EXPERIMENTAL SIMULATION OF RE-INJECTION OF NON-CONDENSABLE GASES INTO GEOTHERMAL RESERVOIRS: GREYWACKE-FLUID INTERACTION

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ABSTRACT

A laboratory experiment was conducted to simulate fluid-rock interaction between greywacke and geothermal brine containing high concentrations of CO_2 and H_2S at 200°C and 35 bars.

The apparatus consisted of a high T-P continuous flow through simulator containing 350 – 500 µm greywacke fragments. The experimental fluid consisted of low pressure separator brine with a dissolved mixture of $CO_2/H_2S/H_2$ (96/4/0.01%). The total experimental time was 66 days. Effluent samples contain high concentrations of CO_2 and H_2S averaging 4000 mg kg^{-1} and 70 mg kg^{-1}, respectively. The pH values during the room T period averaged ~6.2 while after temperature increase to 200^oC they decreased to approximately 4.5 – 5.0. Silica concentrations remained between 700 - 900 mg kg^{-1}.

Upon completion of the experiment, the rock was examined for effects on its geochemistry and mineralogy by XRD and SEM-EDS analysis. Pyrite and calcite were identified as secondary run products by XRD. SEM-EDS examination showed considerable corrosion of ferromagnesian phases and pyrite precipitation from the released ferrous iron. Fluid chemistry demonstrates equilibrium with calcite and pyrite. The distribution of secondary phases suggests that reaction rates are rapid; however, aluminosilicate minerals appear not to have reached full equilibrium.

1. INTRODUCTION

The development of high enthalpy geothermal systems has contributed significantly to the production of renewable energy using the earth’s heat while at the same time having minimal environmental impact.

Geothermal fluid contains many components including dissolved gases mainly CO_2 and H_2S. The gases are dissolved in the fluid at reservoir conditions and partition into the steam phase during boiling. After the steam passes through the turbine, it is condensed leaving these gases as a non-condensable gas (NCG) mixture. The NCG consist mainly of CO_2 and H_2S with smaller quantities of other gases including CH_4, N_2 and H_2, as well as traces of He, Ar, Ne and NH_3. The proportion of each gas varies from one field to another, and sometimes from well to well within the same field. The gas content (by weight) in geothermal fields varies from almost zero in some liquid-dominated fields, for example Wairakei (New Zealand), up to 10% by weight in dry steam fields such as Larderello (Italy) and can be as high as 15% by weight in some fields.

The presence of NCG in geothermal steam degrades the performance of the turbine and condenser. Michaelides (1980, 1982) showed that the gases have a twofold effect on the power produced:

- Their presence decreases the exergy of fluid, thus reducing the available work in the installation;
- The extraction of the gases from the condenser requires the consumption of work by gas ejectors, compressors or pumps.

Moreover, the presence of NCG also reduces the heat transfer coefficient of the heat exchangers and requires a larger surface area than a similar load liquid phase heat exchanger.

The common industry practice is to release the NCG to the atmosphere upon extraction from the condenser. However, with the introduction of tight air quality standards in many countries, along with the United Nations carbon tax credit system to reduce greenhouse gas emissions, it has become an attractive option to re-injection the NCG. The re-injection of NCG has been implemented (Brawley, Coso, Galena and Puna) and/or being considered by several geothermal power developers (Juliusson *et. al.*, 2015) as it provides several advantages including:

- An environmentally friendly way for the disposal of NCG;
- Silica scaling prevention when mixed with silica saturated brine;
- Provide pressure support to the geothermal reservoir;
- Cost saving from not having an H_2S abatement system.

However, the impact of NCG re-injection on the geothermal reservoir can include breakthrough to production wells and the reaction (dissolution) of reservoir rock. The degree in which this fluid-rock interaction occurs is not very well understood. This work investigates and attempts to quantify these fluid-rock interactions to better understand the impact of NCG re-injection on rock and the reservoir permeability.

