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Use of *In-situ* flow-through reactors to study mineral replacement reactions and associated permeability changes in hydrothermal systems

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Mineral replacement reactions and permeability

When a mineral interacts with a fluid with which it is not in equilibrium, a chemical reaction occurs which may result in replacement of all or part of the original (parent) mineral and the formation of a new (product) material. This mineral replacement reaction occurs in 2 stages:

- Dissolution of the parent material until it comes into equilibrium with the fluid (thus changing the composition of the fluid).
- Precipitation of a new mineral assemblage from the fluid that replaces all or part of the parent assemblage.

Critically, the above process can result in new porosity generation at the reaction front (Putnis 2009). Changes in volume associated with mineral replacement reactions induce stress into the system, resulting in micro-fractures and porosity changes that change the permeability of the mineral assemblage (Xia *et al* 2009).

Hydrothermal mineral replacement reactions play an important role in controlling fluid transport in fluid flow environments such as geothermal energy systems. Their role has been studied principally via numerical modelling due to the widely held belief that the timescale of mineral replacement reactions are incompatible with laboratory experiments (Berkowitz 2002). Very little experimental research has been conducted and the relative contributions to permeability of micro-cracks and reaction generated porosity are not empirically verified.

In order to attempt to explore this problem experimentally we have developed *in-situ* flow-through reactors (figure 1). The reactors are used to determine the effect of pressure, temperature, fluid flow rate, fluid composition and pH on mineral replacement reactions and associated changes in permeability.

In-situ flow through reactors

A high pressure high performance liquid chromatography (HPLC) pump was used to generate fluid flow rates of between 1 and 10 ml-min. The pump was capable of maintaining these flow rates at pressures of up to 400 bar (6,750 PSI). The HPLC pump was used in conjunction with a hand loaded back pressure regulator (BPR) providing pressures of up to 400 bar.

A heating jacket, capable of heating to 400⁰C was used to heat fluid prior to its passing through the mineral sample. As heat transference into the BPR could result in increasing pressure over time, the fluid was cooled prior to reaching the BPR. Pressure transducers were placed before and after the sample holder and linked to a data logger so that pressure changes could be used to detect changes in porosity of the sample.

Ultra high pressure reactor

In order to simulate more extreme hydrothermal environments an ultra-high pressure flow-through reactor is being developed.

An ultra-high pressure HPLC pump will generate fluid flow rates of between 0.001 and 5 ml-min. The pump is capable of maintaining these flow rates at pressures of up to 1700 bar (25,000 PSI) in conjunction with a high performance BPR.

The reactor's tubing, sample holding cell and fittings will be constructed from high pressure nickel-alloy (Inconel 625 and Hastelloy C276). Conventional stainless steel components are incapable of withstanding the required temperatures/pressures and have poor corrosion resistance at high temperatures, particularly with saline fluids, resulting in the development of leaks after 24 hours of use. The nickel alloys are capable of withstanding very high pressures (>1500 bar) at high temperatures (>500°C). The alloys are also highly corrosion resistant allowing corrosive fluids such as chlorides to be used at elevated temperatures and pressures for extended periods.

Benefits gained from the reactors include the ability to simulate dynamic rather than static environments for study of mineral transformation reactions. The reactors allow us to independently control pressure, temperature and flow rate so the effect of each on mineral transformation and porosity can be independently assessed.

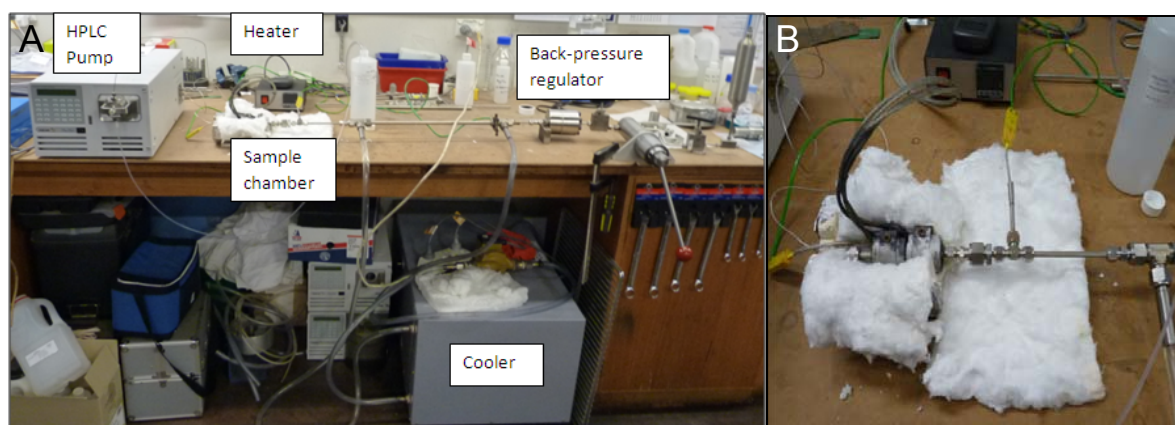


Figure 1: A: Flow through reactor showing (from left to right) HPLC pump, heating element, sample chamber, cooling unit and hand loaded back pressure regulator. Tubing and fittings are stainless steel. Pressure transducers are not fitted. B: A close up image of the heating unit (at left) and sample holder (immediately to the left of the heating unit).

Sample analysis

Samples were non-destructively analysed before and after treatments using a Philips XL40 scanning electron microscope (SEM), Cameca SX-51 electron microprobe with SAMX software and a Skyscan 1072 micro-computer tomography (MCT) analyser. Energy dispersive analysis X-ray (EDAX) analysis was used to determine changes in elemental composition of the samples. MCT analysis allowed construction of 3-dimensional x-ray images of samples from which porosity could be determined using grey-scale analysis.

