Main Menu Programme Author Index

EXPERIMENTAL SIMULATION OF FLUID-MINERAL INTERACTION USING A CONTINUOUS FLOW HYDROTHERMAL APPARATUS

Bruce W. Mountain[1] and Romain Sonney[1]

[1]GNS Science, Wairakei Research Centre, 114 Karetoto Rd., Taupo 3377, New Zealand

b.mountain@gns.cri.nz

Keywords: *Experimental geochemistry, flow-through apparatus, water-rock interaction, silica scaling, re-injection*

ABSTRACT

Experimental simulations of fluid-mineral interactions have been conducted using a continuous flow-through hydrothermal apparatus capable of temperatures up to 400°C, pressures of 500 bars and flow rates as low as 1.5 ml/day.

In the experiments described, New Zealand greywackes were reacted with distilled water and re-injection brines to study the effects on brine chemistry and secondary mineral formation.

Experiments using unaltered greywacke, reacted with distilled water and re-injection brine, showed the formation of clay minerals and possible zeolite phases. Those conducted at re-injection temperatures using re-injection brines showed the formation of amorphous silica deposits whose textural characteristics were affected by the amount of silica polymerisation.

The results from these experiments demonstrated the considerable possibilities for this method. Define your question, we can simulate it.

1. INTRODUCTION

Fluid-mineral interaction studies are undertaken to elucidate the process through the use of computational models or experimental analogs. These can simulate fluid-mineral reactions which are occurring in the natural environment allowing us to predict or explain processes occurring in infrastructure and in the subsurface.

Computational methods to study fluid-mineral interactions include: static, closed-system thermodynamic models such as activity-activity diagrams; more complex, open-system models that have become available through the use of personal computers and even more complex computer modeling software that can incorporate kinetic data, e.g. GWB. Although computational models are convenient to use, they are based on the premise that the thermodynamic data used is comprehensive and correct. This *is* an erroneous assumption.

The alternative to computational models is the use of direct experimentation to reproduce fluid-mineral interactions in the laboratory. This approach simulates the processes occurring in a hydrothermal system using actual rock and fluid allowing observation of the chemical and mineralogical changes occurring subsurface. It allows intrinsic incorporation of thermochemical parameters that may not be available to modeling programs. It's the closest that a geochemist can get to actually being there.

In this contribution, we described results from a set of fluid-mineral interaction experiments undertaken using a continuous-flow hydrothermal apparatus located at GNS Wairakei.

2. EXPERIMENTAL APPROACH

The high T,P flow-through apparatus is located at GNS Science, Wairakei Research Centre. It was constructed by Coretest Systems Ltd., San Jose, California. It is able to simulate fluid-mineral interactions under hydrothermal conditions reaching up to 400°C and 500 bars at a flow rate ranging from 0.06 – 900 ml/hr (Fig. 1)

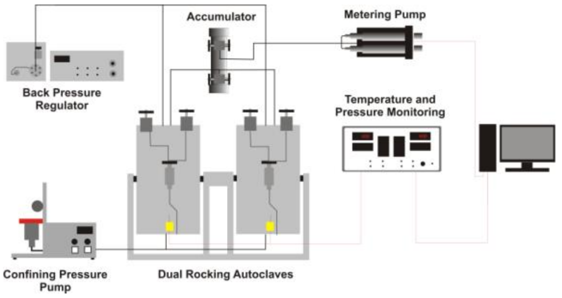

Figure 1: Schematic diagram of flow-through apparatus

Continuous flow is achieved by a double-piston metering pump that pumps distilled water into the titanium accumulator. This contains a diaphragm that separates the distilled water from the study fluid. In this way corrosive and/or saline fluids can to be used without damaging the stainless steel metering pump. The mineral/rock material is held inside a titanium sample holder located inside the autoclaves. Pressure is maintained by an electronic back pressure regulator. The pore fluids samples are collected on the low pressure side of the back pressure regulator.

Pore fluid samples were analysed by ICP-OES for cations, IC for anions, and pH by potentiometry (all at GNS Wairakei). Run products were studied microscopically by SEM at Victoria University Wellington and the University of Auckland.

