Application of the Δ_{48} Proxy to the Real World

Peter K. Swart, Chaojin Lu, and Juntao Zhang[1]

[1)] *Petroleum Exploration & Product Research Institute of SINOPEC*

Project Objectives

- Application of the Δ_{48} proxy to geological materials with constrained histories.
- Apply the Δ_{48} proxy to materials which are known to have formed in isotopic disequilibrium with respect to the Δ_{47} value.

Project Rationale

While there are many reasons for the development of an additional clumped isotope proxy such as the Δ_{48} value, the most important is that it provides a method for resolving instances in which kinetic behaviour affects the Δ_{47} value. However, the measurement of Δ_{48} values is significantly more problematic than that of the Δ_{47} values, not only as a result of the abundance of mass 48 being approximately 10 times lower than that of mass 47, but also because all the variation at mass 48 is principally caused by variations in oxygen and as such is much more sensitive to exchange with H_2O. With the introduction of the generation of instruments such as the Thermo 253-plus, it has been possible to measure abundances of mass 48 and establish a framework similar to the carbon dioxide equilibrated scales (CDES) as developed by Dennis et al. (2011) and the Intercarb CDES (I-CDES) established by Bernasconi et al. (2021) for mass 47 (Fiebig et al., 2016). Finally, the last piece of the puzzle was put in place by developing an empirical calibration between temperature and the Δ_{48} value. This was accomplished by measuring the Δ_{48} values in carbonates precipitated at known temperatures and which had been previously calibrated with Δ_{47} values (Staudigel et al., 2018; Swart et al., 2019). This work (Swart et al., 2021) also agreed with the theoretical line of Hill et al. (2014) and various carbonate minerals which were considered by Bajnai et al. (2020) to have formed in isotopic equilibrium (Fig. 1).

Approach

Once the basic framework of using the Δ_{48} values has been established the next task is to ascertain whether the temperatures suggested by the empirical calibration can be duplicated in materials for which the Δ_{47} proxy appears to give values close to equilibrium, and also whether systems such as corals and speleothems which form carbonates out of equilibrium with respect to Δ_{47}, behave similarly with respect to Δ_{48} values.

Work Proposed

<u>Equilibrium</u>: We have already established a calibration line between the Δ_{48} values and temperature (Fig. 1). We now propose to examine many of the skeletal and non-skeletal components that have been reported to form in equilibrium with respect to Δ_{47} and ascertain whether this is also true for the Δ_{48} value.
<u>Non-equilibrium</u>: We propose to examine the Δ_{48} values in scleractinian corals which form skeletons with Δ_{47} values lower than expected (Saenger et al., 2012) and Δ_{48} values in speleothems which have Δ_{47} values higher than expected. We will use the

model of Guo and Zhou (2019) to model the Δ_{47} and Δ_{48} values and ascertain whether a combination of the two proxies can resolve the original temperature using the approach outlined by Bajnai et al. (2020).

