EXPERIMENTAL STUDIES OF SUPERCRITICAL FLUID-ROCK INTERACTIONS - GEOTHERMAL: THE NEXT GENERATION

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ABSTRACT

The MBIE research programme *Geothermal: The Next Generation (GNG)* is investigating New Zealand's supercritical geothermal resource potential. NZ's unique tectonic setting delivers an exceptional opportunity for the development of these resources and has the potential to provide an unlimited source of renewable energy while minimising carbon emissions.

The exploration and utilisation of supercritical fluids is dependent on accessible and high-quality thermodynamic data. Currently, there is a knowledge gap regarding fluid-rock interactions under the physicochemical conditions which exist under supercritical fluid conditions. This lack of knowledge needs to be addressed.

The GNG programme delivers vital geochemical data to understand the effect of fluid-rock interactions at supercritical conditions. Understanding these processes will provide thermochemical constraints that will be incorporated into numerical models. Such models will facilitate enhanced resource definition and prediction.

To perform fluid-rock interaction experiments at supercritical conditions is technically difficult because of the high temperatures involved. At GNS we have built a unique experimental system to address these challenges. Our continuous flow reactor allows the study of interactions between geothermal brines and NZ reservoir rocks at temperatures and pressures up to 650˚C and 230 bar.

The experimental system will allow the study of the complex reactions that occur when supercritical fluids react with rocks. The results will be used to understand, interpret, and predict the implications of geochemical processes to infrastructure and subsurface conditions.

1. INTRODUCTION

New-Zealand has set a target to shift to 100% renewable energy by 2035 and is aiming to become carbon neutral by 2050. In order to achieve this target, the introduction of new carbon-neutral energy resources will need to take place in the upcoming decades (Change Commission, 2022). NZ's conventional geothermal energy production has a substantial role in the path towards carbon-neutrality. Nevertheless, a much higher potential can be found in deeper, supercritical geothermal heat resources (>400˚C), potentially delivering as much as 10 times more energy than conventional geothermal (Dobson et al., 2017).

High-quality thermodynamic data for interactions between rocks and fluids under supercritical conditions are a necessary requirement for the development of supercritical reservoirs. At present, a wide knowledge gap exists regarding the geochemical interactions taking place at such conditions.

Based on insights from decades of previous research, the Endeavour research programme *Geothermal: The Next Generation (GNG)* aims to minimise exploration and technological risks by elucidating the interactions between NZ rocks and fluids at supercritical conditions (Chambefort et al., 2019). As part of this programme ground-breaking experimental studies at supercritical conditions will be conducted. Experiments will use NZ's basement rocks and brines at supercritical conditions, followed by detailed geochemical examination. This will provide crucial thermochemical constraints that can be incorporated into subsurface numerical models. Such models will facilitate enhanced resource definition and prediction.

Supercritical fluids are found at temperatures and pressures above the supercritical point (>374˚C and >221 bar, for pure water) (Palmer et al., 2004). At these conditions a single, low density fluid phase exits. Heřmanská et al. (2019, 2020) performed several experiments reacting geothermal brines with basaltic rocks at temperatures of 400-420˚C and pressures up to 69 bar. The experimental results showed a significant reduction in the concentration of mineral-forming ions (i.e. SiO_2, Na, K, Ca, Mg, Al). This was attributed to the low density of the supercritical brine. Passarella et al. (2016, 2017) conducted similar experiments at 400˚C and 500 bar that showed extensive alteration of the rock and significantly higher concentrations of the mineral-forming ions in the effluent samples. This is attributed to the effect of pressure on the supercritical fluid density.

In this contribution, preliminary results are presented from a water-rock interaction experiment performed under supercritical conditions at 500˚C and 210 bars. The purpose of this experiment was to investigate fluid-rock interactions between supercritical water and NZ basement greywacke.

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2. METHODS

2.1 Experimental Setup

A novel experimental flow-through system has been constructed to allow the interaction between fluids and rocks at supercritical conditions up to 650˚C and 250 bars. The system consists of a 220 ml custom made reactor (Parr Ints., IL, USA). A high-pressure piston pump (Teledyne ISS, PA, USA) is used to inject fluid into the reactor. The pressure in the system is controlled by a back-pressure regulator (VINCI Tech., France) controlled by a syringe pump (Flox-Lab, France) pressurised with N_2. A disposable syringe is used at the outlet to collect the effluent samples. The process temperature is maintained by a furnace and high-temperature heating sleeve controlled by a series of PID controllers and logged by computer software (Fig. 1, left). All system parts are made from corrosion-resistant materials (e.g., Haynes 230 alloy, Ti and PEEK).

