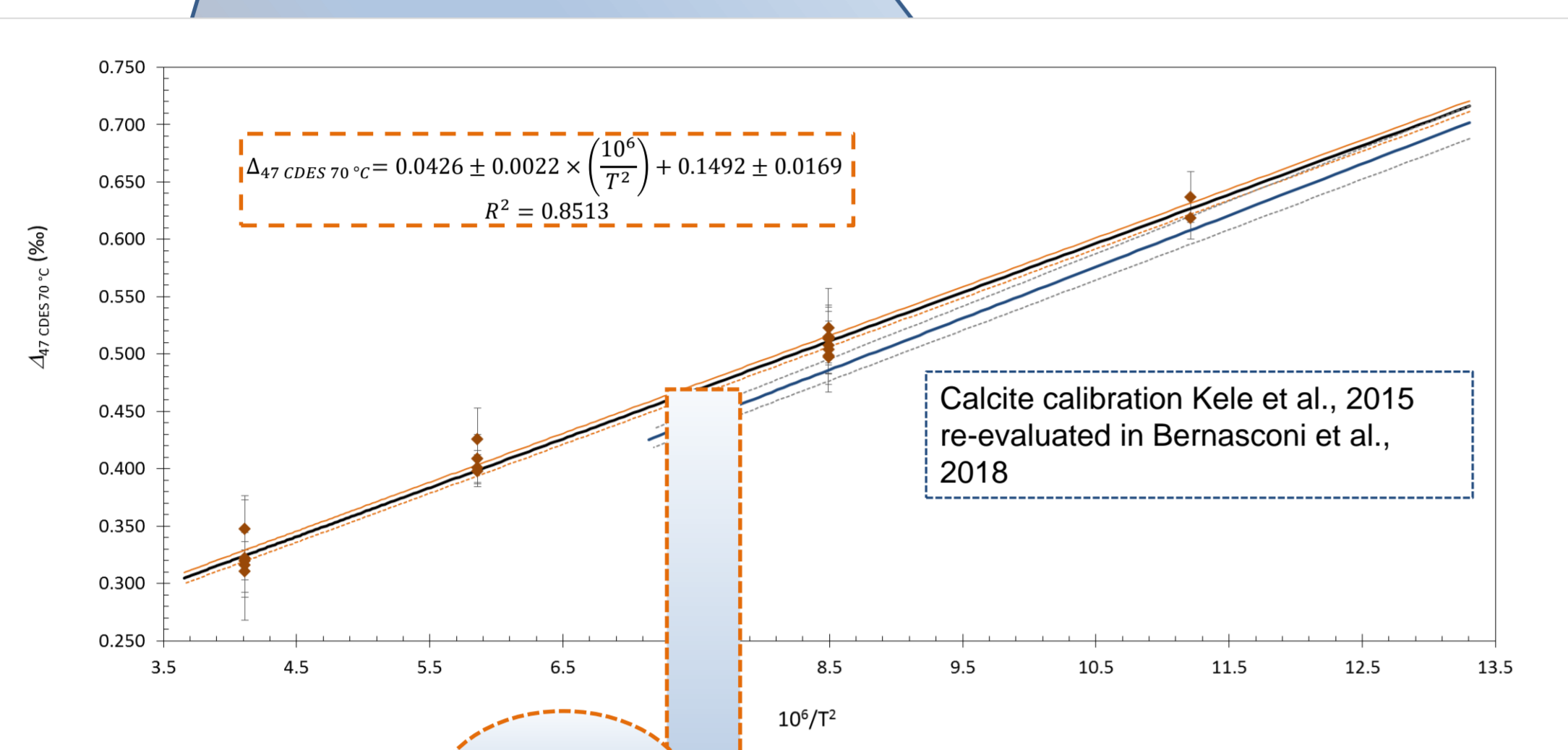
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Recent clumped isotope studies (Guo et al., 2009; Murray et al., 2016; Müller et al., 2017) showed potential differences in the absolute and relative temperature dependent Δ_{47} fractionation during phosphoric acid digestion of different carbonate mineralogies. These remaining uncertainties might cause on one side erroneous temperature estimates and on the other side hamper proper data comparison between laboratories digesting their carbonate samples at different temperatures. In addition to these uncertainties laboratories without own Δ_{47} -T calibration apply calibrations from other laboratories that might react their samples at different temperature or treat their samples with slightly distinct ways of purification. The analysis of identical carbonate standards amongst laboratories is often missing, which hinders proper data comparison between them and legalization to apply calibrations of other laboratories.

