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LABORATORY SIMULATION OF GRANITE-FLUID INTERACTIONS UP TO SUPERCRITICAL CONDITIONS

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ABSTRACT

As a viable resource, any developed Hot Dry Rock (HDR) system must be long-lived, and the chemistry of its fluid-rock interaction processes understood; both for maintaining fluid pathways and field management. We used a recently developed tube-type, flow-reactor system (Bignall *et al*., 2000) to simulate reaction processes in a hypothetical HDR geothermal system, operating at sub-critical to supercritical conditions. Our goal is to elucidate dissolution-deposition processes and the character of induced and natural fractures in the HDR hydrothermal system, both for energy extraction and *in-situ* production of hydrothermal synthetic materials. Two pre-heated (hydrothermal) fluids, (i) deionised (unmineralised) water and (ii) a moderately saline (~1200 mg/kg Cl, ~60 mg/kg Si), mildly acidic fluid, have been reacted with unaltered granite in the flow-type reactor system, at a range of temperatures (up to 425°C), and typical operating pressures of 15-25MPa. Output solutions were analysed, after interaction with the 'reservoir' (granite) rocks, by ICP-AES and AAS techniques and show, for a 400°C/20MPa/H_2O experiment, that an 'apparent equilibrium' fluid is produced, with a major element chemistry of 140ppm Si; 7.1ppm Al; 0.09ppm Fe; 0.03ppm Mg; 0.07ppm Ca; 7.0ppm Na; 5.2ppm K. Zones of granite weight gain/loss, as a result of fluid-rock interactions reflect shifts in Kw, dielectric constant and fluid density, in response to changes in fluid composition and the thermal regime. Dissolution of quartz, feldspar and ferromagnesian mineral phases occur in the zone where temperatures are <340°C, where SEM examination reveal primary minerals have a pitted appearance, although in this zone there is also minor deposition of sericite. In the zone where the thermal regime is between 360°C and about 380°C, there is a strong weight gain, characterised by deposition of quartz and subordinate secondary albite. In zones where the temperature is higher, at >390°C, there is little net weight change, with re-mobilisation of quartz producing minor dissolution of primary crystals, but also occurrence of secondary quartz, together with some sericite and chlorite(?). Our laboratory studies demonstrate that host rock characteristics, fluid chemistry, flow rate, temperature and the temperature gradient are all important factors in dictating mineral dissolution and/or precipitation processes, as well as the condition of the fracture-pathways.

1. INTRODUCTION

The productive lifetime of most conventionally developed geothermal systems is no more than 25 years. A decline in mass output, field temperatures and/or pressures, or a combination of these and other factors, will eventually result in insufficient steam being able to be profitably supplied to the power station, to produce electricity. For this reason, much interest has been shown in developing Hot Dry Rock (HDR) systems, which may compliment 'conventional' geothermal programmes. To be a viable energy option, the developed HDR system must be long-lived, and the chemistry of its fluid-rock interaction processes understood, both for maintaining manageable operating conditions, as well as for the formation and preservation of fluid pathways.

Numerous studies have attempted to model geothermal reservoir conditions, and simulate fluid-rock interactions as a range of pressures and temperatures, using a variety of autoclave systems/reaction vessel experiments (e.g., Savage *et al*., 1986, 1992; Chigira and Watanabe, 1994; and Watanabe *et al*., 1995). Less attention has been paid to the laboratory simulation of interaction processes at the optimum range of temperatures and pressure that an HDR system could operate; that is, at supercritical conditions, under 'flowing' conditions.

This paper reviews granite-fluid interaction experiments at the Research Laboratory of Hydrothermal Chemistry, which have been conducted as part of the 'Research Project on Supercritical Subsurface Boiler", to simulate chemical interaction processes in a hypothetical HDR system. These experiments have been undertaken at sub- to supercritical conditions; using a recently developed flow-through autoclave apparatus which may operate at temperatures of up to 425°C, and pressures of up to 40MPa (Bignall *et al*., 2000).