2.2 Experimental Procedure

To test the performance of the new experimental setup and to study the effect of a supercritical fluid on a rock surface, an 8 x 8 x 4 mm block of NZ greywacke was used. This was held in a holder made of gold wire (Fig. 1) which suspends the block in the supercritical fluid. One of the faces of the block was polished in order to allow a prior- and post- experiment Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (SEM-EDS) mineralogical mapping of the block.

A continuous flow of de-oxygenated, distilled water was injected into the reactor at different flow rates (0.01, 1.3 and 0.02 ml min^{-1}) and a temperature and pressure of 500ºC/210 bar. The effluent was sampled periodically, typically once per day and analysed for room temperature pH and major elements for 30 days, until the experiment terminated due to a technical problem.

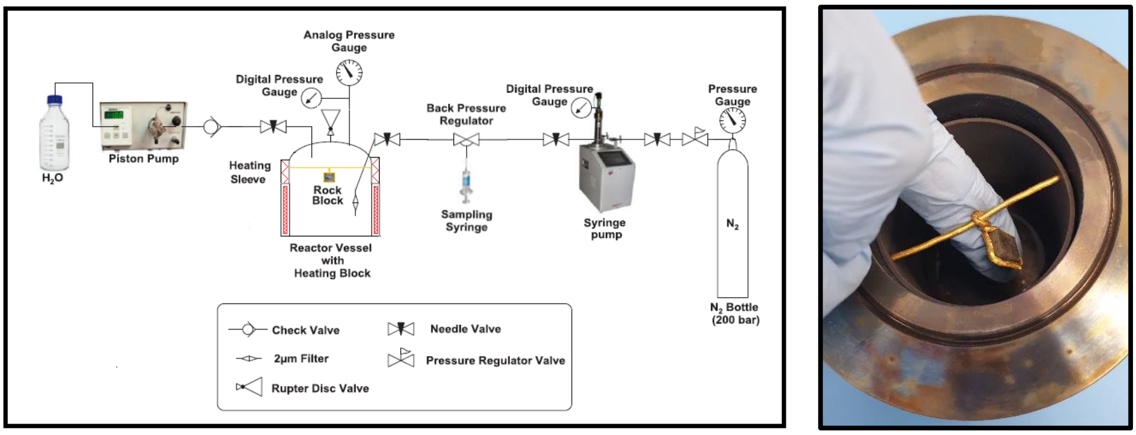

Figure 1: Schematic diagram of the experimental setup (left), greywacke block in gold holder (right)

2.3 Analytical Methods

Major element analyses, including Li, Na, K, Mg, Ca, Sr, Mn, Fe, As, Al, B, and SiO_2, were made by ICP-OES (iCAP 7000, Thermo Scientific), and anions including Cl and SO_4 were analysed by IC (Dionex ICS-5000$^+$ EG), (New Zealand Geothermal Analytical Laboratory, GNS Science). H_2S was determined by the methylene blue method/UV-Vis spectroscopy. Quench pH was measured at room temperature using a standard pH electrode. A JOEL JCM-6000 benchtop SEM-EDS (GNS Science) and a JEOL Field Emission Electron Probe Microanalyzer (University of Auckland) systems were used to characterise the mineralogical and chemical composition of the reacted rock.

3. RESULTS

3.1 Chemical Analysis

Chemical analyses for Li, Na, K, Mg, Sr, Mn, As, Al, and B showed values near or below the detection limit. The effluent room temperature pH is stable over the course of the experiment at ~5.5 (Fig. 2).

