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Revisiting calibration of CO2 based Clumped isotope thermometry - equilibration approach.

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Clumped isotope thermometry is a novel approach for thermometry (Eiler and Shauble, 2004). Here we present experimental observations on low temperature calibration of clumped isotope thermometry for CO_2 -H_2O equilibration at temperatures ranging from 273K TO 333K. The experiment was conducted in a setup which was specially designed and fabricated with compartment for isotopic exchange of CO_2 and H_2O separated by a series of moisture trap to prevent any possible exchange reaction after completion of reaction process. The chamber assembly can be suitably placed inside an oven which can be operated at a temperature range of 253K to 373K and controlled using a compressor and thermal coil. The dimension of experimental chamber was 100 ml. 2ml of water and CO_2 at 1 bar pressure was used for equilibration. The reaction time was specified based on knowledge of reaction kinetics at variable temperatures (Mills and Urey, 1940). We allowed 24 hours of reaction time for experiments conducted between 333K-293K, while prolonged reaction time of 100 hours were given for 273K. The temperature was maintained with a regulator and an independent data logger was used to further verify the uncertainty in temperature or to register fluctuation. Equilibrium temperatures achieved based on this knowledge were 333K±1.5K, 313K±0.66K and 293K±1.04K and 273K±0.73K. CO_2 samples extracted after equilibration were measured using IRMS MAT 253 configured with resistor for measuring m/z 44 to 49. The linear relationship observed by plotting the observed temperature and Δ47 values yielded an empirical relationship:

$$\Delta47= ((0.071\pm0.006\ x(1000x1000))/T^2)+0.119\pm0.091$$

The repetition of experiment conducted in two batches shows range in slope values between 0.075-0.066 while the intercept changes between 0.055-0.183. The average slope and intercept is presented here and matches with the predicted theoretical slope given in Wang et al., (2004). The presentation will discuss the reason behind the uncertainty in slope estimates and possible application of this technique in understanding the thermometry of CO_2 fluid inclusion in rocks, soil air and solid Earth materials.