In examining the interaction processes between supercritical fluids and host (reservoir) rocks, we have aimed to elucidate water/rock interactions during heat extraction in a developed HDR hydrothermal system.

2. METHODOLOGY

Unaltered Iidate Granite, from Fukushima-ken, Northern Honshu, was used in our experiments. The Iidate Granite consists of an interlocking arrangement of medium grained quartz, orthoclase and albite, with subordinate plagioclase and biotite, and various accessory minerals. The mineral content (by volume %) and major element chemistry (wt%) of Iidate Granite is shown in Table 1.

Experiments were conducted in a flow reactor (Figure 1; Bignall *et al*., 2000), typically operating at 15-25MPa, with a thermal gradient and maximum temperature of 425°C (recent modifications now allow operative conditions as high as 500°C and 50MPa), using either deionised water, or a moderately saline fluid (Table 2).

The flow system consists of a central, 1 metre-long reactor tube, designed for modeling the geothermal reservoir, a pre-heat autoclave, pump (with flow rates up to 10ml/min) and sample container. Five heaters are placed around the central reactor, which may be individually controlled, to produce a desired temperature gradient.

The flow reactor tube has an internal volume of 500cm^3, with a cross-sectional area of 5cm^2. The granite was crushed and sieved, with a size fraction of 4-8mm collected, ultrasonically cleaned with deionised water, and dried at 80°C for 24h. Calibration tests were initially performed with 'used' granite chips (later replaced by unaltered samples), with five thermocouples located inside the length of the tube reactor. Porosity in the tube was estimated to be about 35%. In the actual experiments, approximately 700g of fresh granite was reacted for up to 200 hours (average of 100 hours), at 1.0 ml/min.

Weighed granite blocks and polished plates (for XRD and/or SEM analysis) were placed within the tube reactor, so weight change could be assessed, and mineral textures examined. The chemical composition of output solutions collected from the reactor were analysed for Si, Ca, Mg, Al and Fe using ICP-AES, and Na and K using atomic absorption techniques.

3. RESULTS

A thermal gradient is set up in the central reactor tube, with interactions at 20MPa (for experiments described here) able to occur over a range of temperatures (e.g., for the 400°C experiments, the five external heaters enveloping the central flow autoclave were set to produce internal temperatures of 250°C (at inlet), 360°C, 375°C, 400°C and (at outlet) 400°C).

The flow direction for the 400°C experiment was from the 250°C zone to the higher temperature, 400°C zone.

3.1 Weight Change

The weight change of granite samples from the 400°C and 425°C experiments, using deionised water and saline solutions, is shown in Figure 2, together with summary data from an experiment undertaken using similar apparatus and operating conditions at 250-350°C, from Wang *et al*., 1996.

The dissociation capacity of hot water is directly related to the ion product, which has a maximum value around 350°C (i.e. slightly below the critical point for pure water), under saturated vapour pressure, and decreases with decreasing ion product above 340°C. Our operating pressure was higher than the corresponding saturated vapour pressure, which results in a shift in the maximum value of the ion product with higher temperatures.

The mineral species in the unaltered granite, particularly quartz and feldspar, are most readily dissolved in the 250-360°C temperature range, which corresponds to a zone of maximum weight loss in our samples.

Saturated solutions, carrying material dissolved from granite where fluid-rock interactions are occurring at <360°C, flows into parts of the flow reactor where the temperature is >360°C. At the latter conditions, the ion product is not as high, and deposition of secondary minerals results, notably secondary quartz, although minor albite and sericite was noted in some samples, with a corresponding weight gain in that zone.

In the 200-350°C experiment of Wang *et al.* (1996), maximum weight loss occurred where the reaction temperature was about 320-330°C, whilst above 340°C a small weight gain, indicative of mineral deposition.

In the high temperature part of our flow reactor experiment, where temperatures exceed about 390°C, there is little apparent change in mass of the granite samples, although some re-mobilisation of silica is clearly evident, since quartz crystals are pitted and there is some deposition of quartz and other secondary minerals.