3. RESULTS

3.1 Waotu1 (Greywacke – Distilled Water)

This experiment reacted Waotu greywacke (Late Jurassic/Early Cretaceous Manaia Hill Group) with distilled water at 25 - 210°C, 35 bar. This rock was chosen as it is similar to the basement rock in the geothermal areas of the TVZ. The greywacke consists of clasts of siltstone, basalt, quartz, plagioclase, pyroxene and hornblende in a matrix of quartz, feldspar, chlorite, illite, calcite and pyrite. Distilled water was used to see the effects of the rock on a pristine fluid. The initial flow rate for this experiment was 1 ml/hr. Effluent samples were collected daily.

During the initial 25°C period elevated concentrations of Ca and Mg and alkaline pH values were found. This is due to the dissolution of calcite from the greywacke matrix. Trace amounts of Na, K, Al, Sr and SiO_2 were also detected. Upon the temperature shift to 210°C, a sharp increase in the concentrations of K, Na and SiO_2 were measured. As, B, Fe, Li and SO_4 also became detectable but only at trace levels. Ca and Mg dropped to below detection limit. Quench pH stabilise at a value of 7.5. Quartz saturation temperature of 216°C was calculated based on the stabilise SiO_2 concentration agreeing well with the experimental temperature. After six days Ca concentrations increase again to a steady state value of ~1.9 ppm. A decrease in flow rate to 0.5 ml/hr did not affect dissolved component concentrations or pH. This suggests equilibrium with secondary mineral phases had been reached.

SEM examination of fresh unreacted greywacke showed clean unreacted surfaces of quartz, feldspar, pyroxene clasts surrounded by the fine-grained matrix (Fig. 2a). In contrast, run products from this experiment showed significant dissolution of quartz and feldspar. Greywacke clasts also had a semi-continuous coating of secondary phases. EDS examination of a platy, mucaceous phase indicates a Ca - Na - K-bearing aluminosilicate interpreted to be smectite (Fig. 2b). Also present was a euhedral phase that EDS examination showed to be a Ca-Al-Si bearing mineral (zeolite?). Rare secondary calcite was also identified.

3.2 Waotu2 (Greywacke – Reinjection Brine)

To contrast and compare with the simulation with distilled water, in this experiment, Waotu greywacke was reacted with reinjection brine from Wairakei Power Station. The T,P conditions were 25 – 204°C, 35 bar. At room temperature, elevated pH and higher concentrations of Ca, Mg and Sr were found consistent with dissolution of calcite. Upon the temperature shift to 204°C, sharp declines in pH, Mg and As occurred. Other components, excluding SiO_2, remained at their re-injection brine concentrations and appeared to be unaffected by fluid-mineral interactions. SiO_2 concentration in the input brine is 567 ppm and at room temperature this concentration dropped to 530 ppm. After the temperature shift to 204°C, a steady state SiO_2 concentration of 440 ppm was reached. This concentration represents a $T_{quartz} = 241^oC$, $T_{chalcedony} = 231^oC$ and $T_{amorph\ SiO2} = 116^oC$.

The surface of reacted grains from this experiment showed a different assemblage of secondary minerals. Rosettes of a Mg-Fe-Al bearing silicate, most likely chlorite, were found in abundance (Fig. 3a). Also common were coatings of a anhedral flaky/mucaceous aluminosilicate phase composed of varying amounts of a Ca, Na, and K, most likely a clay mineral (smectite?) (Fig. 3b). Less common phases included a euhedral Ca-Al-Si phase (Fig. 3c) resembling a zeolite (clinoptilolite?) and overgrowths of potassium feldspar (Fig. 3d).

3.3 K50-1 (Re-injection Aquifer – Re-injection Brine)

In this experiment, re-injection aquifer greywacke from a New Zealand geothermal area was reacted at 154°C, 27 bars, to simulate a re-injection scenario. The flow rate for this experiment was initially 1 ml/hr, then it was decreased to 0.5 ml/hr near the end of the experiment. The initial SiO_2 concentration in the brine was 980 ppm. Measurement of monomeric silica content of the input brine showed that it had polymerised and that only ~180 ppm of the SiO_2 was monomeric.