Here we discuss examples of Δ_{47} studies on different carbonate mineralogies and the advantages of analyzing the corresponding carbonate standards for an improved data comparison (Bernasconi et al., 2018) and to anchor Δ_{47} data to Δ_{47} -T calibrations done in other laboratories.

Dolomite specific Δ_{47} -T calibration for acid digestion at 70 °C (Müller et al., in review)



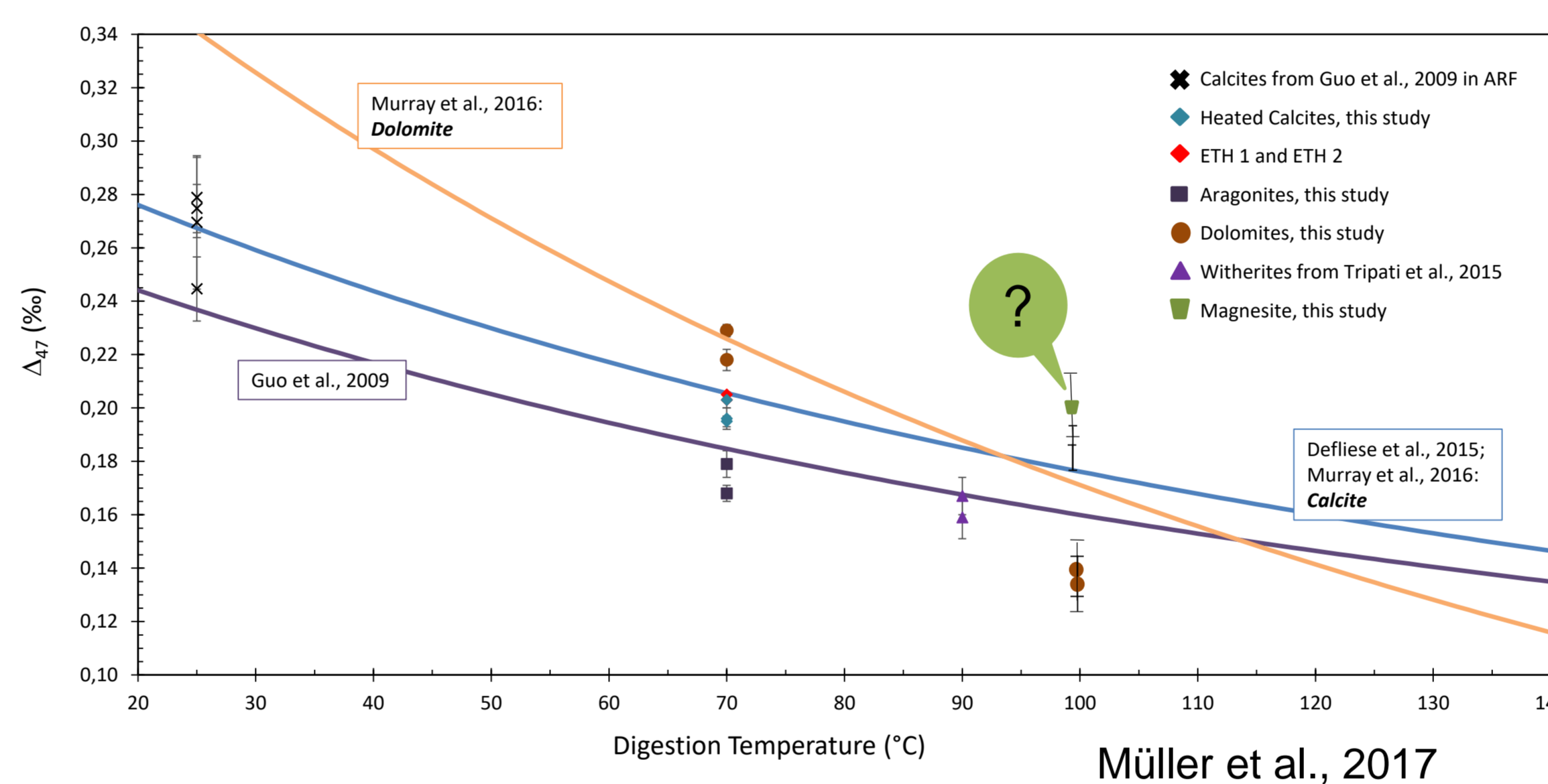
Conclusions and outlook

- dolomite specific clumped isotope temperature calibration for 70 °C acid digestion significantly above calcite calibration
- big uncertainty in acid fractionation correction for dolomite
- dolomite standards (SRM 88b, Sansa, Rodolo) available for better data comparison
- aragonite specific clumped isotope acid fractionation correction needs further investigation with aragonitic samples from well constraint growth conditions
- magnesite clumped isotope acid fractionation calcite (need for homogenous magnesite standards)
- calcite: well constraint acid fractionation, standards available (Interlab Comparison and Bernasconi et al., 2018)

Instrumental setup at Utrecht University for Δ_{47} analysis of calcite, aragonite and dolomite



Kiel IV carbonate device (70-95 µg replicates), 102 % phosphoric acid 70 °C, porapak Q trap held at -40 °C, connected to 253 Plus (Thermo Fisher Scientific).

