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The effect of mineral replacement reactions on sandstone composition and porosity development in hydrothermal environments

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ABSTRACT

Mineral replacement reactions may result in porosity change, altering fluid flow rates within hydrothermal mineral systems. Little experimental research has been conducted on the role of environmental variables such as temperature and pressure on porosity development in geothermal systems.

In order to simulate hydrothermal reactions experimentally, we developed *in-situ* flow-through reactors and subjected mineral samples, consisting of quartz cemented by gypsum, to sodium carbonate solution under varying pressure and temperature regimes. The rate of calcification of the mineral samples and associated porosity generation was determined.

Further work will involve studying mineral transformation reactions on cementing materials commonly found in sandstones associated with areas of geothermal interest. It is hoped to determine conditions optimal for ensuring high fluid flow rates in geothermal systems.

1. INTRODUCTION

Hydrothermal mineral replacement reactions play an important role in controlling fluid transport in fluid flow environments such as geothermal energy systems. 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 two 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).

These reactions have been studied principally via numerical modeling due to the belief that mineral replacement reactions occur over a timeframe incompatible with laboratory experiments (Berkowitz 2002). Very little experimental research has been conducted on the relative contributions of environmental variables such as temperature and pressure on porosity development.

Our research aims were to study and quantify the effects of temperature, pressure and timescale on mineral replacement reaction rates. To this end, a pilot experiment was performed whereby gypsum was used to cement a quartzite base and the resultant matrix exposed to varying pressure-temperature regimes. Changes in cement composition and associated porosity development were determined.

The goal of this research was to identify the hydrothermal conditions and mineral compositions optimal for attaining the fluid flow rates necessary for geothermal energy development. It will provide an experimental basis for predictive modeling to identify potential future geothermal well locations.

2. METHODS

In order to simulate hydrothermal reactions experimentally we have developed *in-situ* flow-through reactors (figure 1).

A HPLC pump was used in conjunction with a backpressure regulator to generate a fluid flow rate of between 0.1 and 10 ml-min and pressures of up to 1200 bar. The fluid was heated via a heating jacket to temperatures of up to 200^0C prior to passing through the mineral sample.

The reactors were developed with tubing, sample holding cell and fittings constructed from high pressure nickel-alloy (Inconel 625 and Hastealloy C276). The nickel alloys are capable of withstanding very high pressures (>1500 bar) at high temperatures (>500^OC). The alloys are also highly corrosion resistant allowing corrosive fluids such as chlorides to be used at elevated temperatures and pressures for extended periods.

The reactors were used to determine the effect of pressure, temperature, and fluid composition on mineral replacement reactions and associated changes in permeability. Sample material, consisting of quartz grains cemented with gypsum, was placed in the reactors and exposed to 0.1 molar sodium carbonate solution at a flow rate of 5 ml minute. The samples were subjected to varying temperatures (140^0C to 200^0C) and pressures (200, 450 and 1200 bar) for varying time periods (1 hour to 1 week).

Samples were non-destructively analyzed for porosity changes using a Skyscan 1072 micro-computer tomography (MCT) analyzer. MCT analysis allowed construction of 3-dimensional x-ray images of samples from which porosity could be determined using grey-scale analysis. Sample compositional changes were determined using x-ray diffraction techniques.