To achieve this goal we have used an experimental approach to simulate (at a small scale) the fluid rock interaction between greywacke rock and geothermal brine containing high concentrations of dissolved CO_2 and H_2S.

2. EXPERIMENTAL APPROACH

The experimental apparatus (Fig. 1 and Fig.2), located at the Wairakei Research Centre, GNS Science, allows simulation of fluid-rock interaction at temperatures and pressures up to 400°C and 500 bars (Sonney and Mountain, 2013). Continuous flow is achieved by a computer-controlled double-piston pump with a flow rate range of 0.001 - 15 ml min^{-1}. The pump system injects distilled water into a cylindrical titanium accumulator containing a movable piston. The experimental fluid is located above the piston which isolates it from the distilled water. As distilled water is injected below the piston by the metering pump, the experimental solution is forced out and through the experimental apparatus. This set-up prevents the experimental solution from coming in contact with the stainless steel metering pump. The rock material is enclosed in a titanium pressure vessel externally-heated in the high temperature oven. After passing through the pressure vessel the fluid exits via the digital back pressure regulator and collects in a disposable plastic syringe. The exit tubes from the pressure vessel are heated to prevent silica scaling.

The rock used in the experiment was Late Jurassic/Early Cretaceous Manaia Hill Group greywacke sourced from the Waotu quarry 56 km southeast of Hamilton, New Zealand. It consists of clasts of siltstone, basalt, quartz, plagioclase, pyroxene and hornblende in a matrix of quartz, feldspar, chlorite, illite, calcite and pyrite. It was chosen as it is similar to the basement greywacke in the geothermal areas of the TVZ a common lithology of the re-injection aquifers in the Taupo Volcanic Zone. The rock was crushed and sieved to retrieve the 355 - 500 µm size fractions. This was cleaned several times in an ultrasonic bath using distilled water. The pressure vessel contained 23.7 g of greywacke. The fluid utilised was low pressure separator brine from a New Zealand geothermal power station. At the start of the experiment, 1.5 liter of brine was de-oxygenated using high purity N_2 containing 100 mg kg^{-1} H_2. The NCG mixture was provided by an external tank containing $CO_2/H_2S/H_2$ (96% / 4% / 0.01%) at 6 bar. The NCG were added by the following procedure (Fig. 3):

1. Approximately 800 ml of de-oxygenated brine was drawn into the chamber of the accumulator by withdrawing the piston (Fig 3a);
2. The NCG mixture was attached to the accumulator and the tubing was evacuated;
3. Approximately 200 ml of gas mixture was then drawn into the accumulator by withdrawing the piston (Fig. 3b);
4. The fluid/gas mixture was then compressed to experimental pressure (35 bar) to dissolve the gases into the brine (Fig. 3c);
5. Due to the high gas concentration, a strong density gradient is created and the gas does not mix evenly through the brine. In order to mix the gas, the accumulator was removed and inverted which was sufficient to cause mixing (Fig. 3d).

A thorough mixing of the gas was confirmed by relatively constant fluid: gas ratio in the effluent syringe. This procedure was repeated once during the experiment in order to refill the accumulator. Fluid flow at 1 ml hr^{-1} was initiated at room temperature and 35 bar. This was maintained for six days after which temperature was increased to 200°C. After 38 days the flow rate was changed to 0.5 ml hr^{-1} to test for equilibrium. The total experimental time was 66 days.

Effluents were analysed for Li, Na, K, Mg, Ca, Sr, Mn, Fe, As, Al, B, and Si with inductively coupled plasma-optical emission spectroscopy (ICP-OES); Cl^- and SO_4^- with ion chromatography (IC). Detection limits vary between elements: Li, 0.01; Na, 0.8; K, 0.9; Mg, 0.01; Ca, 0.05; Sr, 0.003; Mn, 0.007; Fe, 0.08; As, 0.015; Al, 0.15; B, 0.3; Si, 0.6; Cl^-, 0.04 and SO_4^-, 0.1 (mg kg^{-1}). CO_2 was analysed by back titration (>20 mg kg^{-1}) and H_2S by methylene blue reaction and UV-Vis spectroscopy (>0.01 mg kg^{-1}). X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the mineral/chemical composition of the reacted material.

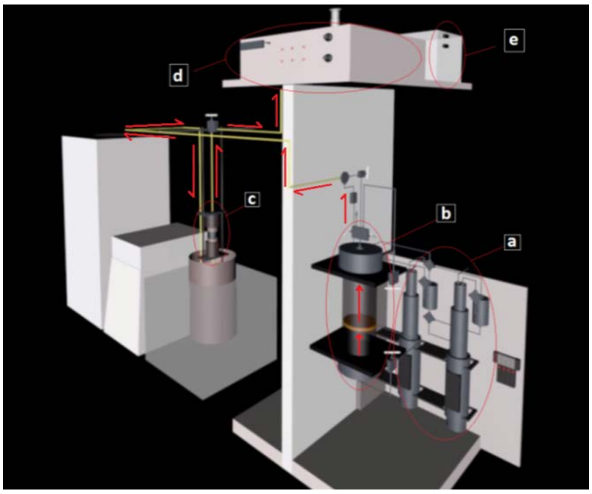

Figure 1: 3D view of the high temperature-pressure hydrothermal apparatus and its components: (a) double piston pump; (b) accumulator containing the metal piston below which distilled water is pumped and above which contains the experimental fluid; (c) pressure vessel containing rock material which is surrounded by the oven; (d) back pressure regulator control unit; (e) back pressure regulator.

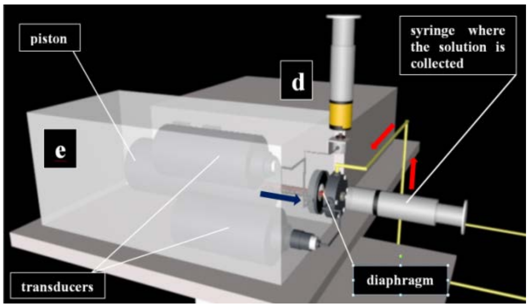

Figure 2: 3D view of the (d) digital back pressure regulator controller and (e) back pressure regulator used to maintain fluid pressure the experiment.

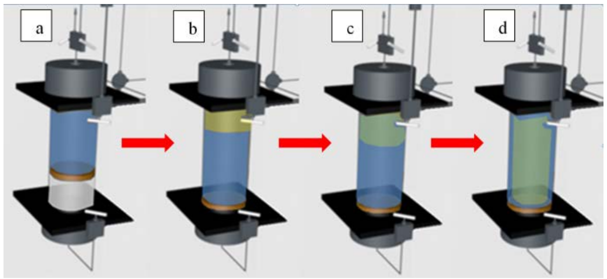

Figure 3: 3D view of the titanium accumulator showing different steps used to dissolve the NCG mixture into the brine: a) filling with de-oxygenated brine to 800 ml; b) filling with NCG mixture; c) compression of gas-brine mixture; d) inversion and mixing of combined fluid.

