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Application of Clumped Isotope Palaeothermometry to reconstruct thermal evolution of recrystallised calcite in fine-grained micrites

Alexandra Sarah Robinson[1], Dr Cédric M John[1], Dr Annabel Dale[2], and Dr Mark Osborne[2]
[1]Imperial College London, Earth Science and Engineering, London, United Kingdom of Great Britain and Northern Ireland (alexandra.robinson17@imperial.ac.uk)
[2]BP Exploration & Production, Sunbury on Thames, United Kingdom of Great Britain and Northern Ireland

Previous studies have shown that within fine-grained dolomites, recrystallisation that occurs at shallow burial depths (<1 km) and low temperatures (<40 °C) can alter the carbonate clumped isotope signature of the minerals. Dolomites are, therefore, no longer representative of the environment of deposition, but rather capture temperatures present during burial. Currently, we do not understand isotopic re-setting of carbonate clumped isotopes during calcite recrystallisation during burial within micritic formations and whether the temperatures measured are representative of maximum burial temperatures reached. This study thus aims to determine if recrystallisation in fine-grained calcitic micrites show similar degrees of isotopic alteration to early dolomites; this is important as temperatures measured could be representative of temperatures reached during burial and serve as a proxy to reconstruct the thermal evolution of a formation and burial diagenetic processes. We have combined carbonate clumped isotope palaeothermometry with SEM/EDS imaging to study calcite recrystallisation under moderate burial (<1.8 km).

We analysed 17 samples collected from outcrops located on the West of the Eagle Ford Shale outcrop belt, Texas. The Eagle Ford is an ideal study location as it contains abundant fine-grained carbonate mixed with clastic material. The burial depth and temperature reached are understood through previous studies using organic proxies, giving this study a reasonable calibration for temperatures obtained through clumped isotope palaeothermometry. Results confirm that the Eagle Ford Shale is mixed formation, with nearly all samples showing 50:50 carbonate to clastic material. Clumped isotope analysis show variability in both measured clumped isotope temperatures ($T(\Delta_{47\ calcite})$, 35 to 105 °C) and calculated water oxygen isotope composition ($\delta^{18}O_{vsmow}$, -1.93 to 6.96 ‰). The results show higher temperatures than reconstruction based on organic matter matutuation index. This indicates that thermal evolution of calcite recrystallisation can differ from that of organic matter transformation, probably because different kinetics exist for the two reactions. Organic matter transformation depends on both temperature and time, whereas carbonate recrystallisation can occur instantaneously and depends on temperature and the fluid present. A correlation also exists between $T(\Delta_{47\ calcite})$ and $\delta^{18}O_{vsmow}$; the higher $T(\Delta_{47\ calcite})$, the higher $\delta^{18}O_{vsmow}$. This correlation is interpreted to be evidence of burial recrystallisation via dissolution/re-precipitation within a closed system, therefore with minimal to no change in the

$\delta^{18}O_{calcite}$. We suggest that even with the large range of measured T($\Delta_{47\ calcite}$), these variations could be a result of recrystallisation via dissolution/re-precipitation during burial and therefore representative of maximum burial temperatures, which are not recorded by the organic temperature proxies.