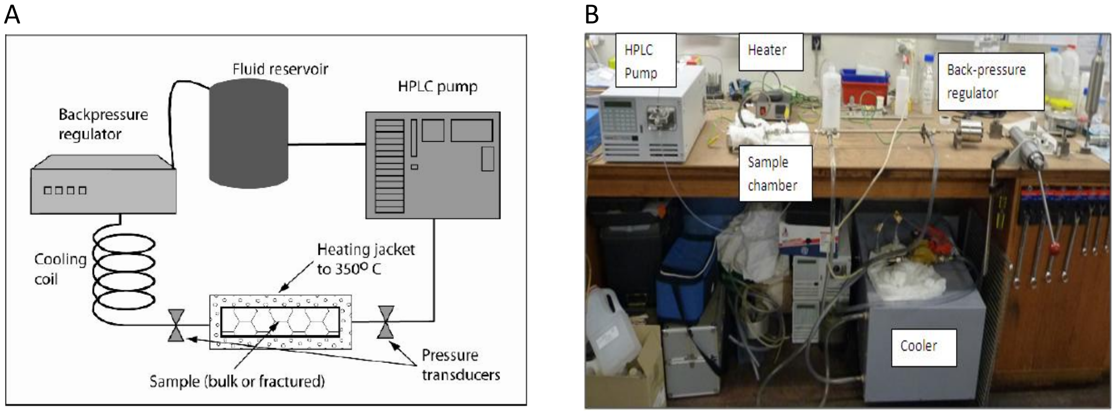


Figure 1: The flow through reactor system showing high pressure pump and backpressure regulator.

3. RESULTS

3.1 Mineral replacement reactions over time.

XRD analysis of the time series experiment showed that at experimental conditions of 140^0C temperature 450 bar pressure and a 5 ml per minute flow rate, no mineral replacement reaction was evident after 1 hour. After 24 hours some replacement of the gypsum with calcite had occurred. After 1 week, all of the gypsum had been replaced with calcite (figure 3,ABC). As expected, porosity development followed the same pattern (figure 2C) with, little change in porosity over 24 hours, but an increase from 2 percent to 25 percent over the next 144 hours.

3.2 Mineral replacement reactions and pressure

At a pressure of 200 and 450 bars (temperature 140^{0}C), no mineral transformation reaction occurred over an 8 hour period. Increasing pressure to 1,200 bars resulted in replacement of gypsum by calcium sulphate and calcite over 8 hours (figure 3, DEF). At all pressure levels, porosity was of the same order (approximately 2 per cent) after 1 hour. After 8 hours, porosity remained at 2 percent at 200 and 450 bar but increased to 18 percent at 1,200 bar (figure 2A).

3.3 Mineral replacement reactions and temperature

Over a 1 hour timeframe there was no significant change in sample composition or porosity at temperatures between 140 and 200^{0}C. Over 8 hours, porosity increased to 4 percent at 160^{0}C, 15 percent at 180^{0}C and 19 per cent at 200^{0}C, reflecting the increased rate of calcification of the sample at elevated temperatures (figure 2B).