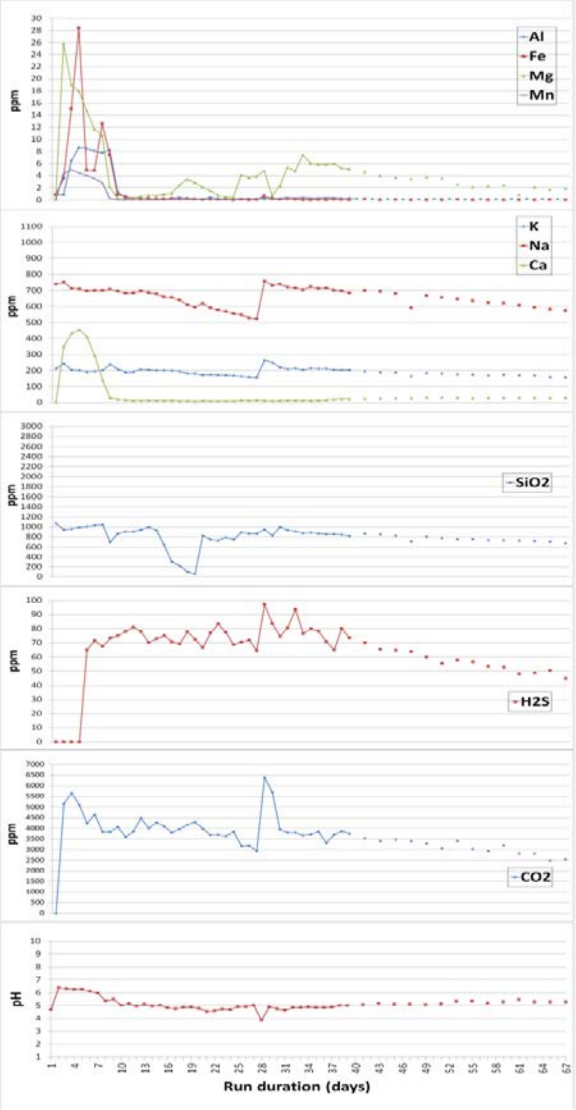

Figure 4: Effluent chemistry from greywacke-NCG brine experiment plotted versus experimental time. Dashed line (1.0 ml hr^{-1}), Dotted line (0.5 ml hr^{-1}).

3. RESULTS

3.1 Greywake – geothermal brine/NCG

The geothermal brine had an initial pH of 5.0. It contains high concentrations of Fe, Mg, Mn, Ca and Al, intermediate concentrations Bi and As and high concentrations of SiO_2, Na and K are expected for a low pressure separated geothermal brine. SiO_2 concentration was 1120 mg kg^{-1}. The first six days of the experiment was conducted at 25˚C. Ca concentration increase rapidly from 4 mg kg^{-1} to 450 mg kg^{-1} with a concomitant increase of pH to stable values of ~6.2. Al, Mg, Mn and Fe all became detectable in the fluid because of simple leaching. K, Na, B, Li values instead remained stable.

After the temperature was shifted at 200˚C there was a sharp drop in pH up to a stable value of ~5.2 while the solubility of SiO_2 drop to 702 mg kg^{-1} and stayed stable between 700 and 900 mg kg^{-1} up to the end of the experiment. After 13 days from the increase of temperature there was a large decrease due to silica scaling in the apparatus. This caused a block in the tubing and required replacement to continue the experiment. Up to 28 days it is noticed that K, Na, B, and Li all decrease continuously. This is an experimental artifact caused by distilled water leaking past the piston and into the brine. Ironically, this defect allows one to determine which elements are being buffered by mineral reactions. Note that other dissolved components do not display this continuous decrease including Mg, Ca, SiO_2, H_2S and CO_2. This is evidence of mineral buffering. After refilling the accumulator at 28 days (note increase in Na and K) Al, Fe, Mg, Mn and As below the detection limit; K, Na, B and Li decrease slowly over the remainder of the experiment. Ca concentration drop significantly to 28 mg kg^{-1} and then rose slowly over the experiment. CO_2 and H_2S concentrations were relatively constant in solution for all the duration of the experiment averaging 3200 mg kg^{-1} and 70 mg kg^{-1} respectively. Both appear to decrease slightly over the last 25 days. High picks in concentration and low pH in the twenty-eight day are due to the refilling of the accumulator with new geothermal brine. Changing in flow rate from 1 l/hr to 0.5 ml/hr at 40 days did not affect dissolved component concentrations or pH, confirming a steady state was achieved (Fig.4).