At the lowest flowrate, during the first 11 days of the experiment, Fe, Ca, and H_2S have measurable, but declining concentrations, while SiO_2 is higher, reaching ~13 mg kg^{-1} (Fig. 3). When the flowrate was increased (Day 11 to 22), SiO_2 concentrations decline significantly and reach a new steady state value of ~2 mg kg^{-1}, while Fe, Ca, and H_2S show near detection limit values. After Day 22, when the flowrate was decreased again, SiO_2 concentrations increase reaching a steady state value of ~6 mg kg^{-1}. Ca attains a low but constant concentration while Fe peaks immediately after the flowrate reduction.

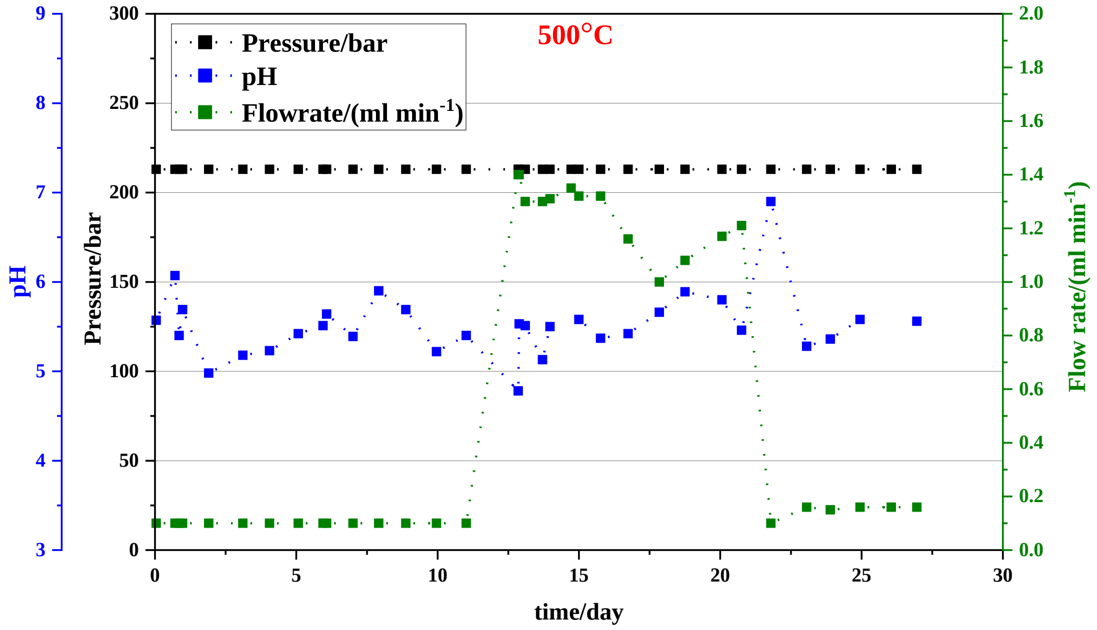

Figure 2: Pressure (bar), pH, and flow rate (ml min^{-1}) vs. time (day) during the experiment