Samples collected during the inital room temperature period showed increases in pH, Ca, Mg and Sr, consistent with the dissolution of the calcite from the greywacke. SiO_2 concentration decreased by 70 ppm during reaction with the greywacke at room temperature. After the temperature shift to 154°C, pH decreased to 6.9 and then reached a steady state value of approximately 7.5. Other major elements, excluding SiO_2, remained relatively unchanged from brine concentrations. SiO_2 decreased to a steady state value of 640 ppm. This concentration represents a $T_{quartz} = 276^oC$, $T_{chalcedony} = 275^oC$ and $T_{amorph\ SiO2} = 153^oC$. Although the last temperature agrees with the experimental temperature, it must be remembered that the silica in the input brine is partially polymerised and thus measured silica is not representative of the actual monomer present in the experiment.

The sample holder contains about 25 g of crushed, sieved (0.5 – 2.0 mm) and cleaned greywacke. The input fluid enters the sample holder at the bottom. The fluid is furthest from equilibrium with the rock at the entry point. At the slow flow rate utilised, the flow is not turbulent and mixing is mininal. This means that the brine and rock see the maximum exchange of components at the bottom of the sample holder while at the exit the brine and rock are at their closest equilibrium.

Run products from the K50-1 experiment were split into portions based on their position in the sample holder. SEM examination showed that those at the bottom were coated with a continuous covering of amorphous silica (Fig. 4a). No other secondary minerals were identified. The coating covered all clast types and the matrix material. It consisted of a continous very fine-grained silica layer encompassing larger spherulitic shaped bodies (Fig. 4b). Greywacke fragments from the top of the sample holder were free of this coating and appear similar to the unreacted material.

3.4 K50-2 (Re-injection Aquifer – Depolymerised re-injection brine)

The experimental set-up for this experiment was similar to K50-1, however, in this case, two ovens were used. The re-injection brine was pumped into the first oven at 350°C. The residence time in the empty sample holder in this oven is approximately 50 hours. This is sufficient time for the polymeric silica in the brine to be depolymerised afterwhich it flows in the second oven containing the re-injection aquifer greywacke. The tubing between the two ovens is heated to minimise re-polymerisation of the silica. Although the apparatus is capable of operating the ovens at different temperatures, it must be isobaric throughout. As a result, the pressure in both sample holders was maintained at 209 bars. The temperature of reaction in the second sample holder for this experiment was 157°C.

The effluent chemistry from this experiment showed an increase of pH from 6.0 to 7.8 within three days. During the same period, SiO_2 concentration dropped to 400 ppm and then rose to a steady value of 600 ppm. This represents a $T_{quartz} = 270^oC$, $T_{chalcedony} = 267^oC$ and $T_{amorph\ SiO2} = 147^oC$. All other major components in the brine remain at close to their input values. In this case, it is assumed that all the silica was monomeric when it entered the sample holder and thus the fluid appears to have been close to equilibrium