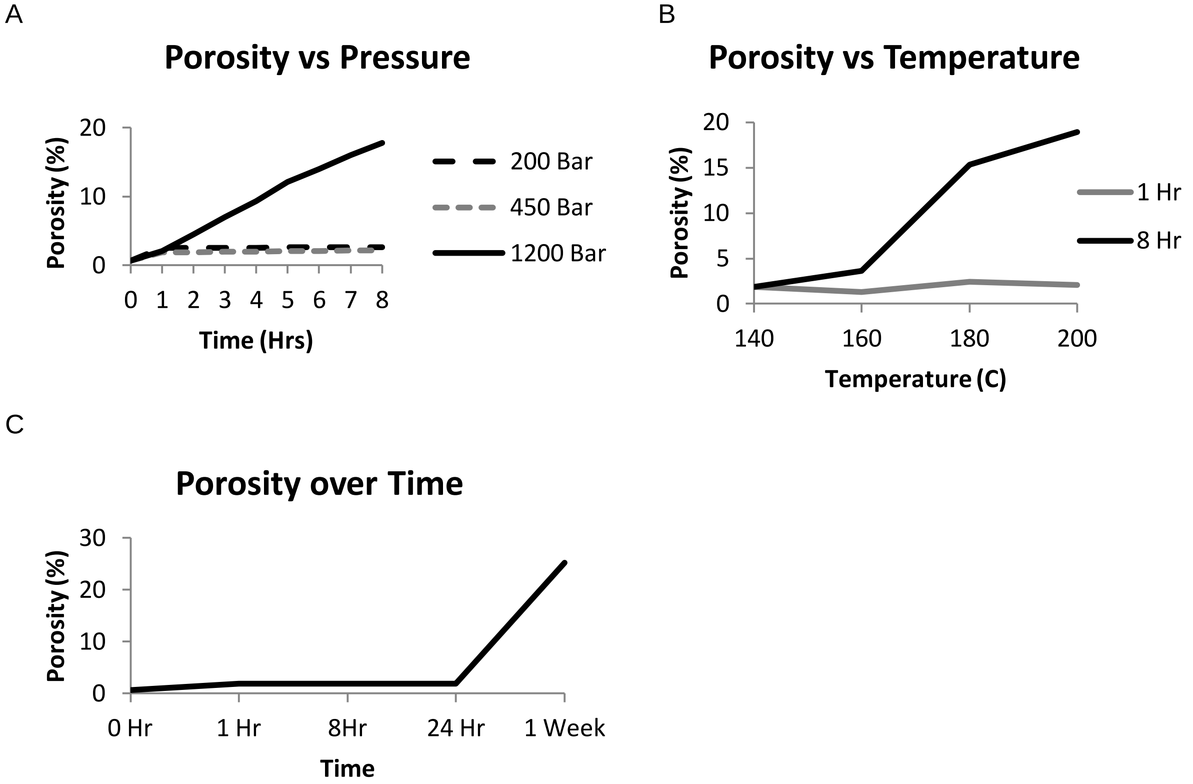
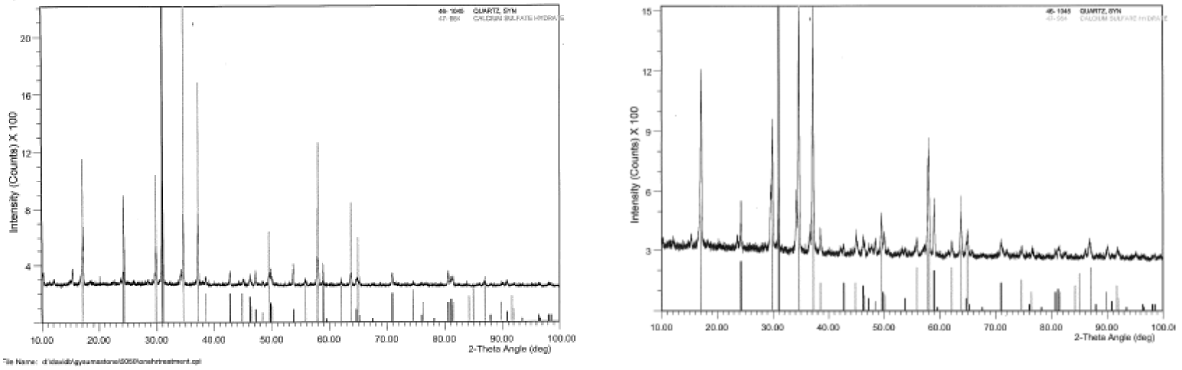
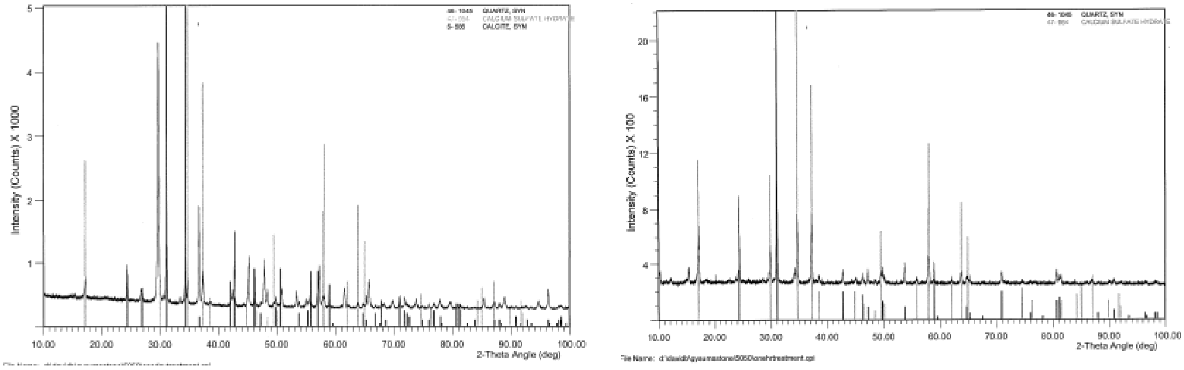


