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SiO_2 PRECIPITATION ACCOMPANYING FLUID FLOW THROUGH GRANITE HELD IN A TEMPERATURE GRADIENT

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Abstract In experiments simulating the rise of hydrothermal fluids from a geothermal reservoir, water was flowed at a low rate down a temperature gradient through fractured and intact cylinders of Barre and Westerly Granite. Temperatures ranged from 80 to 105°C at the outer edges of the cylinders to 250 to 300°C along a central borehole which housed the heating coil. As a result of mineral deposition, particularly SiO_2, at low temperatures in the granite samples, permeabilities were reduced 10- to 100-fold in periods of 1 to 3 weeks. Chemical analyses were made of the low-temperature fluids discharged from the cylinders. Early-sampled fluids were supersaturated with respect to several minerals at low temperatures in the granites. Of the oversaturated species, SiO_2 showed the most rapid decrease with time, and in an experiment with low initial flow rate, the solution reached equilibrium with quartz at the low-temperature edge of the cylinder within about 6 days. Increasing the maximum temperature of the gradient at constant confining pressure led to higher SiO_2 concentrations in the discharged fluids. However, increasing confining pressure along with maximum temperature resulted in lower dissolved SiO_2 contents, because of enhanced reaction at the reduced flow rates accompanying the pressure increase. The behavior of SiO_2 contrasted with most other dissolved species, which were affected by changes in temperature but not flow rate in the time of the experiments.

Introduction A series of permeability experiments was conducted to model the flow of fluids from high to low temperatures across granitic rocks. As a result of several days of slow flow, the permeability of each granite specimen was reduced to 1 to 10% of its value prior to heating (Morrow and others, 1981). As an aid in determining the causes of the permeability reductions, the fluids discharged from the granite specimens were collected for chemical analysis (Moore and others, in press). An unexpected finding of the fluid analyses was that the variations in dissolved silica concentrations with changing experimental conditions differed from those of the other species in solution. The distinctive behavior of silica and its effect on the permeability of the granites form the subject of this summary paper.

Experiments The experimental design is shown in Figure 1. Cylindrical samples of granite 3" in diameter and 3-1/2" long contained a 1/2"-diameter borehole in which a coiled resistance heater produced a temperature gradient between the center and .outer edge. Distilled water was flowed radially through the granite from high to low temperatures. Gold shims were placed

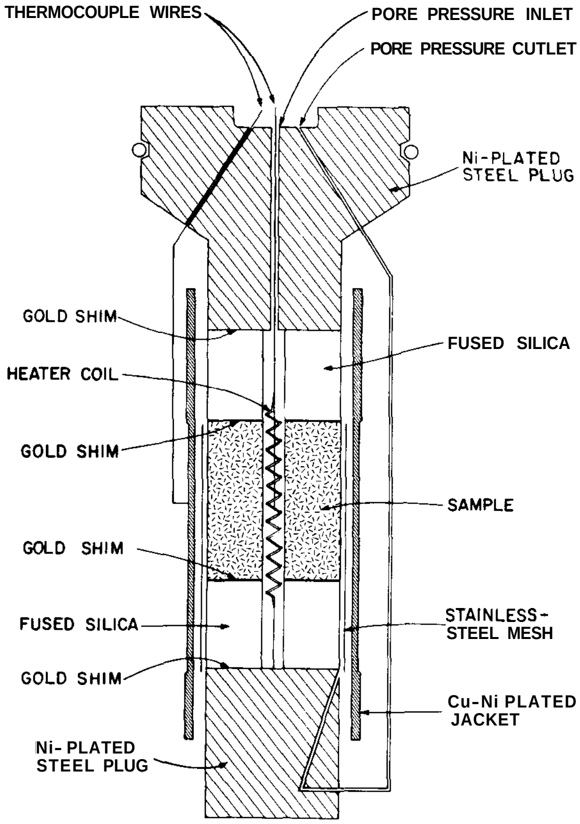

Figure 1 Schematic sample assembly.

at the ends of the granite samples to seal them from the adjoining fused silica cylinders that served as thermal insulators. Other exposed metal around the borehole was gold-plated to prevent contamination of the fluids. The sample assembly was separated from the containing jacket by a stainless steel mesh that allowed drainage of the discharged, low-temperature fluids away from the rock cylinder.

The experiments conducted are sumnarized in Table 1. Cylinders of Barre and Westerly Granite, both biotite-muscovite granodiorites, were used in different experiments. Temperatures within the boreholes ranged from 250 to 300°C, and those at the outer edges were 80 to 105°C. Confining pressures of 300 bars were coupled with pore pressures of 100 bars, corresponding to 1.2 km thickness of overburden with fluid pressure resulting from the hydrostatic head. Confining pressures of 600 bars and pore pressures of 200 bars were also used. A 5 to 10 bar pore pressure differential produced a low rate of fluid flow. Distilled water was the starting fluid in the experiments listed in Table 1. An additional experiment using a $NaHCO_3$-$CaCl_2$ solution rather than distilled water resulted in similar permeability reductions.

Nine dissolved species were analyzed from 1.5 ml fluid samples, collected as separate 1.25 and 0.25 ml samples. Details of the analytical techniques and many fluid compositions are contained in Moore and others (in press). The 0.25 ml sample was analyzed for SiO_2 using the molybdate-blue method of spectrophotometric analysis (ASTM, 1974; p. 401-402). From the larger fluid sample, the cations Ca, Na, K, and Mg were determined using atomic absorption techniques. The bicarbonate content was determined from measurements of total inorganic carbon, made with a carbon analyzer. The anions Cl, F, and sulfate were determined using an ion chromatograph with integrator attachment.

Some of the fluid compositions were analyzed with the SOLMNEQ computer program of Kharaka and Barnes (1973), which determines the states of reaction (ΔG_R) of the solutions at a given temperature with respect to up to 158 mineral species. In order to determine the differences in reactivity of a given fluid across the sample, most of the solution compositions analyzed by SOLMNEQ were run at both the high- and low-temperature extremes of the granite cylinders.

Permeability Changes The variation in permeability with time was determined from measured changes in mass flow rate over the constant pore pressure differential, using the radial flow model of Darcy's Law. As an example of the trend of permeability decrease, the normalized permeability changes with time for NWD22 and 24 are shown in Figure 2. The granite cylinders in each experiment showed a rapid initial permeability drop followed by lower rates of decrease. At constant confining presures, an increase in borehole temperature resulted in a more rapid rate of permeability reduction. In addition, the larger the volume of fluid flowed through the cylinders, the greater the permeability drop.

Textural Evidence of Reaction Thin-section and SEM examinations yielded some evidence of mineral reaction and precipitation in the granite cylinders during the experiments. Observations of high-temperature mineral reaction were confined to narrow concentric zones around the boreholes. There, calcite showed pronounced etching along cleavage

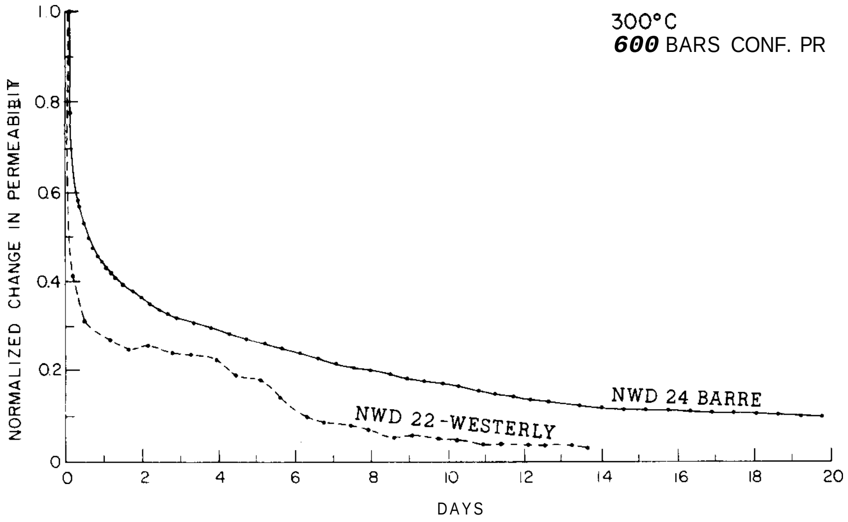

Figure 2 Normalized changes in permeability with time

Table 1. Experimental Conditions

Experiment	Rock Type	Temp. Gradient (°C)	Confining Pressure (bars)	Pore Pressure (bars)	Pore Pres. Differential (bars)	Duration of exp. (days)	Vol. Fluid Flow (mL)	Permeability initial k(da)	Permeability final k(da)
NWD10	Barre	80-250	300	100	5	18.0	41.8	7.9(10^{-5})	1.6(10^{-5})
NWD20	Barre	104-280	300	100	5	12.9	32.3	4.9(10^{-8})	1.7(10^{-8})
NWD21	Westerly	84-250	300	100	5	11.9	134.2	7.4(10^{-7})	4.5(10^{-8})
NWD22	Westerly	92-300	600	200	10	12.9	34.0	2.4(10^{-7})	9.3(10^{-9})
NWD23	Barre	103-250	300	100	5	9.0	114.0	2.0(10^{-6})	3.0(10^{-8})
NWD24	Barre	94-300	600	200	10	19.9	23.7	7.4(10^{-8})	5.6(10^{-9})

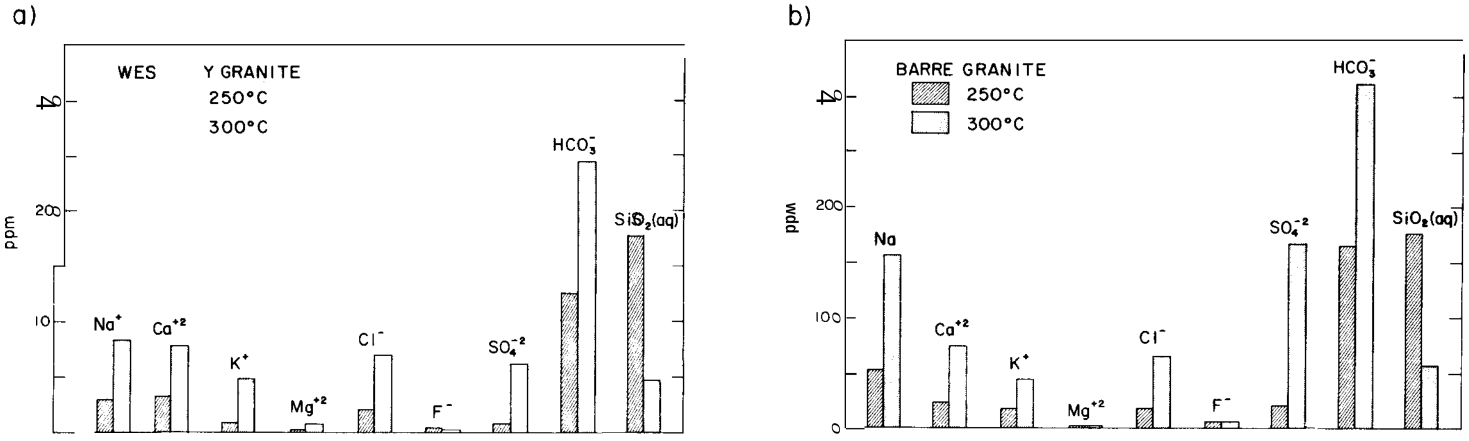

Figure 4 Effect of temperature on the composition of fluids discharged from a given granite type at similar times during an experiment: (a) Westerly Granite, fluid samples collected at 10.0 days; b) Barre Granite 6.0 days.

and fracture traces and phyllosilicate alteration minerals in plagioclase had changed color from green to yellowish-brown. A few early experiments were conducted using samples containing a through-going fracture (Morrow and others, 1981). After the experiments, the fracture surfaces showed traces of mineral deposition near the low-temperature sides. Most of the deposits consisted of patchy masses and fibers of silica which formed on exposed quartz grains (Fig. 3). In addition, some Ca-rich fibers grew on plagioclase crystals.

Chloride and Sulfate Neither Cl nor S are major constituents of any mineral in Westerly or Barre; instead, they are concentrated in intergranular fluids and adsorbed onto grain surfaces (Ellis and Mahon, 1964). Considerable amounts of both ions were removed by flushing cold water through the rock cylinders for 3-5 days prior to heating. Nevertheless, the concentrations of both species in solution rose again upon initial heating with the higher-temperature water the more effective leaching agent (Fig. 4). Subsequently, both ions dropped rapidly to low values.

Na, Ca, K, Mg, F, and HCO_3 Unlike Cl and sulfate the concentrations of these 6 species are related to mineral solubilities, with temperature the major control on solution concentrations. The higher Na contents an Na/Ca ratios in Fluids derived from Barre Granite (Fig. 4) are consistent with the occurrence of a more Na-rich plagioclase and a separate albitic alteration phase in Barre. In the same way, the slightly Mg-enriched solutions from Westerly are related to the higher Mg contents of minerals in that granodiorite. The amounts of Na, K, and Ca in solution doubled or tripled with a 50°C temperature increase (Fig. 4). The bicarbonate concentration also doubled, which contrasts with the negative temperature dependence of calcite solubility but which can be explained by differences in solution pH. The Mg and F contents were controlled by the solubility of mafic minerals and of accessory fluorite, respectively. The concentrations of these 2 ions did not increase with temperature, because minerals such as chlorite and fluorite show slightly negative solubility relationships in that temperature range (Ellis, 1971; Mahon, 1964). In the same way, the slightly Mg-enriched solutions from Westerly are related to the higher Mg contents of minerals in that granodiorite.

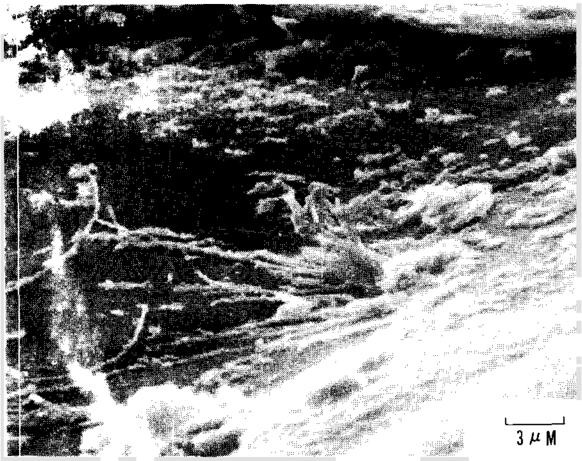

Figure 3 Low-temperature deposition of silica fibers on a quartz grain exposed along a fracture surface. SEM photomicrograph, 30,000 x magnification.

Table 2. Temperatures at which the SiO_2 contents and Na, K, and Ca concentrations for selected fluid samples would be equilibrium values.

Sample	Quartz	Na-K-Ca
NWD20		
20	170	198
28	167	171
NWD21		
34	182	218
53	172	208
NWD22		
63	104	250
69	99	263
70	72	225
NWD23		
77	186	265
83	171	229
84	154	221
NWD24		
93	119	237
99	142	217
100	130	208

Changes in the ionic concentrations with time may reflect partial reaction of the solutions at lower temperatures in the granites. Equilibrium temperatures of selected fluid compositions calculated using the Na-K-Ca geothermometer of Fournier and Truesdell (1973) are listed in Table 2, along with quartz temperatures. Nearly all of the initial Na-K-Ca temperatures were below the borehole temperatures and they also decreased with time. The gradual decreases in temperature indicate increasing reaction of the solutions at low temperatures as flow rates decreased.

Throughout most of the 250°C experiments the solutions were undersaturated with respect to calcite at the lowest temperatures in the cylinders, and bicarbonate concentrations increased with time. In contrast, the solutions were oversaturated wih calcite at the low-temperature edge for most of the 300°C experiments, and the bicarbonate concentrations decreased with time in an apparent attempt to reach equilibrium concentrations.

Ca concentrations decreased steadily during the experiments, particularly those at 300°C. The ratio Ca/HCO_3 also decreased with time. The lowered Ca contents relative to HCO_3 suggests that some limiting mineral solubility other than calcite, such as the precipitation of a Ca-zeolite or Ca-montmorillonite, may have caused Ca concentrations to decrease.

Silica The presence of silica in the fluids is controlled most strongly by the dissolution of quartz, which shows marked increases in solubility with increasing temperature (for example, Kennedy, 1950) and is by far the most reactive mineral in granodiorite subjected to flow of hydrothermal fluids (Charles, 1978). For experiments run at the same confining pressure with the same rock type (NWD20 and 23), a 30°C increase in temperature led to somewhat higher dissolved silica Concentrations. However, increasing confining pressure as well as temperature resulted in much lower silica contents (Fig. 4) and correspondingly lower equilibrium temperatures (Table 2). The lower concentrations at higher temperatures and confining pressures contrast markedly with the behavior of the other dissolved species that show positive temperature-dependent solubilities (Fig. 4).

None of the discharged fluids was saturated with respect to quartz at the borehole temperatures of the granite cylinders. However, silica phases such as quartz, chalcedony and a-cristobalite were oversaturated in at least some fluids at the low-temperature side. The values of ΔG_R for silica species decreased with time in an experiment, consistent with silica deposition from the low-temperature, oversaturated solutions. