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Pushing the frontiers in paleohydrology using the calcite hygrochronometer

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Calcite is the quintessential hygrochronometer, providing records of fluid composition through an abundance of elemental and isotopic proxies, which can be linked to conditions in deep-time using absolute chronology (i.e. using LA-ICP-MS U-Pb dating). Some methods were established decades ago, such as bulk carbon and oxygen isotopes, whereas others, such as clumped isotopes have grown rapidly in the last few years. It is evident that calcite can exhibit resolvable compositional zonation at the micron-scale, therefore, all methods should be considered an average of that particular analyte volume. As the spatial resolution of these methods improves, so can the correlative power between different datasets. So, what are the current limitations and where can improvements be made? Here we document examples of the *state-of-the-art* across several different environmental settings, variably combining petrographic techniques with trace element mapping, isotopic mapping, *in situ* U-Pb dating, *in situ* C-O isotopes, and clumped isotopes.

Fault-hosted vein-calcite in the Faroe Islands, NE Atlantic Margin, record contrasting length-scales of paleohydrological change. These hydrothermal veins record deep cycling of meteoric water that utilizes the permeability created by protracted faulting of the host flood basalts. Notably, trace elements record rapidly changing redox conditions that are decoupled from C-O isotopes.

Fracture-hosted calcite mineralization in the deep subsurface provides a record of bacterial activity, and is thus one of the few minerals that acts as an absolute biospheric chronometer. In the Paradox Basin, USA, discrete growth bands (~10 µm in width) of Pliocene age overgrew fracture-fill calcite formed during earlier stages of basin burial, and record $\delta^{13}C$-excursions related to microbial methanogenesis.

Calcite cements in sedimentary formations provide a record of evolving diagenetic processes, along with changes in pore-hosted fluid and vapour compositions during burial and uplift. In the Jurassic Brae Formation, UK North Sea, fine-scale cements record a pattern of mineral formation and replacement that relates to Jurassic burial and diagenesis, followed by CO_2 charging during the Cretaceous. Fingerprinting these cements across a range of stratigraphic levels through U-Pb, C-O and Sr isotopes, allows us to track the spatiotemporal pattern of CO_2 migration and trapping.