3.2 Fluid Chemistry

The chemistry of output solutions from representative 400°C and 425°C flow reactor experiments, with starting solutions being either deionised water or a saline fluid, are shown in Figures 3-5.

The major element chemistry of output solutions from the 400°C, 20MPa flow reactor experiment, using deionised water as starting solution, is shown in Figure 3.

An initial period of heating of 1.5 to 2 hours is required for the five heaters to attain their intended operating temperature. During this period, thermal expansion of fluid in the reaction tube results in a rapid increase in the internal pressure of the system, with the output volume of reacted fluid exceeding the amount pumped into the system. After 1.5 hours the major element concentrations of the reacted fluid reaches a maximum, but later, after re-equilibration of the system, there is little variation in the major element chemistry of output solutions, so after about 12 hours the system attains an 'apparent' equilibrium condition.

Figure 4 shows comparative major element concentrations of output solutions from the 400°C, 20MPa flow reactor experiments (over the initial 60 hours), using deionised water and the saline fluid. These curves show a similar pattern and reflect the chemistry of the initial (starting) 'hydrothermal' fluid. In each case, an 'apparent' equilibrium condition is reached, after which the chemistry of the output solution is little changed (Table 3).

A comparison of output solutions, using deionised water, for the 400°C and 425°C experiments is shown in Figure 5, together with summary data for the 200-350°C experiment conducted by Wang *et al*., 1996.

3.3 Secondary Mineralogy

Granite samples in the 'inflow' part of the flow reactor (i.e. where temperatures are between 250°C and 360°C) occur in a 'weight loss' zone, and contain quartz and feldspar crystals that have a pitted appearance (Figure 6). The feldspar grains are strongly altered, with sericite infilling spaces in the crystals, whilst primary quartz have numerous microfractures.

In the central part of the reaction column, where the internal temperature is <400°C, there is a strong weight gain, reflecting the precipitation of quartz and secondary albite, and lesser amounts of sericite, which deposits into fractures, cleavage planes, on feldspar surfaces and in intergranular spaces. The precipitation of secondary quartz in this zone, reflects its solubility under the prevalent physical conditions; taking into account fluid density and the thermal regime.

In the 'upper' (400°C) zone, a small weight loss is indicated, with dissolution of feldspar (Figure 7) and ferromagnesian phases and microfracturing and alteration of primary quartz, being matched by precipitation of minor secondary quartz, sericite (Figure 8), chlorite(?) and trace calc-silicate phases (Figure 9). The decreased rate of dissolution of mineral species in the 400°C zone corresponds to lower Kw values and a preference for some mineral species to precipitate under these physical and chemical conditions.

4. DISCUSSION

The character of hydrothermal solutions, and their fluid-rock interactions, vary according to the physical P-T conditions, as well the chemical (salt) composition of the fluid. The value for the ionic product, low Kw, has a maximum value in pure water of 10-11 at 250-300°C, under saturated vapour pressure, but decreases above about 350°C, with resultant deposition. The Kw value, and dielectric constant change in response to a shift in fluid composition, whilst the vapour pressure will decrease and critical point will increase with an increase in salt concentration.

Such factors have a large influence on fluid-rock interaction processes, and the degree to which dissolution-deposition reactions will proceed in a HDR hydrothermal system.

These effects, and their implications for the exploitation of HDR systems as an energy resource are poorly understood. Whilst numerous studies of dissolution-deposition processes at equilibrium conditions have been undertaken using batch-type autoclave systems, less work has been conducted for multicomponent systems under non-equilibrium 'flowing conditions'.

We have found that fluid-rock interactions, are affected by several factors, not only temperature (and thermal gradients), pressure and compositions of the hydrothermal fluid and the type of reservoir rocks, but the flow rate of the hydrothermal fluid, shape and width of the fracture surface/permeable channel and condition of the fracture/mineral surfaces.

In a developed HDR system, the nature of induced fractures will change in shape and form, by the interaction of injected (heated) fluid, which is mixed with hydrothermal (reservoir) fluids, and the host rocks. This is an important consideration for controlling heat extraction for electricity generation, and other potential applications of HDR resources. Increasing thermal efficiency and utilizing HDR energy resources in the subsurface setting, where the geothermal energy is actually stored, will minimize energy loss, both for electricity generation and for related technologies.