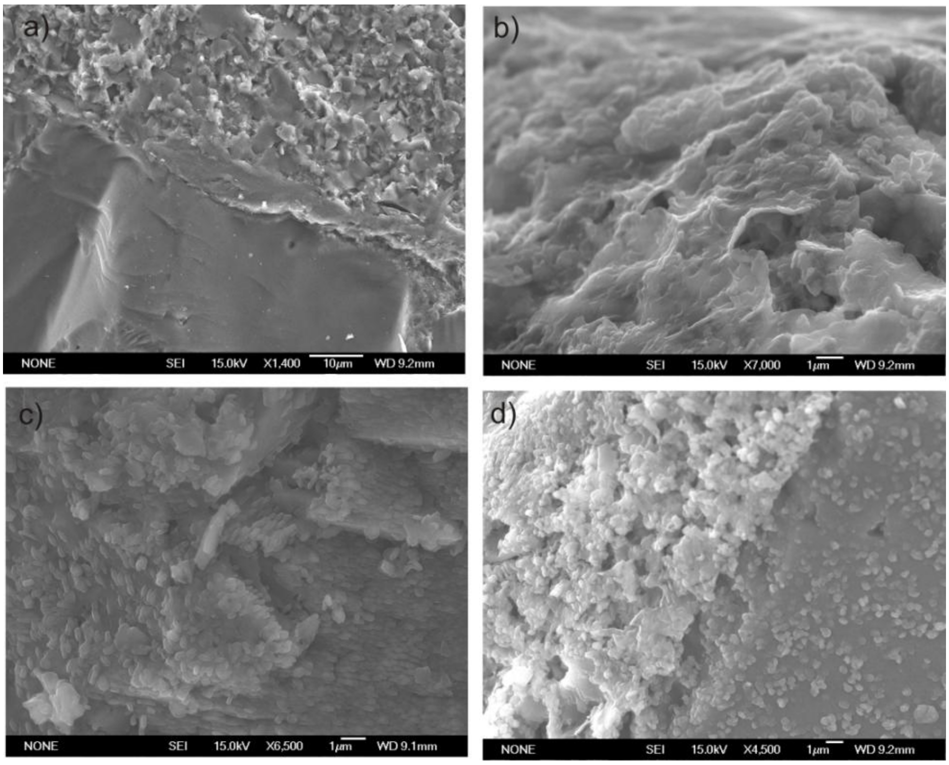

Figure 2: Photomicrographs of: a) unreacted greywacke showing the matrix and adjacent quartz clast; b) reacted greywacke with a coating of secondary minerals (smectite); c) euhedral Ca-Al-Si phase (zeolite?); and d) possible zeolite phase on the matrix and adjacent quartz clast (right).

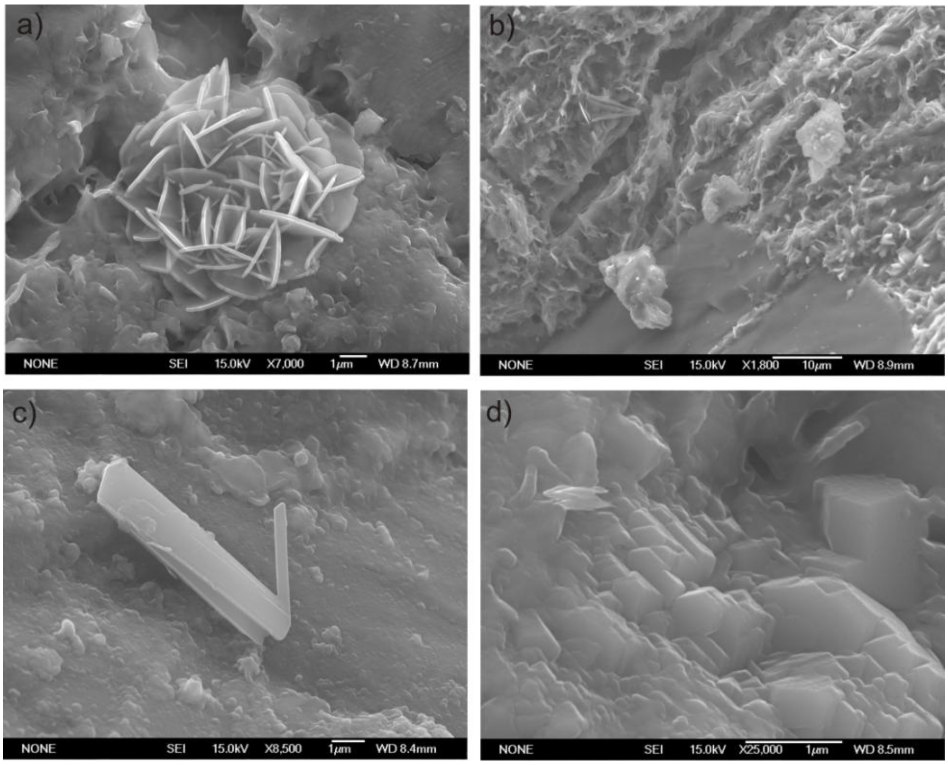

Figure 3: Photomicrographs of: a) chlorite rosettes; b) coating of smectite (?) adjacent to a quartz clast; c) Ca-Al-Si phase (clinoptilolite?); d) secondary K-feldspar overgrowths.

