Episodic growth of vein calcite in a stable continental setting: potential application of U-Pb dating by LA-ICPMS and ID-TIMS methods

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The application and utility of LA-ICPMS and ID-TIMS for U-Pb isotopic dating of secondary fracture calcite infilling has been explored. These complementary methods were applied to test a hypothesis regarding the timing of emplacement of joints and calcite-filled veins within the Devonian Lucas Formation on the eastern flank of the Michigan Basin, in southern Ontario, Canada.

Outcrop fracture cross-cutting relationships, vein morphology consistent with generation under high pore fluid pressure, and knowledge of a basin-scale concentric fracture pattern were interpreted to suggest that prominent NNW-striking and broadly ENE-striking fracture populations were emplaced contemporaneously during the Paleozoic Era.

Initial trials determined that calcite-filled vein samples collected from shallow core (< 35 m depth) and shoreline outcrops had high U (1-10 ppm) concentrations and sufficent radiogenic Pb to permit successful dating by laser ablation. LA-ICPMS analyses of the calcite infilling (n = 141) defined two age clusters in all veins regardless of their orientation, one with a relatively small number of analyses at around 56 Ma and a broader peak around 100 Ma. These results were independently confirmed by ID-TIMS with single-grain analyses at 51±2 Ma and over the range 85±2 Ma to 109±4 Ma.

Agreement between the two methods suggests that the LA-ICPMS ages are reliable. The results indicate that new crystal growth occured episodically during the Late Cretaceous and early Paleogene, although the age of fracturing may have been older. The LA-ICPMS method appears to be suitable for yielding meaningful U-Pb isotopic ages and represents a useful geochronologic tool for interpreting the timing of vein emplacement.

Berea Sandstone permeability pre and post reaction with supercritical CO_2 in 1% NaCl brine

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The injectivity of CO_2 into saline formations greatly depends upon the properties and behaviour of geological materials close to injection points. We have constructed custom built geochemical reactors and permeability apparatus to investigate the behaviour of geological materials in response to CO_2 sequestration. Samples being tested include drill core material from a future Australian CO_2 sequestration reservoir-seal set [1, 2] and well-characterised materials such as Berea Sandstone to validate our procedures. Two different sized cubic sister sample sets of Berea Sandstone cut aligned to bedding laminations were obtained for initial experiments.

The permeability of as-received samples of Berea Sandstone was found to be compromised by surface deposits of mineral fines thought to be the product of sample cutting and milling. Permeability in the bedding plane for as-received samples was also less than the orthogonal to bedding orientation. In contrast, the permeability of samples gently cleaned using a sonic bath was significantly higher, and gave the expected result of bedding plane permeability being greater than the perpendicular to bedding orientation.

The brine permeability of sonic bath cleaned Berea Sandstone increased 14% (from 240 to 275 mD) following reaction with supercritical CO_2 immersed in 1% NaCl for 360 hours at 50 ºC and 10 MPa. Geochemical analysis of the dissolved ions in the experiment water indicated significant mobilisation of cations, especially calcium, magnesium, iron, manganese, potassium, and silicon, thought to be the product of carbonate and reactive silicate dissolution and clay cation exchange. SEM-EDS analysis of unreacted samples detected partially pore-filling ankerite and also vermiculite-smectite alteration of phlogopite flakes. Dissolution of reactive minerals observed, especially ankerite, is one possible reason for the measured permeability increase [3].

[1] Farquhar *et al*.. (2013) *MinMag*, this volume. [2] Pearce *et al*.. (2013) *MinMag*, this volume. [3] Moore *et al*.. (2004) *Geophys. Res. Lett*.. 31, L17610.

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