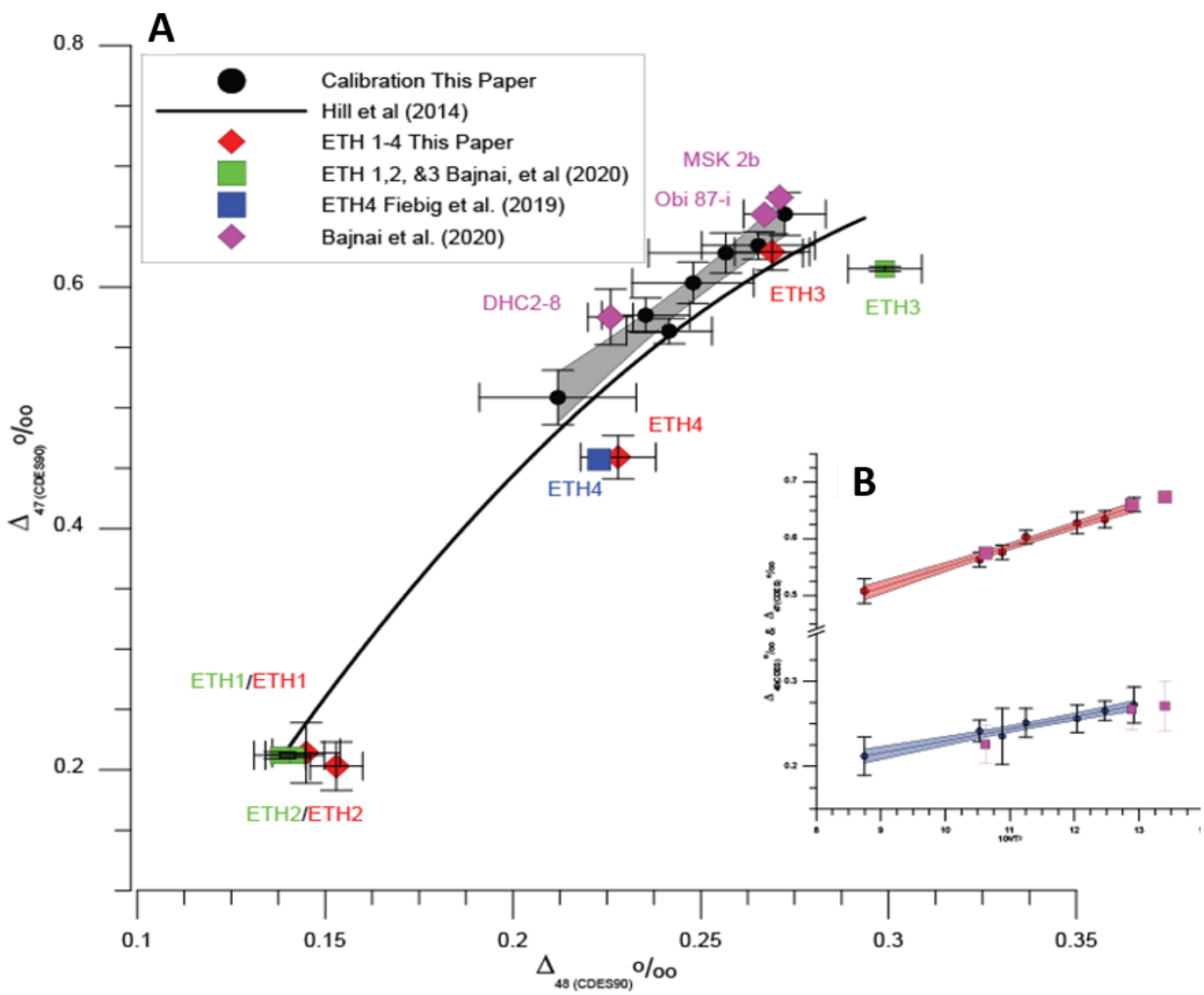

Figure 1: (A) Relationship of Δ_{48} and Δ_{47} values measured on the calibration presented by Swart et al. (2021) (black circles) and ETH samples (red diamonds) compared to the theoretical line from Hill et al. (2014) and the data from Fiebig et al. (2019)(ETH4) (blue square) and (ETH1, 2, and 3) (green squares). The DHC2-8 sample reported to have formed close to 33.7°C (Coplen, 2007) has Δ_{48} and Δ_{47} values that fall within error of the calibration. Other values reported by Coplen (2007) for Obi-87i and MSK 2b fall within error of the calibration line.

(B) Shows the Δ_{48} and Δ_{47} values of DHC2-8, Obi-87i, and MSK 2b samples plotted relative to the calibration lines. Note that Δ48 and Δ47 values for MSK, OBI and DHC2-8 were not processed using equilibrated gases directly, but using long-term CDES values obtained for ETH standards. All values fall within the 95% confidence limits of the analyses and the calibration line.

Figure from Swart et al. (2021).