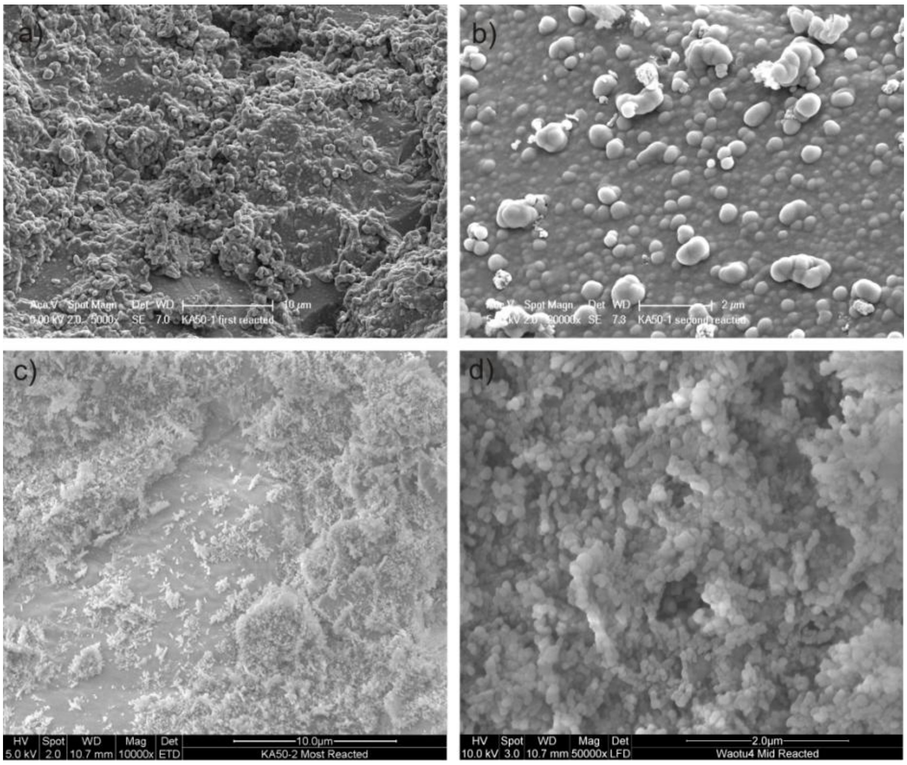

Figure 4: Photomicrographs of: a) re-injection aquifer greywacke with coating of amorphous silica from experiment K50-1; b) close-up of silica coating from K50-1; c) amorphous silica coating from experiment K50-2; and d) close-up of silica coating from K50-2.

solubility with amorphous silica as it exited.

SEM examination of the run products from the bottom of the sample holder shows a deposit of amorphous silica (Fig. 4c). No other secondary phases were identified. The amorphous silica consists of a discontinous coating of small spherules 10 – 20 nm in diameter (Fig. 4d). This contrasts with the silica coating in the previous experiment (K50-1) where the coating is continuous and there are silica spherules that are much larger and more diverse in size. Greywacke fragments from the top of the sample holder in K50-2 are clean and have no amorphous silica coating. Assuming that pressure has a minimal effect on silica precipitation, it is evident that the depolymerisation of silica has had a marked effect on the texture of the precipitate.

2. SUMMARY

Experimental hydrothermal apparati provide the opportunity to study fluid-mineral interactions in a wide variety of natural/industrial situations. The experiments described above represent a small selection of possible simulations that can be conducted. Unlike geochemical modelling, real time experiments with real fluids and actual host rocks overcome the problems of the lack of thermodynamic and kinetic data required for mathematical models. Although these experiments may be site-specific, they can provide useful insights into what fluid-mineral interaction processes are occurring. Our apparratus at GNS can be used to study many questions relevant to the geothermal industry including:

1) the process of fluid-mineral interactions at temperature up to 400^{o}C and pressures of 500 bars;
2) the thermodynamic stability of metal complexes and alteration minerals in geothermal systems and power stations;
3) the temperature stability and chromatography of tracer chemicals (e.g. NDS tracers) in the geothermal environment;
4) the modification of rock properties due to fluid-mineral interaction;
5) the formation of scaling and corrosion products in re-injection aquifers and power station infrastructure.

Laboratory simulations are currently the closest we have to simulating, studying and understanding the geothermal environment.