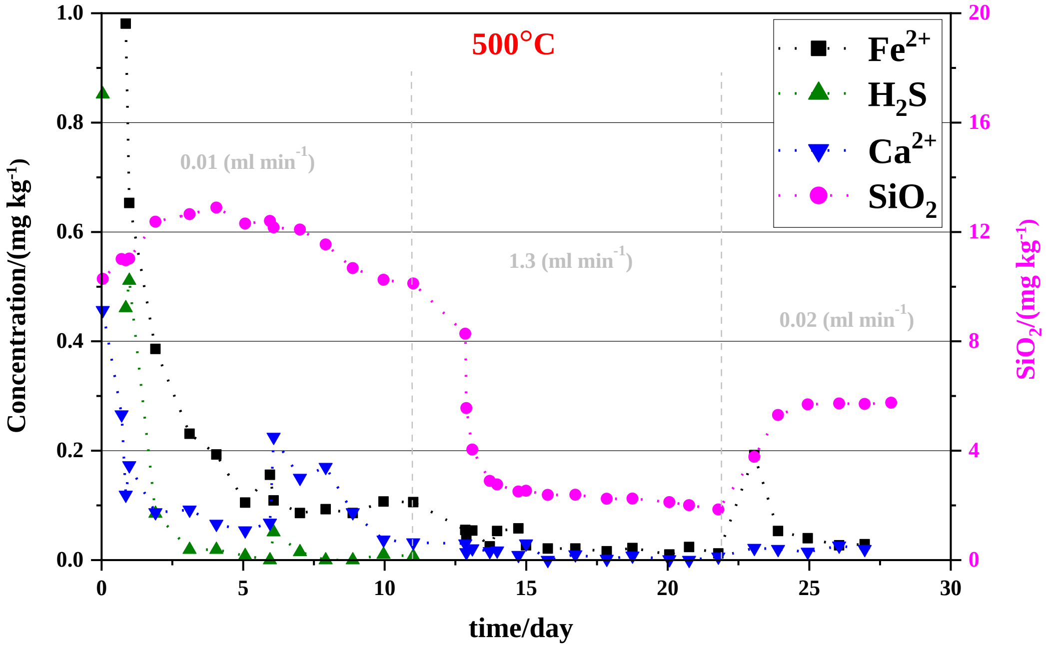

Figure 3: Fe, Ca, H_2S, and SiO_2 (mg kg^{-1}) vs. time (day) during the experiment

3.2 Mineralogical Analysis

Extensive mineral alteration was observed on the polished face of the rock (Fig. 4). The most significant observation is the complete dissolution of quartz crystals from the rock, leaving notable cavities (Fig. 5 left). Other observations include changes in mineral colour and an increase in surface roughness due to the dissolution and reprecipitation of new phases.

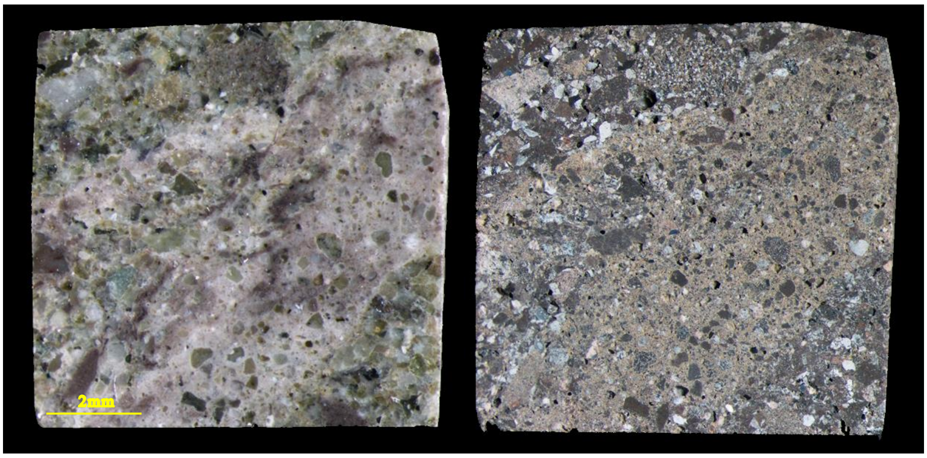

Figure 4: Light microscopy of the polished face of the greywacke block before (left) and after (right) the experiment

Field Emission Electron Probe microanalyzer SEM images reveal the extensive alteration on the rock surface (Fig. 5) with significant transformation of the surface by new mineral precipitation and re-precipitation of primary phases. SEM-EDS maps (Figure 6 and 7) show examples of the surface alteration that occurred on the rock surface. The change from red-coloured grains into purple-coloured grains represents the loss of Na from the original albite being replaced by K and Ca-rich phases andesine and orthoclase. Other primary phases like pyroxene and chlorite are altered to clinopyroxene, hornblende and clay phases (e.g. illite).