We have used the flow-reactor system to demonstrate that there is little net weight change of granite samples under conditions of about 400°C and 20MPa, and that whilst there is some re-mobilisation of silica, dissolution (of primary minerals), this is balanced by precipitation of quartz, sericite and other secondary minerals. The problem of (mainly) silica deposition around 350°C requires further consideration.

Our observations support the contention that an HDR system might be developed at near supercritical conditions, and by taking into account mechanisms of mineral dissolution and/or precipitation we may deduce the optimum physical and chemical conditions whereby induced and natural fracture-pathways can be maintained.

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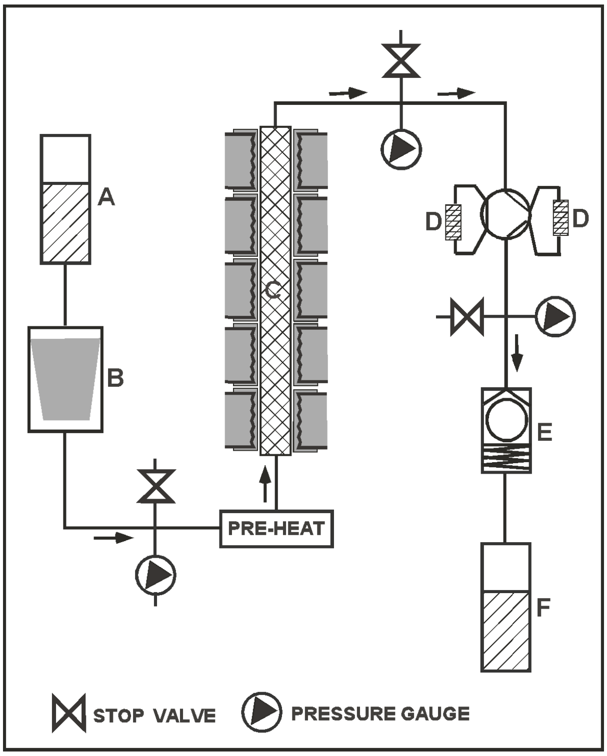

Figure 1. Schematic illustration of the HDR flow reactor-autoclave system. A: Tank for starting solution; B: Pump; C: Central autoclave with five external heaters; D: Filter System; E: Pressure regulator; F: Sample Solution. Arrow shows direction of fluid flow.

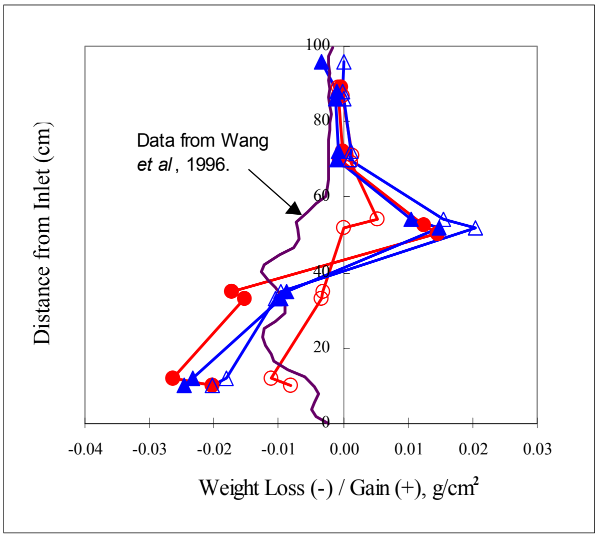

Figure 2. Weight change after fluid-rock interactions. Symbols: ● H_2O starting solution; O 400°C, NaCl starting solution; ▲ 425°C, H_2O starting solution; Δ425°C, NaCl starting solution; - 350°C, H_2O starting solution (after Wang *et al*, 1996).