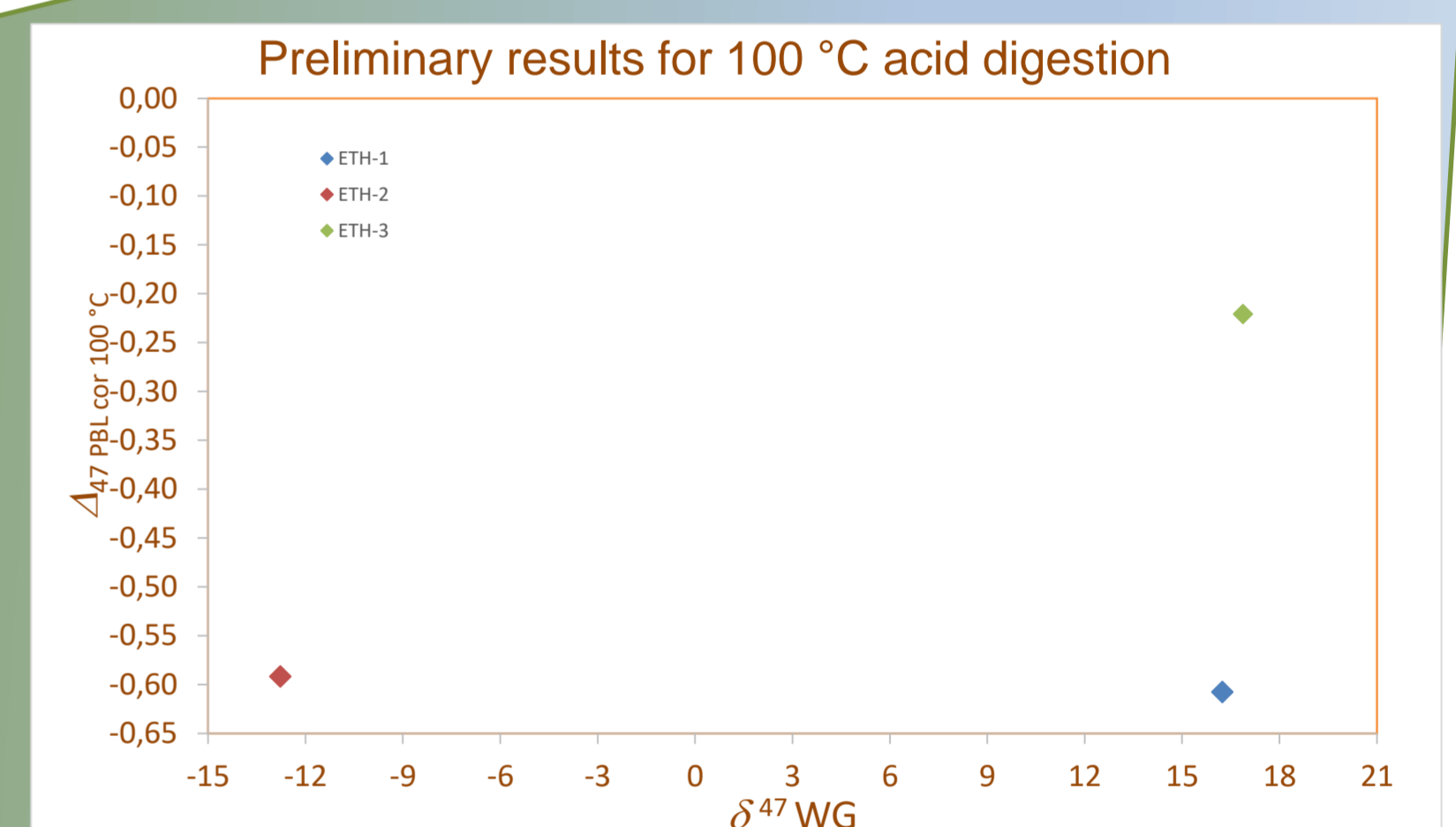


Identifier	$\delta^{13}C_{VPDB}$ (‰)	$\delta^{18}O_{VPDB}$ (‰)	Δ_{47} CDES 70 °C (‰)	#
Aragonites				
Bilin 1 (H)	3.10±0.01	-8.36±0.01	0.165±0.009	64
Bilin 2 (H)	-10.99±0.06	-5.59±0.05	0.176±0.013	38
Average			0.169±0.007	102
Calcites				
MS 2 (H)	2.06±0.01	-1.91±0.02	0.183±0.008	88
ETH 4 (H)	-10.20±0.01	-18.72±0.02	0.187±0.008	107
Merck (H)	-41.91±0.02	-15.62±0.01	0.192±0.009	66
Average			0.187±0.005	258
Dolomites				
Rodolo (H)	-3.89±0.02	1.78±0.04	0.229±0.009	91
Sansa (H)	1.29±0.02	-3.68±0.04	0.226±0.010	57
Average			0.227±0.007	148

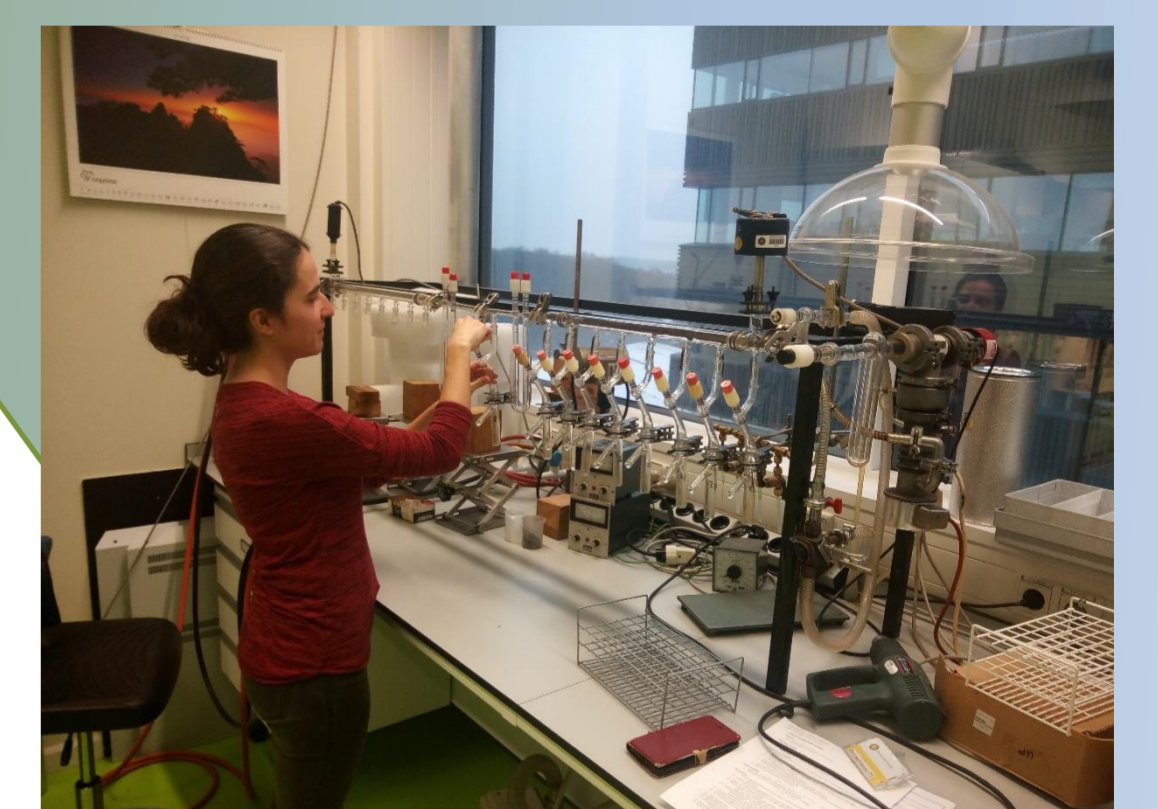
All uncertainties are displayed at the 95% CL

Absolute Δ_{47} acid fractionation for 70 °C reaction temperatures of various carbonates (Müller et al., 2017 re-evaluated in Müller et al., in review)

Magnesite clumped isotope fractionation:



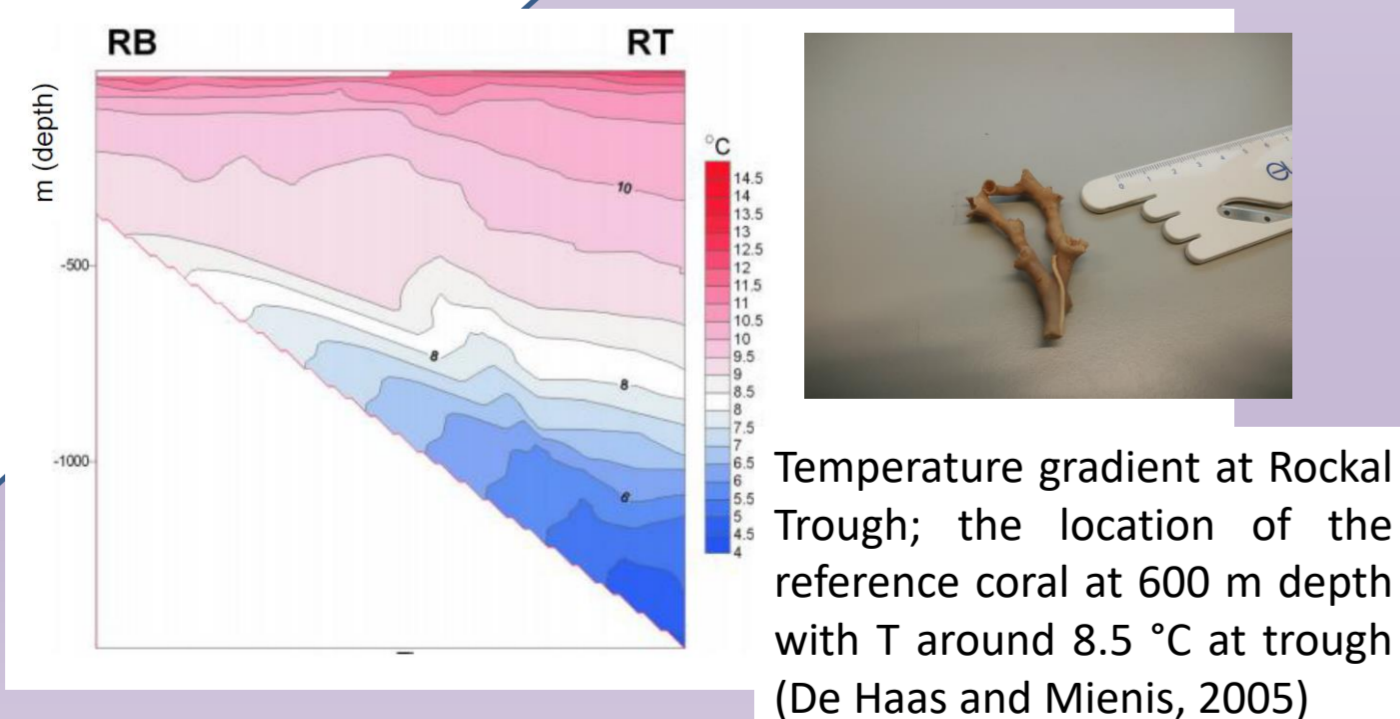
Magnesite heated in cold seal pressure vessel at 700 °C for 10, 24 and 58 hours