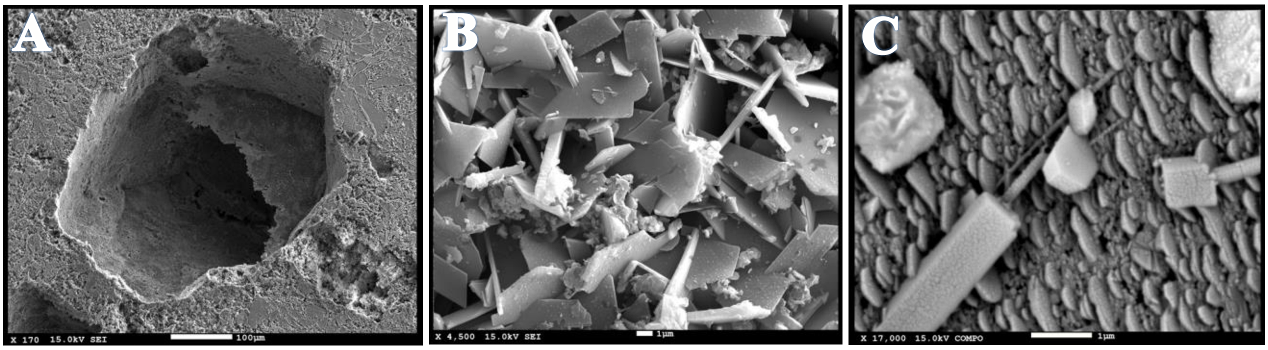

Figure 5: Cavities left in the block surface where quartz grains have been dissolved (A), precipitated clays (B), altered surface of pyroxene, showing its reprecipitation into hexagonal crystals (C).

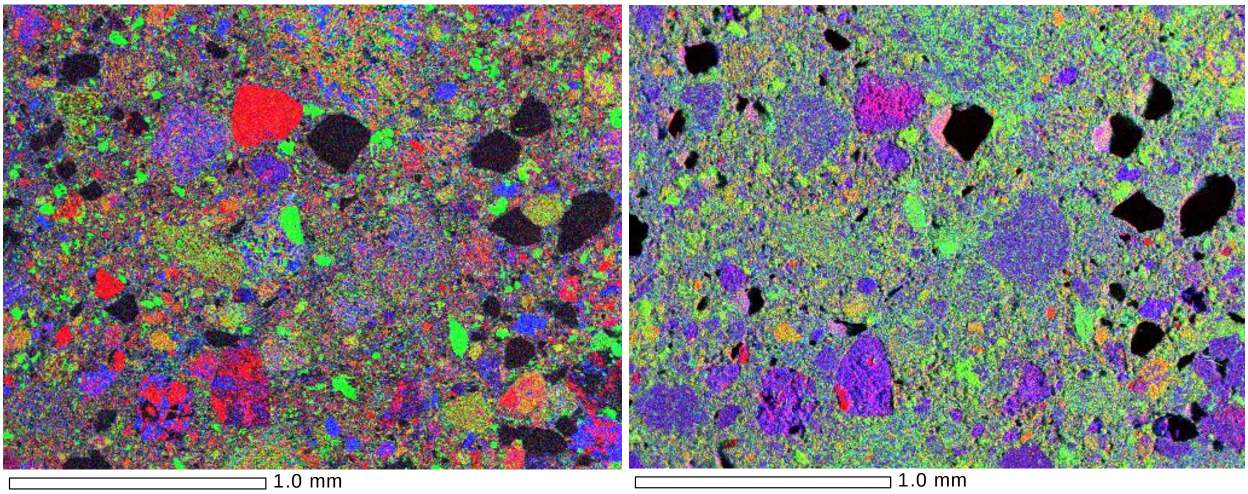

Figure 6: SEM-EDS maps of the rock surface before (left) and after (right) reaction, Na, Ca, and K are represented by the colours red, green, and blue, respectively. Notice the depletion of Na (red) and the relative enrichment of Ca (blue) and K (green).