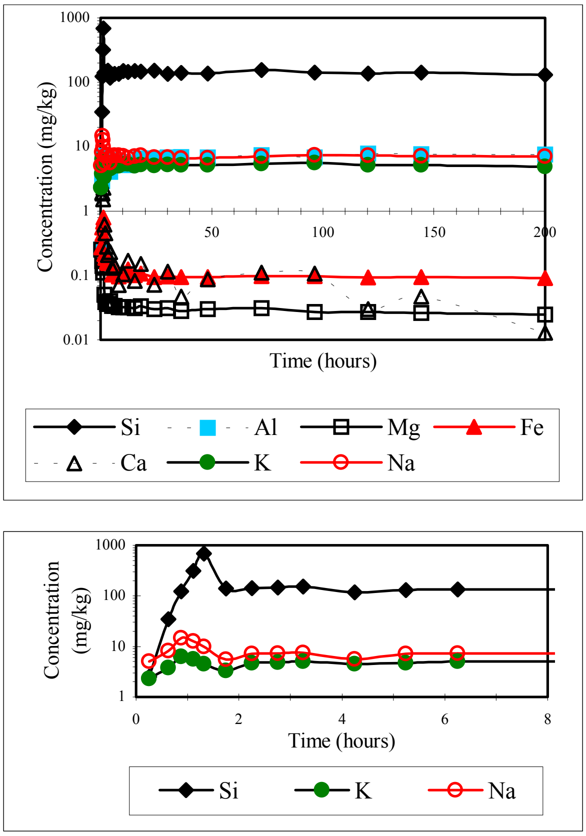

Figure 3a (top). Major element chemistry (ppm) of output solutions from 400°C, 20MPa flow-reactor experiments; H_2O as starting solution. Figure 3b (bottom) expanded view of Si, Na and K data, from the 400°C, flow-reactor experiment, over the first 6 hours of the simulation.

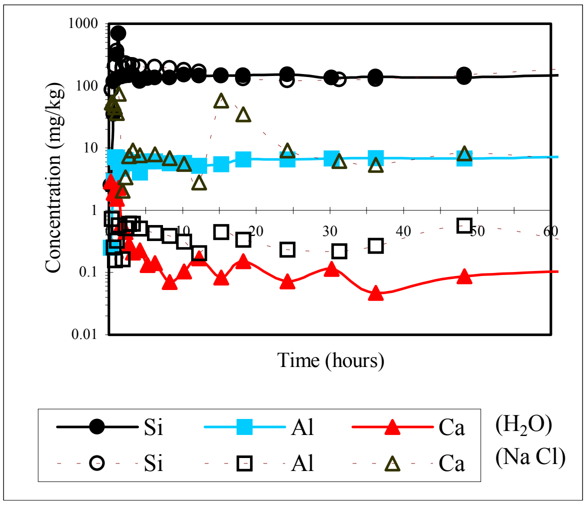

Figure 4a. Comparison of major element chemistry (Si, Al and Ca) of output solutions from 400°C, 20MPa flow-reactor experiments, using H_2O (filled symbols) and NaCl fluid (open symbols) as starting solutions.

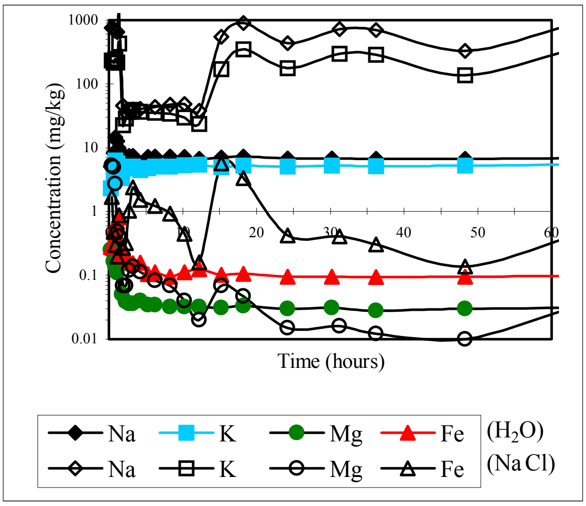

Figure 4b. Comparison of major element chemistry (Na, K, Fe and Mg) of output solutions from 400°C, 20MPa flow-reactor experiments, using H_2O (filled symbols) and NaCl fluid (open symbols) as starting solutions.