Preliminary studies

Dolomitisation of marble

Pilot dolomitisation experiments were performed on a 12mm by 7 mm marble sample at 30 bar pressure and 200°C. The sample was pre-cracked to allow fluid flow through the marble and provide a

region of interest to monitor for dolomitisation. Pressure transducers linked to a data logger were used to monitor for pressure changes across the marble sample resulting from changes in porosity. A magnesium/calcium solution was pumped through the sample at a flow-rate of 10 ml-min.

Initial results showed a 16 bar pressure difference across the marble sample over 10 days, indicating a significant change in porosity had occurred. Analysis using a SEM and electron microprobe showed dolomitisation occurred both at the front face of the marble sample and along the crack (figure 2). The dolomitisation extended from the crack into the marble along the calcite grain boundaries.

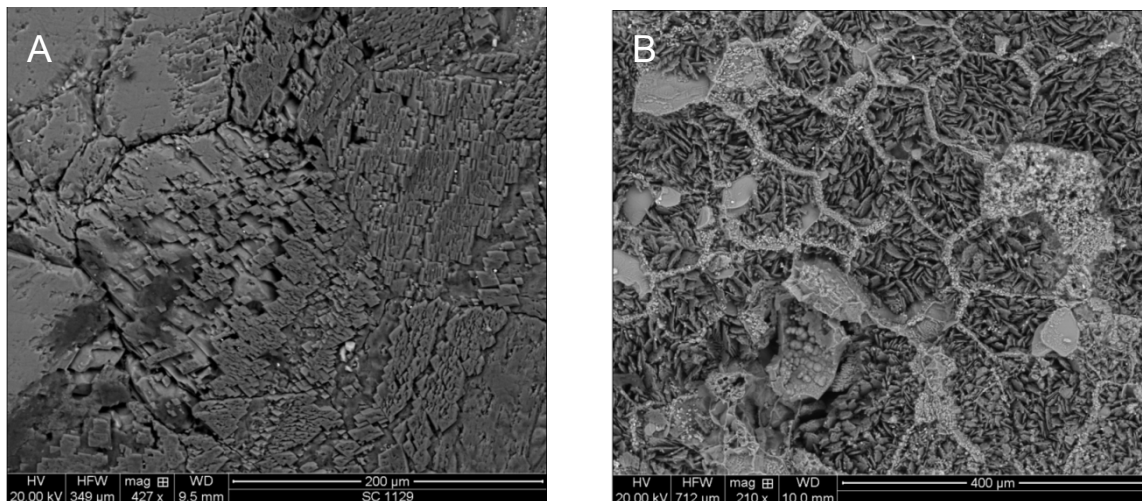


Figure 2: Dolomitisation of marble at A: front face of marble. The image is a backscattered electron image sample (Quanta 450 FEG ESEM, 60 Pa) of the unpolished sample. The lighter grey areas are calcite; the darker grey areas are dolomite B: Looking along the crack. The lighter grey boundaries are proto-dolomite with low amounts of calcium. The interior of the grains is magnesium carbonate. Large crystals of silicate minerals are also visible.

Isolation of variables affecting dolomitisation of limestone

The reactors have also initially been used to isolate the effect of fluid flow rate on the rate of mineral transformation and analyse associated changes in porosity. Dolomitisation of limestone was selected as an appropriate process to study the phenomena. Mineral samples analysed were 4.3mm in diameter by 4mm length, to allow optimal resolution during MCT analysis (5 microns). Sample's were wrapped in Teflon and placed in a vespel plastic sheathing before being placed in the reactor's sample holder to ensure a fluid tight fit.

Reaction fluid was composed of 1 molar magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and 1 molar calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) as suggested by Kaczmarek and Sibley (2011). A magnesium/calcium ratio of 1.14:1 was used to minimise time needed for substantial dolomitisation of the limestone to occur (i.e. less than 48 hours for > 50% dolomitisation). Other variable values used in the experiment are shown in table 1. The samples were placed in the reactors for 24 hours.

Table 1: Parameters for variable flow rate experiment and level of dolomitisation achieved and associated porosity.

| | | |
|------------------------|--------|--------|
| Flow rate (ml/min) | 1 | 10 |
| Temperature (°C) | 200 | 200 |
| Pressure (Bar) | 250 | 250 |
| Mg:Ca ratio | 1.14:1 | 1.14:1 |
| % proto-dolomitisation | 36 | 19 |
| Porosity % | 17 | 10 |

Formation of proto-dolomites occurred within 24 hours and was negatively correlated with fluid flow rate (table1). It is likely that faster flow rates inhibited nucleation of the dolomite onto the limestone surface. Porosity increased with dolomitisation due to the smaller volume of the replacement dolomite (because of magnesium's smaller ionic radius) compared to calcite.

Future work

Further work on mineral transformations in hydro-thermal systems will involve analysing the independent effect of fluid composition, pressure, and temperature on transformation rates and porosity generation.

The above methodology is being applied to mineral samples taken from the Otway Basin Geothermal Well (Ladbroke Grove 1). Mineral permeability varies at this site depending on whether the sample is taken from above or below the oil-water contact point. We will use our flow through reactors to simulate these environments and, by subjecting samples to differing pressure/temperature regimes, alter their porosity, thus gaining an understanding of the diagenetic processes responsible for the sample's natural permeability.

The ultra high pressure/temperature reactors under development will also allow us to simulate and study more extreme pressure/temperature regimes. The data gathered may then be used to develop reactive fluid flow models linking pressure, temperature, fluid flow rate and fluid composition to mineral transformation and permeability in hydrothermal systems.

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