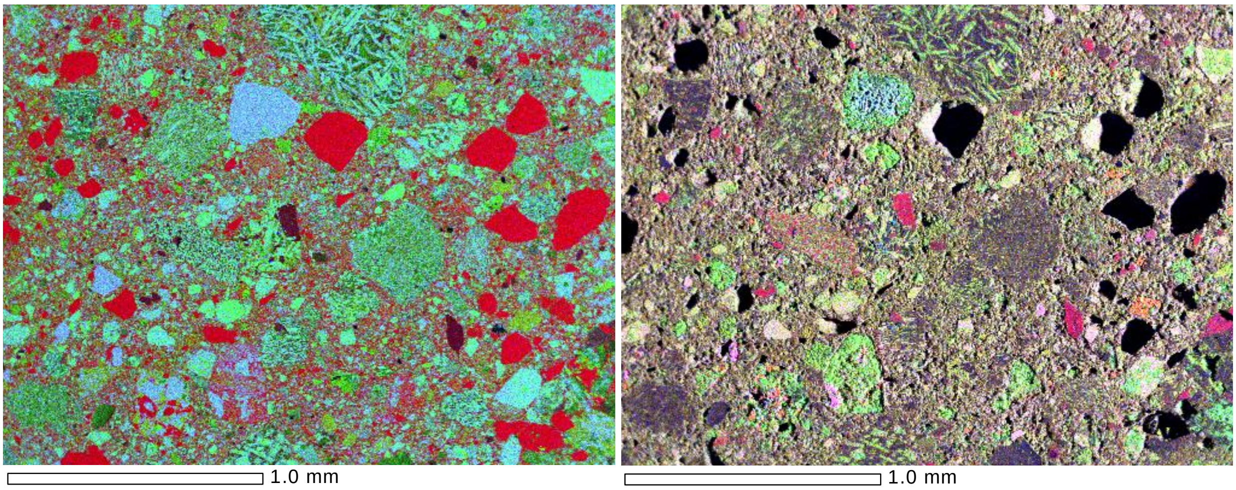

Figure 7: SEM-EDS maps of the rock surface before (left) and after (right) reaction. Si, Al, and Na are represented by the colours red, green, and blue respectively. The surface roughness of the reacted block is emphasised by the shadows (black). Note the loss of Na (blue).

3. DISCUSSION

Very low solute concentrations are found in the effluent solutions, due partially to the high fluid/rock ratio, relatively low surface area when compared with rock grains or powder, but mainly due to low fluid density under supercritical conditions.

At temperatures below supercritical (<374˚C), along the saturated water vapour curve, there are two coexisting phases (gas and liquid). Above the supercritical temperature, only a single phase will exist. According to the Helmholtz Function (Haar et al., 1984), the density of supercritical fluids is strongly related to the pressure. The density of pure water at the experiment conditions (0.072 kg m^{-3}) is 7.2% that of water at standard conditions. Previous works show that the solubility of solutes can be an order of magnitude lower in supercritical fluids compared to subcritical fluids due to the extreme change in the fluid density (Fournier and Potter, 1982; Leusbrock et al., 2010, 2009). This emphasises the need for measurement of mineral solubilities under supercritical conditions.

SiO_2 concentrations in the experimental effluent can provide a preliminary estimate of the solubility of quartz. By assuming that early in the experiment quartz was the main source of silica and that the effluent solution reached equilibrium, quartz solubility is estimated to be ~12 mg kg^{-1} at $500^{o}C$/210 bar (Fig. 3). When the flow rate was increased, it is concluded that the system reached a steady state condition rather than equilibrium, thus the measured SiO_2 concentrations cannot represent quartz solubility. During the third stage of the experiment, when the flowrate was decreased, SiO_2 concentrations increase as expected, potentially regaining equilibrium. Although equilibrium may have been regained, it is suggested that at this stage, quartz may have been depleted, and the measured SiO_2 is from other silicate phases.

Measured Fe and H_2S concentrations are attributed to the dissolution of pyrite (FeS_2), while Ca concentrations are attributed to the dissolution of anhydrite ($CaSO_4$), both minerals are known to be present in the unreacted rock (Fig. 3).

Figures 4 - 7 show extensive mineralogical alteration of the rock surface. Considering the low solubility of minerals in the low-density fluid, the extensive surface alteration observed gives rise to questions as to the mechanism by which the rock is altered. It is hypothesised that a nano-layer of fluid condenses on the rock surface. This condensed layer may facilitate the transport of dissolving solutes from one region of the rock surface to another. Further research is needed to assess this hypothesis.

4. SUMMARY AND CONCLUSIONS

Experimentation under supercritical conditions is a challenge due to the technical difficulties involved. This contribution presents preliminary results of an innovative flow-through experiment reacting a greywacke block with supercritical water at a temperature of 500˚C/210 bars.

Although minerals are less soluble in low density supercritical fluids, the experimental results show extensive mineral alteration on the rock surface. This implies that the transport on solutes take place on the molecular scale. The alteration clearly shows a transition from low grade greenschist facies into intermediate grade amphibolite facies as expected at such high temperatures.

The experimental fluid/rock ratio limits the interpretation of the geochemical process that occur. Future experiments with lower ratios will provide further understanding of these processes.

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