Experimental Geochemistry for Geothermal Solutions: Advancing Industry Practice at ESNZ

Bruce W. Mountain[1], Pedro M. Rendel[1], Lucjan Sajkowski[1]

[1] The Experimental Geochemistry Laboratory (EGL), Earth Science New Zealand (ESNZ), Wairakei Research Centre, Aotearoa New Zealand

Contact: b.mountain@gns.cri.nz

ABSTRACT

The Experimental Geochemistry Laboratory (EGL) at Earth Science New Zealand (ESNZ) has expanded its capabilities to include the supercritical pressure-temperature region. With experimental work spanning water-rock interactions, mineral solubilities, scaling/corrosion simulations, and CO_2 reinjection, the laboratory contributes to advancing geochemical understanding and industry practices in the geothermal setting. With expanded capabilities the lab can conduct such studies at the more extreme temperature and pressure conditions of the supercritical environment. New innovative experimental methods at supercritical conditions include seawater - basalt interaction, water/brine - greywacke interaction, CO_2 – brine co-injection, and mineral thermochemistry measurement. The experimental approach aids in understanding geochemical processes at sub/supercritical conditions in geothermal reservoirs and in current and future power station infrastructure.

Keywords: experimental geochemistry, water-rock interaction, scaling, corrosion, CO2 re-injection, mineral solubility, supercritical geothermal

1. INTRODUCTION

The study of water-rock interactions under high temperature and pressure conditions has long been a cornerstone of geochemical research, particularly in the context of geothermal energy exploration and production. As the demand for sustainable and efficient energy sources grows, the need for advanced experimental techniques to replicate and understand chemical reactions that occur within geothermal reservoirs and power facilities has become increasingly important. The Experimental Geochemistry Laboratory (EGL) at Earth Science New Zealand (ESNZ) has taken a significant advance in this field by expanding its capabilities into the supercritical pressure-temperature region.

With the acquisition of state-of-the-art equipment, the EGL now supports experimental work at temperatures reaching up to 700°C and pressures up to 500 bars. This expansion was made possible through capital equipment investments by GNS Science and supported by funding from the *Geothermal: The Next Generation* (GNG) programme. The laboratory's enhanced capabilities allow experimental simulation of geochemical processes under subcritical and supercritical conditions.

By simulating these extreme environments, the EGL contributes not only to the advancement of geochemical understanding but also to the development of practical solutions for the geothermal industry. The laboratory's work supports the sustainable development of geothermal resources in New Zealand and aligns with global efforts to enhance the efficiency and sustainability of geothermal energy production, reducing the carbon footprint of this important renewable energy source.

2. EXPERIMENTAL WATER-ROCK INTERACTION

2.1 Basalt - Seawater Interaction

To investigate the interaction between seawater and basalt at supercritical conditions (400˚C/500 bar) a new experimental method was developed (Passarella, 2021). This method marked the first time that fluid-rock

interactions with continuously flowing seawater were achieved under such extreme conditions. The experiments utilised EGL's older hydrothermal flow simulators (Coretest Systems), which are capable of maintaining continuous fluid flow through rock substrates at temperatures up to 400°C and pressures of 500 bars (Fig. 1).

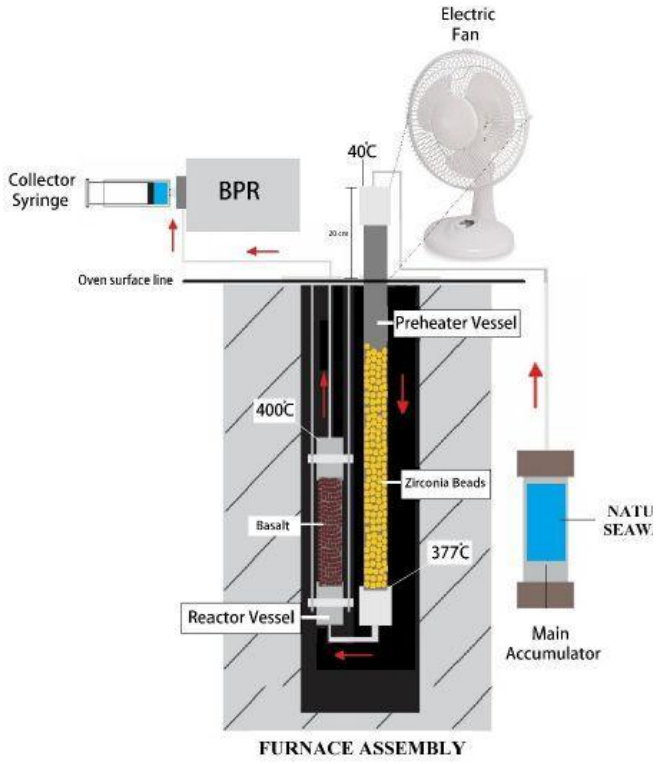


Figure 1: Continuous flow set-up for seawater-basalt interaction at supercritical conditions. BPR – back pressure regulator.

The new method employed a "temperature gradient" pressure vessel designed by the EGL (Preheater in Fig. 1). Seawater is introduced at the top of the Preheater at approximately 40°C and then moves through an extreme temperature gradient, reaching up to 377°C. As the seawater descends, retrograde solubility mineral phases including anhydrite, caminite, and brucite, precipitate. This process prevents these minerals from precipitating further along the flow path, which would cause rapid blockage of the small-bore titanium tubing. Zirconia ceramic beads, ~2 mm in diameter, are placed inside the Preheater to provide surface area for mineral precipitation.

The use of a continuous flow method through the rock allowed the identification of distinct alteration fronts including glass dissolution, chloritization, and anhydrite precipitation. The identification of these fronts would be impossible using standard batch reactor approach. The experiments also highlighted the extensive chloritization and fast rate of reaction at which Mg is fixed by the rock (Fig. 2).

2.2 Greywacke – Water Interaction

In 2020, the EGL acquired two new experimental reactors (Parr Instruments). These included the ultra-high temperature supercritical reactor, capable of reaching temperatures up to 700°C and pressures of 300 bar, which was specifically designed for the EGL and is globally unique (Fig. 3). This reactor was further enhanced with an HPLC pump and back pressure regulator to facilitate continuous fluid flow under supercritical conditions. The second reactor was a Parr large volume stirred autoclave, which operates up to 350°C and 300 bar, designed to process up to 1000 ml of geothermal brine for silica polymerisation testing at temperatures above 100°C.

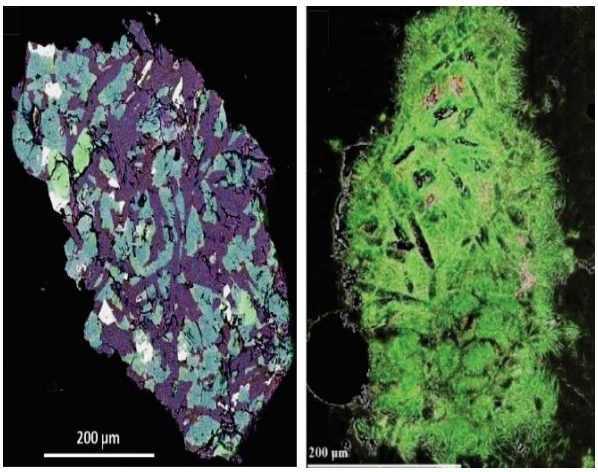


Figure 2: False colour SEM-EDS maps of unreacted basalt (left) and basalt reacted with seawater at 400°C (right). Minerals in the unreacted basalt: plagioclase (purple), clinopyroxene (turquoise), olivine, (light green), and Fe-Ti oxides (white). Minerals in the reacted

basalt: chlorite (green) and Fe-Ti oxides (red).

As part of the *Geothermal: The Next Generation* (GNG) programme, several experimental studies were conducted to explore the effects of supercritical fluid-rock interactions on mineralogy and fluid chemistry. These studies utilised typical New Zealand greywacke as the rock substrate, which was reacted with various fluid chemistries. The greywacke was specifically chosen because it is anticipated that supercritical geothermal fluids will be encountered in the greywacke basement rocks of the Taupo Volcanic Zone.



Figure 3: The ultra-high temperature continuous flow reactor at EGL.