SEM-ESD examination of fresh unreacted greywacke showed clean surfaces composed of sedimentary clasts surrounded by a fine-grained matrix of clay mineral, quartz, albite, illite and minor opaque minerals (Fig. 5a). Reacted grains showed significant dissolution of the primary mineralisation (Fig. 5b). Most effected were the ferromangnesian mineral phases including chlorite and pyroxene (Fig. 6a,b). Many reacted mineral surfaces were covering in coatings of pyrite (confirmed by XRD). Of note was the higher density of pyrite coatings on ferromagnesian phases and on the matrix of the greywacke (Fig. 7a – c). Of note, many ferromagnesian clasts had significantly higher concentrations of pyrite crystals than their surrounding matrix (Fig. 8a –c), indicating the released ferrous iron had limited mobility in the presence of high concentrations of hydrogen sulphide.

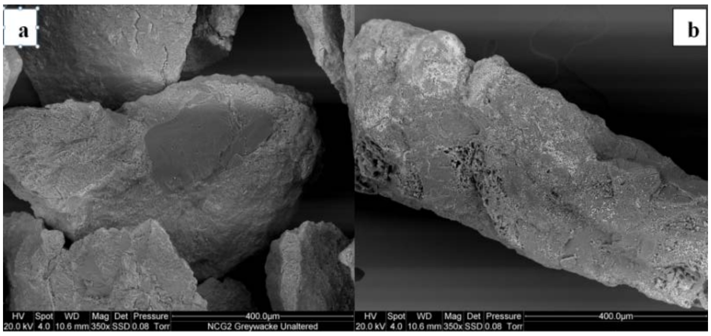

Figure 5: Back scatter electron photomicrographs of (a) unreacted grain of greywacke showing a large quartz clast surrounded by finer matrix and (b) reacted grain of greywacke showing pyrite crystals (bright spots) and dissolution cavities in ferromagnesian minerals.

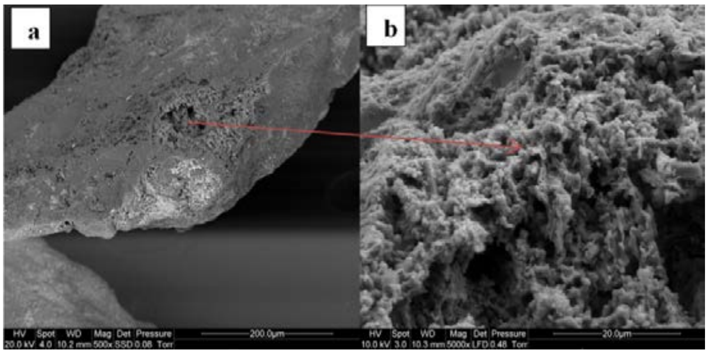

Figure 6: Photomicrographs of a reacted grain (a) in detail (b) a clast of heavily corroded chlorite.