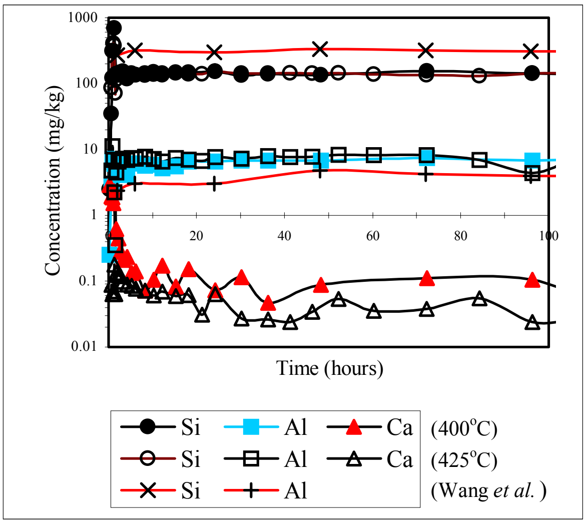

Figure 5a. Comparison of major element chemistry (Si, Al and Ca) of output solutions from 400°C (filled symbols) and 425°C (open symbols), 20MPa, flow-reactor experiments, using H_2O as starting solution. Results for 350°C experiments (Wang *et al*., 1996) is also shown (× and + symbols).

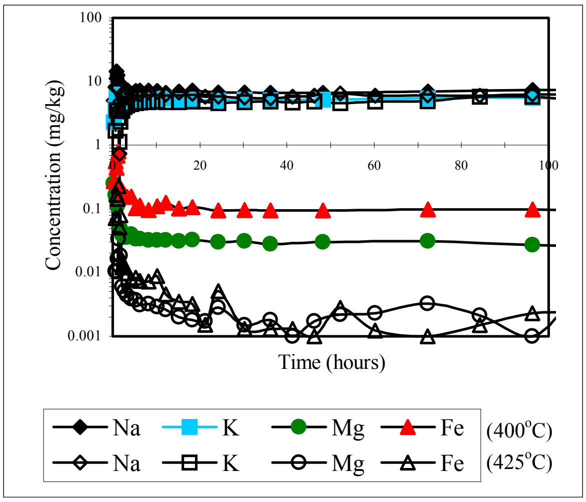

Figure 5b. Comparison of major element chemistry (Na, K. Fe and Mg) of output solutions (same symbols as Figure 5a).

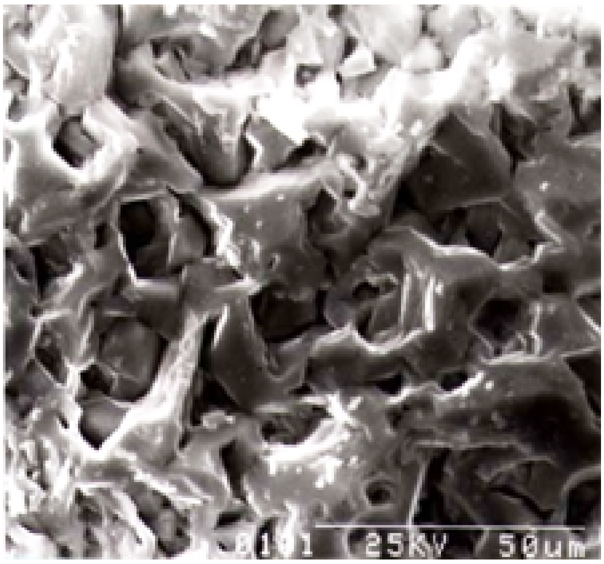

Figure 6. SEM micrograph of pitted quartz; 400°C, 20MPa. Starting solution was a NaCl fluid. Scale bar 50µm.

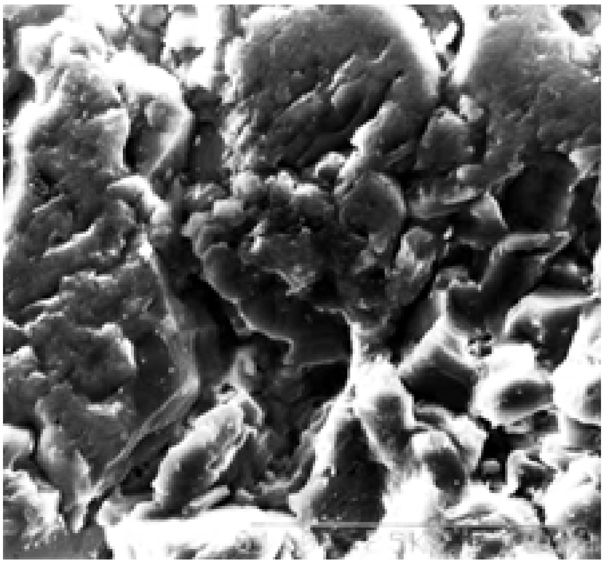

Figure 7. SEM micrograph of corroded alkali feldspar; 425°C, 20MPa, deionised water. Scale bar 50µm.

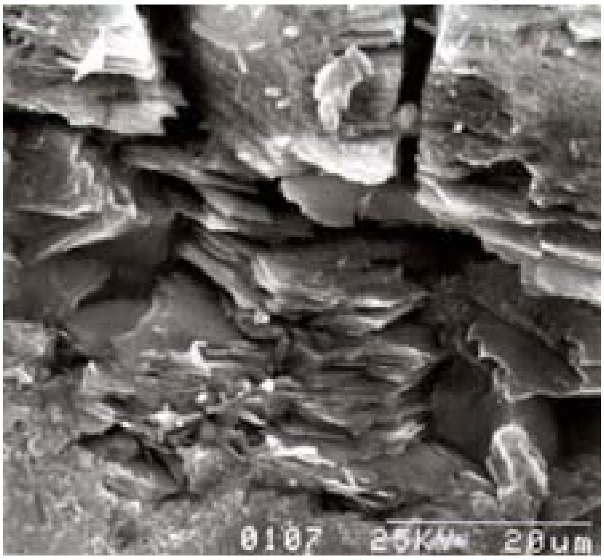

Figure 8. SEM micrograph of sericite infilling a fracture in orthoclase; 400°C, 20MPa, deionised water. Scale 20µm.

Figure 9. SEM micrograph of calc-silicate crystals on orthoclase; 400°C, 20MPa, NaCl fluid. Scale 20µm.

Table 1. Mineral nontent (vol%; top) and major element chemistry (wt%; below) of Iidate Granite (Wang *et al,* 1996).

Mineral	Quartz	Orthoclase	Albite	Anorthosite	Biotite
Volume %	37%	23%	24%	10%	6%

SiO_2	TiO_2	Al_2O_3	FeO	MgO	MnO	CaO	Na_2O	K_2O	Total
72.09	0.20	14.53	1.99	0.33	0.05	2.02	4.13	3.61	98.95

Table 2. Major element chemistry (in ppm) of saline, ‘mineralised’ fluid used in our flow-system experiments.

	Si	Al	Fe	Mg	Ca	Na	K
Conc.	60	0.02	0.30	0.44	0.46	680	250

Table 3. Major element chemistry (ppm) of output, ‘apparent equilibrium’ fluids, from 400°C and 425°C experiments, using distilled water and the saline fluid. Key: A=400°C/H_2O; B=400°C/NaCl; C=425°C/H_2O; D=425°C/NaCl.

Expt.	Si	Al	Fe	Mg	Ca	Na	K
A	140	7.1	0.09	0.03	0.07	7.0	5.2
B	139	0.32	0.33	0.02	5.07	602	247
C	141	7.4	0.00	0.00	.04	6.0	5.0
D	150	1.15	0.03	0.01	1.2	557	253