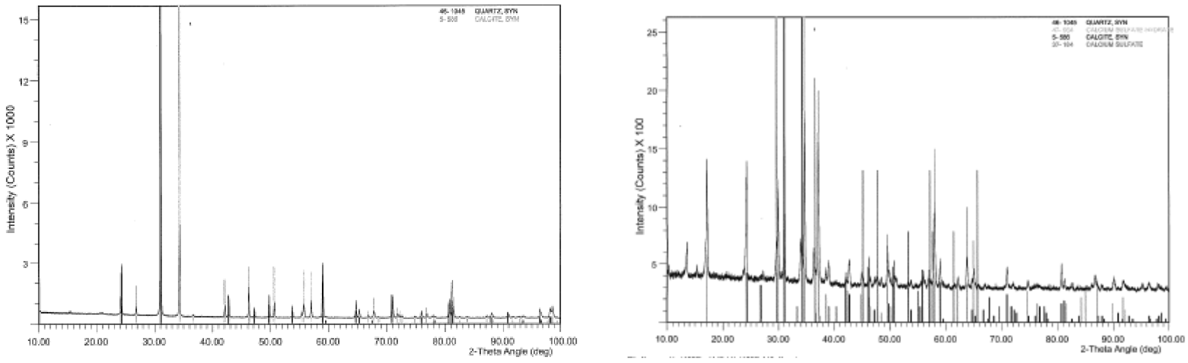
Figure 2: Effect of: A. pressure on porosity development over time at 140^{0}C. B. Temperature on porosity development (pressure = 450 bar) C. Timescale of the mineral replacement reaction (pressure 450 bar, temperature 140^{0}C)


A 1 Hr Quartzite/Gypsum

D 200 Bar 1 Hr Quartz/Gypsum


B 1day Quartzite/Gypsum/Calcite

E 450 Bar 1 Hr Quart/Gypsum


C 1 Week Quartzite/Calcite

F 1,200 bar 1 Hr Quartz/Gypsum/Calcium Sulphate/Calcite

Figure 3. XRD charts showing: ABC, replacement of gypsum with calcite over time (pressure 450 bar, temperature 140^0C), DEF effect of pressure increase on calcification of gypsum (Time = 1 Hr, temperature = 140^0C)

4. CONCLUSION

The increase in porosity that occurred as the gypsum cement was replaced by calcite may be attributed to the lower molar mass and solubility of calcite compared to gypsum. The rate at which this mineral replacement reaction occurs has been shown to be highly dependent on environmental conditions such as pressure and temperature with reaction rate increasing at temperatures over 160^0C and pressures beyond 450 bars. This is an application of Le Chatelier's principle that states that a system in equilibrium that experiences a change (e.g. increasing pressure) adapts to minimize the effects of the change (hence gypsum is replaced by more compact calcite to offset the pressure increase).

Further work will involve studying cementing materials commonly found in sandstones associated with areas of geothermal interest, (carbonates, kaolinite, illite/smectite, zeolites), to fluids of a composition representative of those found at geothermal drill sites. By determining the pressures and temperatures at which mineral replacement reactions occurs and its effect on mineral porosity, it is hoped to determine conditions optimal for ensuring high fluid flow rates in geothermal systems.

5. ACKNOWLEDGMENTS

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6. REFERENCES

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