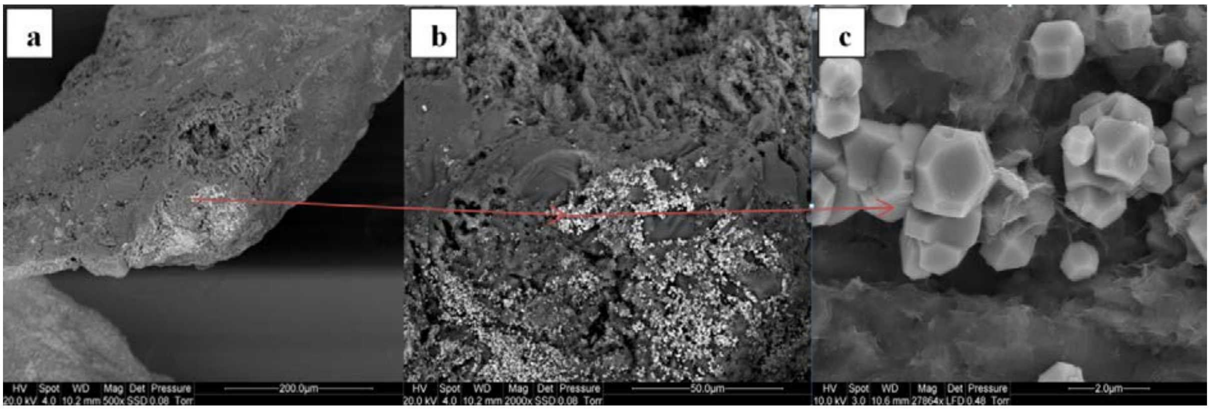

Figure 7: Photomicrographs of the same reacted grain of Fig.6 (a) with evident pyrite formation in bright spot where the iron is accumulated due to the partial dissolution of greywacke matrix (b); crystals of pyrite (c).

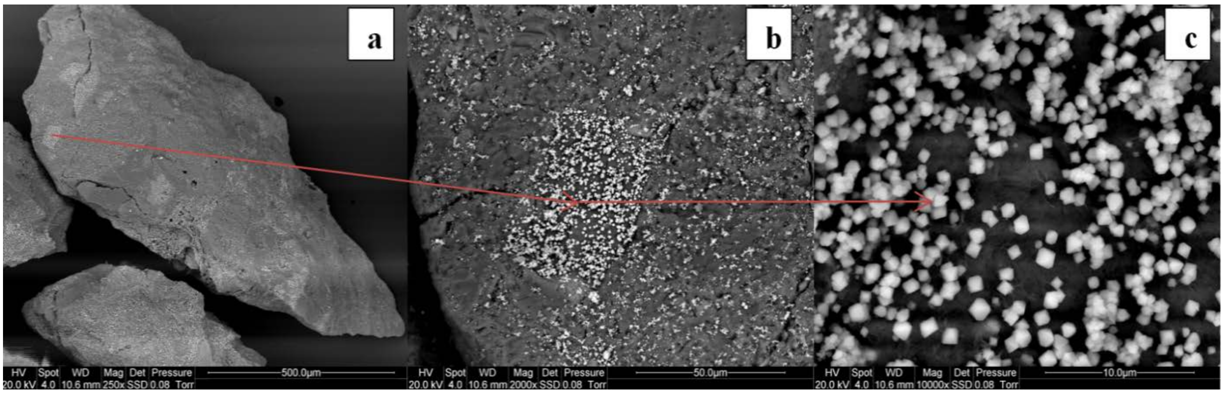

Figure 8: Photomicrographs of (a) an altered grain. In detail showing a clast of pyroxene (b) densily covered by pyrite (c).

4. DISCUSSION

The addition of high concentrations of CO_2 and H_2S to the brine means that fluid pH decreases, i.e.,

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$
$$H_2CO_{3(aq)} \leftrightarrow HCO_3^{-} + H^+$$
$$HCO_3^{-} \leftrightarrow CO_3^{--} + H^+$$

$$H_2S_{(g)} \leftrightarrow \mathrm{H}_2S_{(aq)}$$
$$\mathrm{H}_2S_{(aq)} \leftrightarrow HS^- + H^+$$

At room temperature, the acidifed fluid reacts rapidly with any carbonate or sulfate minerals in the greywacke resulting in elevated concentrations of Fe, Mg, Mn and, particular, Ca through the carbonate dissolution reaction attributed to carbonate dissolution with production of OH^-

$$CaCO_3 + H_2O \leftrightarrow Ca^{2+} + HCO_3^{-} + OH^{-}$$

Cation exchange reactions between feldspars, clays, etc. can also contribute to modification of cation concentration, as well as, rapid dissolution of fine material. Taken together these reactions cause the pH to rise to values above 6.0 (Fig.

After temperature has been increased to 200°C, behavior of the major elements including SiO_2, Al, Ca, and Mg, is controlled by the precipitation of clay mineral or zeolite phases. Although we did not observe any zeolites there were coatings of an unknown Ca-aluminosilicate phase (resembling smectite) found in the SEM. Calcite and magnetite were also identified as secondary phases by XRD but was only rarely observed by SEM.