Magnesite phosphoric acid digestion at 100 °C, sample purification from H₂O and NonCond with vacuum line

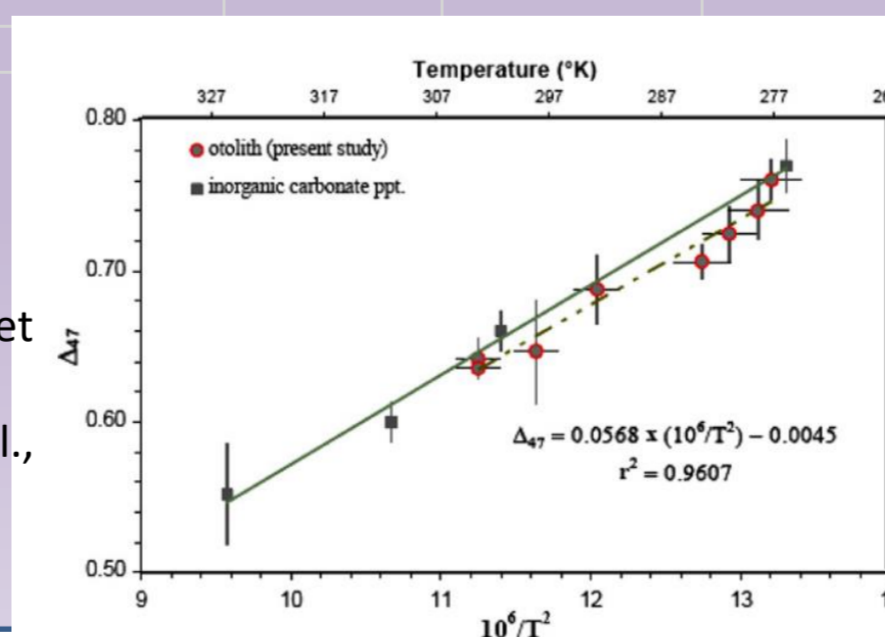
Aragonitic reference coral: aragonite Δ_{47} acid fractionation equal to calcite?