These experiments used both the older hydrothermal flow simulators and the new ultra-high temperature continuous flow supercritical reactor. The typical initial step in fluid-rock interaction simulations is to react the rock substrate with distilled water. While distilled water is not naturally occurring, its use allows the resulting fluid compositions to be primarily influenced by the rock. Several experiments have been conducted where greywacke was reacted with distilled water under supercritical conditions, with temperatures ranging from 400°C to 500°C and pressures between 220 and 250 bar.

Under supercritical conditions with distilled water, the primary reaction observed is the dissolution of quartz from the rock. This is expected, as the distilled water lacks dissolved SiO_2. The SiO_2 concentrations ranged from 10 to 200 mg kg^{-1}, which are much lower than those found under subcritical conditions. Other dissolved species, such as Na, K, Ca, Mg, Al, and Fe, are present in minimal to undetectable amounts. Despite this, SEM analysis of the rock surfaces reveals significant growth of new mineral phases at 400°C and 450°C. These coatings include the minerals albite, andesine, chlorite, and unidentified phases that appear to be amphiboles.

These observations suggest significant mobility of chemical components near the rock surface, although they were not transferred into the bulk fluid. The low concentrations of dissolved cations can be attributed to the low density and dielectric constant of pure water under supercritical conditions (note that SiO_2 is uncharged). This raises the question of how such extensive restructuring of rock components can occur when their concentrations are so low. One possible explanation, which requires further investigation, is the presence of a condensed water layer on the rock surfaces at supercritical conditions.

At 500°C, the pattern of mineralisation changed significantly, with the grains being coated by a semi-continuous layer of cristobalite (Fig. 4c). This suggests that at this temperature, only SiO_2 was notably mobile, while other rock components were unable to mobilise into the low-density fluid. If a condensed layer were present at the lower temperatures, as speculated above, it would appear to have been absent at 500°C.

2.3 Greywacke – Brine Interaction

Two experiments were conducted at 350°C/300 bar and 400°C/250 bar, in which greywacke was reacted with a re-injection brine from a New Zealand power station. In this case, the fluid is expected to dominate the exchange of components between the fluid and the rock due to its high concentrations of dissolved solutes. This scenario could occur, for instance, if a conventional re-injection brine were introduced into a geothermal system at near-supercritical or supercritical conditions.

At 350°C/300 bar, the dominant reaction observed was the dissolution of quartz, which is expected as the re-injection brine was undersaturated with respect to this mineral under these conditions. The rock surface was also coated with newly formed minerals, primarily albite (Fig. 5a). It is important to note that at 350°C/300 bar, the fluid density is approximately 0.7 g cm^{-3}, allowing it to carry significant concentrations of dissolved solutes.

In contrast, at the higher temperature, the rock is coated with newly formed phases, including quartz and at least two unidentified phases that are likely amphiboles (Fig. 5b). At 400°C/250 bar, the density of water is approximately 0.3 g/cm^3. Under these conditions, quartz is undersaturated in the entering fluid, leading to its precipitation.

The implication is that the introduction of a conventional re-injection brine into a supercritical system is not advised as extensive precipitation of secondary mineral phases is expected.

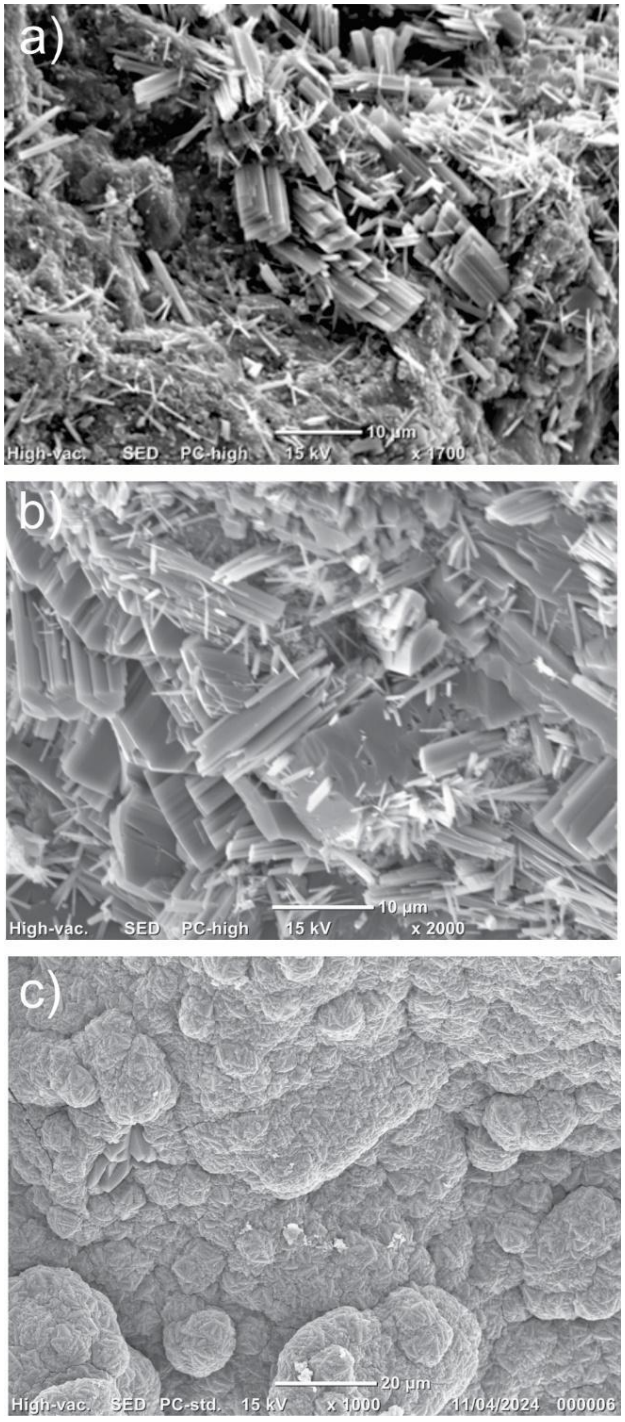


Figure 4: SEM images of greywacke reacted with distilled water at a) - b) 400°C and c) 500°C. At 400°C extensive restructuring of rock components occurred while at 500°C the rock is covered in a monomineralic coating of cristobalite.

2.4 Greywacke – Brine – CO_2 interaction

A single experiment was conducted at 400°C/250 bar, simulating the re-injection of a conventional brine with added CO_2 at a concentration of 2000 mg kg^{-1}. The purpose of this experiment was to evaluate the potential for CO_2 sequestration in the greywacke under supercritical conditions.

In the SEM examination of the rock surface, extensive dissolution and restructuring of rock components were observed (Fig. 6a). The newly formed minerals included albite, anhydrite, and an unidentified phase, likely an amphibole (Fig. 6b). Quartz was not observed as a new mineral phase in this experiment. This suggests that the introduction of high CO_2 concentrations, which would lower the fluid pH, significantly mobilised rock components. Consequently, SiO_2 was consumed in the precipitation of other aluminosilicate phases and quartz remained undersaturated.

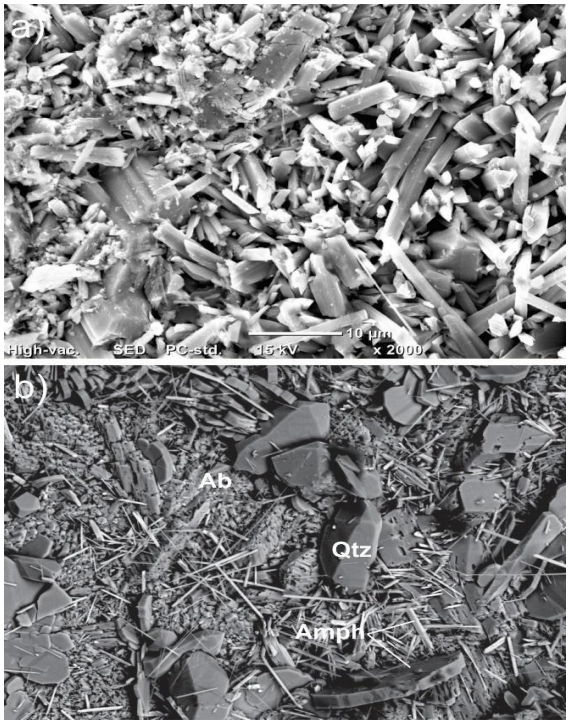


Figure 5: SEM images of greywacke reacted with geothermal brine at a) 350°C and b) 400°C. At 350°C the rock is covered with a coating of primarily albite while at 400°C quartz and two unidentified minerals (Amph) are found.

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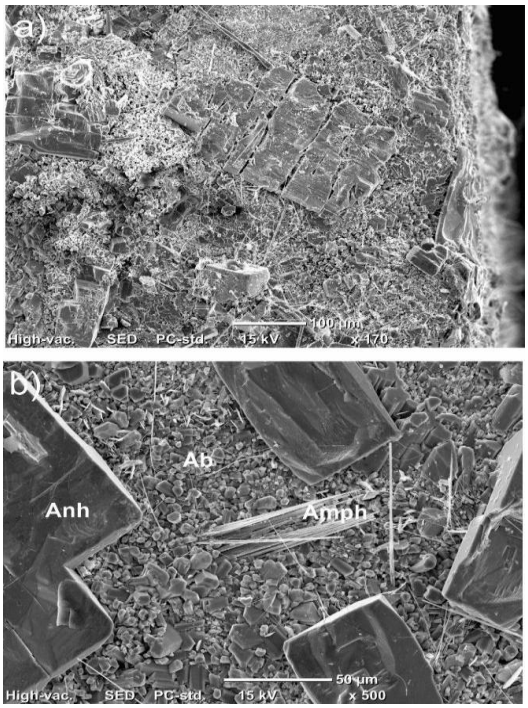


Figure 5: SEM images of greywacke reacted with geothermal brine + CO_2 at 400°C/250 bar. In a) extensive corrosion of the rock surface is observed. In b) newly formed phases include albite (Ab), anhydrite (Anh), and an unidentified phase (Amph).

No carbonate phases were identified in the experiment; however, extensive mobilisation of calcium was observed, as indicated by the presence of anhydrite. This suggests that CO_2 sequestration by greywacke is not an active mechanism under the tested conditions.

3. MINERAL SOLUBILITIES

The measurement of the thermodynamic parameters of key minerals like quartz and anhydrite at supercritical conditions is vital for the design and implementation of supercritical power generation systems. At EGL, we have conducted detailed studies on the solubility of these two minerals under supercritical conditions.

3.1 Quartz

The solubility of quartz in distilled water has been measured within the temperature and pressure range of 375 to 600˚C and 200 to 270 bars (Rendel and Mountain, 2023). This specific temperature and pressure range was selected because it approximates the conditions expected to be found in deep geothermal systems in the Taupo Volcanic Zone. The experiments utilised the supercritical continuous flow reactor (Fig. 3 and 7). The resulting data, which were used to refine the empirical equation of Fournier and Potter (1982), provide valuable data on quartz solubility under these conditions. This had not been previously well-defined.

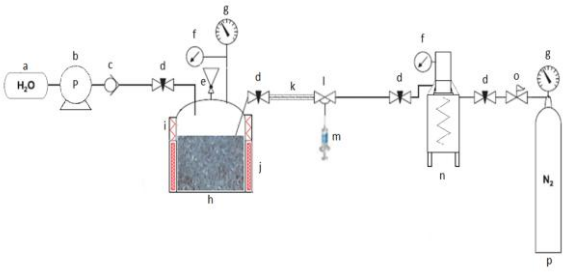


Figure 7: Schematic diagram of the ultra-high temperature simulator: (a) inlet water reservoir; (b) piston pump; (c) check valve; (d) needle valve; (e) rupture disc; (f) pressure transducer; (g) pressure gauge; (h) pressure vessel filled with quartz grains; (i) heating mantle; (j) furnace; (k) cooling loop; (l) back pressure regulator; (m) sampling syringe; (n) syringe pump; (o) pressure regulator valve; (p) nitrogen cylinder.

3.2 Anhydrite

The solubility of anhydrite in distilled water has recently been measured in the temperature and pressure range of 380 to 625°C and 220 to 270 bars (Rendel et al., 2024). The experiments also used the ultra-high temperature reactor (Fig. 3 and 7). Prior to these experiments, anhydrite solubility in this temperature and pressure range had been poorly defined. The new data have been employed to refine the empirical parameters for the Dolejš and Manning (2010) solubility equation.

Figure 8 shows the experimental results at two different scales. Note that the vertical axis is in units of µg kg^{-1}. It is evident that the solubility of anhydrite is extremely low under supercritical conditions reaching less than 1 mg kg^{-1} at 380°C (Fig. 8a). At higher temperatures the solubility is less than 10 µg kg^{-1} (Fig. 8b). The results also demonstrated that the solubility of anhydrite is not congruent under supercritical conditions.

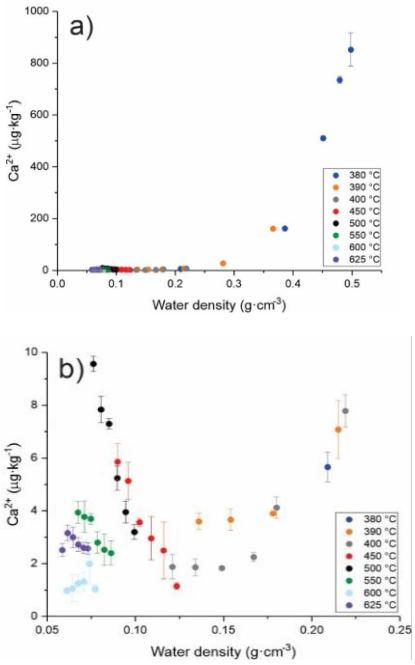


Figure 8: The solubility of anhydrite under supercritical conditions.

Data shown on graphs at two difference scales in µg kg^{-1}.

4. THE GEOTHERMAL PROCESS SIMULATOR (GPS)

The EGL has recently installed a new hydrothermal flow apparatus, the Geothermal Process Simulator (GPS), built by VINCI Technologies, France. This instrument can reach temperature and pressure conditions of 600°C and 500 bar (Fig. 9). It is comprised of two high temperature reactors and two injection pumps. One injection pump is located between the reactors allowing injection of a second fluid into the fluid flow without preheating. The instrument was specially designed for the EGL and will be able to test:

1) pH dosing and its effect on silica scaling rate;
2) the efficacy of chemical injection (anti-scalant/anti-corrosion compounds) in geothermal infrastructure;
3) the effects of brine ± NCG reinjection on reservoir quality and scaling rates;
4) accurate measurement of material stability and corrosion rates at subcritical and supercritical conditions up to 600°C.



Figure 9: The Geothermal Process Simulator (GPS).

5. CONCLUSIONS

The Experimental Geochemistry Laboratory (EGL) at Earth Science New Zealand (ESNZ) has made significant advancements in understanding water-rock interactions under supercritical conditions. Using existing and newly acquired equipment, combined with funding from the Geothermal: The Next Generation (GNG) programme, the EGL has expanded its capabilities to conduct experiments at temperatures up to 700°C and pressures up to 500 bars. With experimental work spanning water-rock interactions, CO_2 re-injection, mineral solubilities, and scaling/corrosion simulations, the laboratory contributes to advancing geochemical understanding and industry practices in the geothermal setting.

ACKNOWLEDGEMENTS

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REFERENCES

Dolejš D. and Manning C. E. (2010) Thermodynamic model for mineral solubility in aqueous fluids: Theory, calibration and application to model fluid-flow systems. *Geofluids* **10**, 20–40.

Fournier, R.O., Potter, R.W. (1982) An equation correlating the solubility of quartz in water from 25° to 900°C at pressures up to 10,000 bars. *Geochim. Cosmochim. Acta*. 46 (1982). https://doi.org/10.1016/0016-7037(82)90135-1.

Passarella, M. (2021). Basalt-fluid interactions at subcritical and supercritical conditions: An experimental study. PhD Thesis, Victoria University of Wellington, Wellington, New Zealand. 362 p.

Rendel, P.M., Mountain, B.W. (2023) Solubility of quartz in supercritical water from 375°C to 600°C and 200-270 bar. Jour. Supercritical Fluids 196. https://doi.org/10.1016/j.supflu.2023.105883

Rendel, P.M., Mountain, B.W., Sajkowski, L. Solubility of anhydrite in supercritical water from 380˚C to 625˚C and 220 bar to 270 bar (in review).