On observation that was quite evident was the corrosion of the ferromagnesian phases including chlorite (clasts and in the matrix) and pyroxene and basalts clasts. The high density of pyrite precipitation on the clasts and in the matrix indicates that high carbonic acid concentrations led to ferromagnesian mineral dissolution. The release ferrous iron was then quickly fixed by dissolved sulfide to form pyrite by the reaction

$$Fe^{2+} + 2HS^- \leftrightarrow FeS_2 + 2H^+$$

The proximity of the precipitated pyrite to its iron source and not on other phases such as quartz, and the lack of detectable iron in the effluent samples, indicates that the reaction rates were relatively fast.

Activity-activity diagrams for Ca-Na-K aluminosilicate minerals at 200˚C and 35 bars are shown in Fig.9a-f. The diagrams show that fluid SiO_2 concentrations are close to amorphous silica saturation although we did not observe any obvious amorphous silica precipitates. In K^+/H^+-SiO_2, Ca^{2+}/H^{+2}-SiO_2, K^+/H^+-Na^+/H^+ and Na^+/H^+-SiO_2 space fluid compositions lie within the stability fields of end member zeolites phases (clinoptil-K and mordenite-Na) consistent with the findings of Sonney and Mountain (2013); however, we did not find any zeolite phase in SEM examination. In Fig. 9b, both at 1 ml hr^{-1} and 0.5 ml hr^{-1}, the fluid composition has achieved calcite saturation which was confirmed by XRD analysis.

Fig. 9f, drawn assuming SiO_2 activity in the fluid is controlled by quartz; it is evident that Na and K concentrations lie along the metastable extension of the albite-k-feldspar join. Given the abundance of these minerals in the original greywacke this could be expected and that total equilibrium has not been attained between the aluminosilicate phases.

5. CONCLUSION

The high T-P hydrothermal apparatus has been used to simulate the interaction between greywacke and geothermal brine containing high concentrations of CO_2 and H_2S at geothermal conditions.

The fluid was prepared by using a mixture of non-condensable gases (including CO_2, H_2S and H_2) with low pressure separator brine. Thorough mixing was confirmed by relative constant fluid:gas ratios in the effluent syringe and from low pH values of the solution.

During the first week of fluid-rock interaction at room temperature, carbonate dissolution resulted causing elevated Ca concentrations in solution as well as higher pH values (~6.2). Upon temperature increase to 200˚C, SiO_2 concentrations remained between 700 and 900 mg kg^{-1} and pH dropped to approximately 4.5 – 5.0. Elements including Na, K, Li, Ba behaved conservatively.

SEM-EDS analysis showed an accentuated dissolution of the primary mineralization especially of ferromagnesian minerals such as chlorite and pyroxene. All the Fe^{2+} was fixed as pyrite by the reduced sulfur in the solution. Activity-activity diagrams show that the fluid compositions lie within the clinoptilolite and mordenite-Na stability field which may be a proxy for the zeolite phase. From geochemical calculations the fluid achieved calcite saturation, confirmed by XRD.

The experiment demonstrated the utility of this simulation to interpret reaction occurring in aquifer during re-injection of geothermal brine high in CO_2 and H_2S. This helps to have a better understanding on the behavior of these substances in terms of capture and new mineral formation in greywacke.

The experimental approach demonstrates the potential of real time simulation using representative fluids and rocks to overcome some of the deficiency of thermodynamic and kinetic data used in reservoir simulation. The best approach is a combination of both types of studies to give the most comprehensive outcome.