Deep sea coral *Madrepora oculata*



Replicates	$\delta^{13}C_{VPDB}$ final	$\delta^{18}O_{VPDB}$ final	$\delta^{18}O_{SMOW}$	$\delta^{18}O_{SMOW}$ fluid	Δ_{47} CDES 25 °C	T (°C) AC	T (°C) calcite
Average	-3.21	1.22	32.17	-2.18	0.760	2	7
SD	0.01	0.03	0.03	1.39	0.026	6	6
Std Error	0.00	0.01	0.01	0.34	0.006	1	1
95% CL	0.01	0.02	0.02	0.71	0.013	3	3

Δ_{47} -T calibration of aragonitic otoliths offset to calcite aragonite calibration (Ghosh et al., 2007)



Potential causes of offsets or non offsets: -vital effects; -different acid fractionation; -contamination derived of organic matter within carbonate

References

Bernasconi S.M., Müller I.A., Bergmann K.D., Breitenbach S.F.M., Fernandez A., Hodell D.A., Jaggi M., Meckler A.N., Millan I. and Ziegler M. (2018) Reducing uncertainties in carbonate clumped isotope analysis through consistent carbonate-based standardization. *Geochemistry, Geophysics, Geosystems* **19**, 2895-2914.

Bonifacie M., Calmels D., Eiler J. M., Horita J., Chaduteau C., Vasconcelos C., Agrinier P., Katz A., Passet B. H., Ferry J. M. and Bourrand J.-J. (2017) Calibration of the dolomite clumped isotope thermometer from 25 to 350 °C, and implications for a universal calibration for all (Ca, Mg, Fe)CO₃ carbonates. *Geochimica et Cosmochimica Acta* **200**, 255-279.

Defliese, W.F., Hren, M.T., Lohmann, K.C., 2015. Compositional and temperature effects of phosphoric acid fractionation on Δ_{47} analysis and implications for discrepant calibrations. *Chemical Geology* **396**, 51-60.

De Haas H. and Miens F. (2005) Cold water corals and carbonate mound formation at the Pen Duick Escarpment (Gulf of Cadiz) and Rockall Bank, Cruise 64PE237. Den Burg, Internal NIOZ Report.

Ghosh P., Eiler J., Campana S.E. and Feeney R.F. (2007) Calibration of the carbonate clumped isotope paleothermometer for otoliths. *Geochimica et Cosmochimica Acta* **71**, 2736-2744.

Guo, W., Mosenfelder, J.L., Goddard III, W.A., Eiler, J.M., 2009. Isotopic fractionations associated with phosphoric acid digestion of carbonate minerals: Insights from first-principles theoretical modeling and clumped isotope measurements. *Geochimica et Cosmochimica Acta* **73**, 7203-7225.

Kele S., Breitenbach S. F. M., Capezzuoli E., Meckler A. N., Ziegler M., Millan I. M., Kluge T., Deák J., Hanselmann K., John C. M., Yan H., Liu Z. and Bernasconi S. M. (2015) Temperature dependence of oxygen- and clumped isotope fractionation in carbonates: A study of travertines and tufas in the 6-95 °C temperature range. *Geochimica et Cosmochimica Acta* **168**, 172-192.

Müller I.A., Violay M.E.S., Storck J.-C., Fernandez A., van Dijk J., Madonna C. and Bernasconi S.M. (2017) Clumped isotope fractionation during phosphoric acid digestion of carbonates at 70 °C. *Chemical Geology* **449**, 1-14.

Müller I.A., Rodriguez-Blanco J.D., Storck J.-C., Santilli do Nascimento G., Vasconcelos C., Benning L.G. and Bernasconi S.M. (in review for Chemical Geology) Calibration of the oxygen and clumped isotope thermometers for dolomite based on synthetic and natural carbonates.

Murray, S.T., Arienzo, M.M., Swart, P.K., 2016. Determining the Δ_{47} acid fractionation in dolomites. *Geochimica et Cosmochimica Acta* **174**, 42-53.

Tripati, A.K., Hill, P.S., Eagle, R.A., Mosenfelder, J.L., Tang, J., Schauble, E.A., Eiler, J.M., Zeebe, R.E., Uchikawa, J., Coplen, T.B., Ries, J.B., Henry, D., 2015. Beyond temperature: Clumped isotope signatures in dissolved inorganic carbon species and the influence of solution chemistry on carbonate mineral composition. *Geochimica et Cosmochimica Acta* **166**, 344-371.