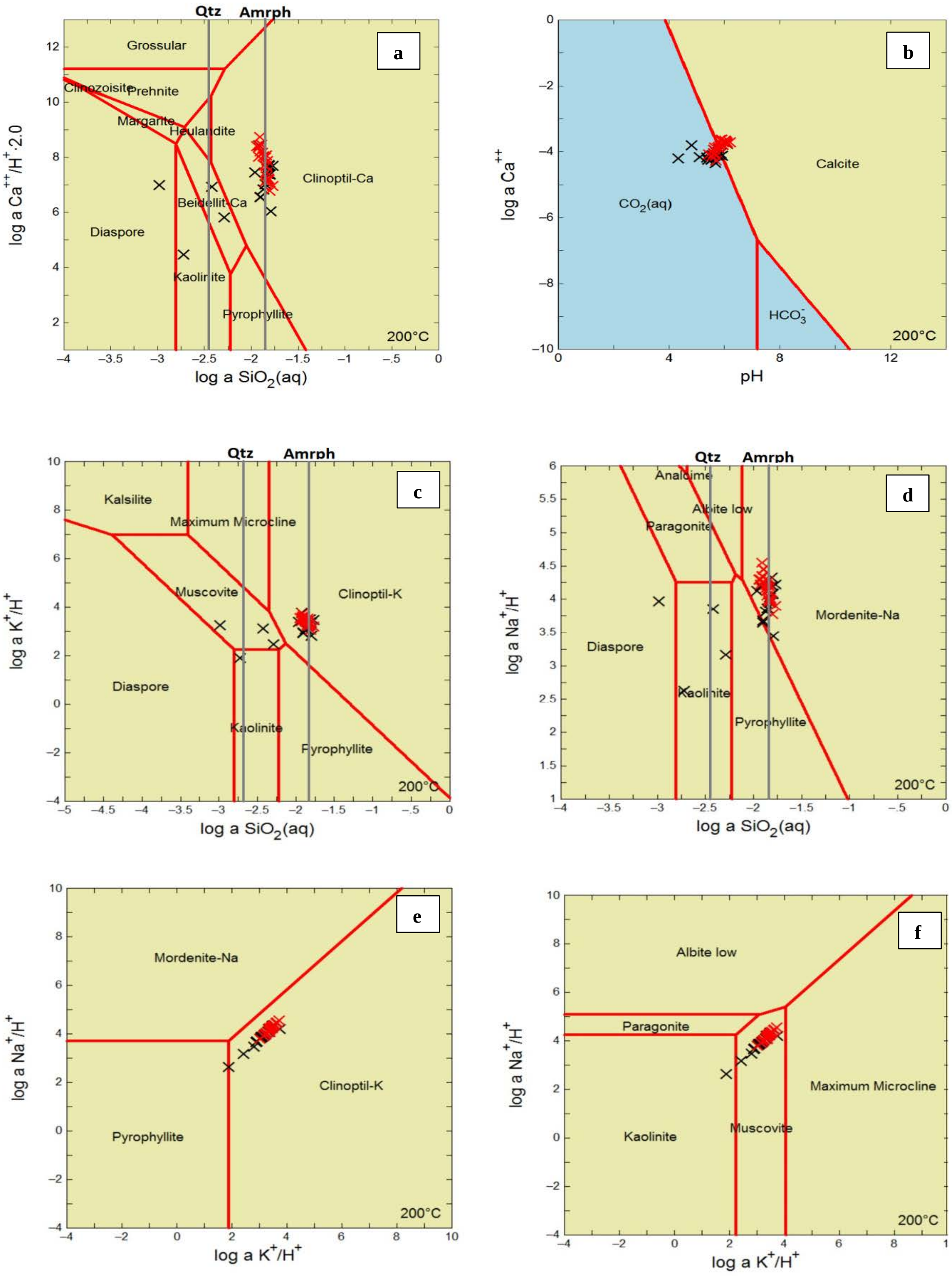

Figure 9a-f: Activity-activity diagrams at 200°C and 35 bars. Black and red crosses show activity ratios in the experiment effluents from greywacke fluid-rock interaction at 1ml hr^{-1} and 0.5 ml hr^{-1} respectively. Grey vertical lines show quartz and amorphous silica saturation. Graph (f) has been drawn assuming SiO_2 activity in the fluid is controlled by quartz.

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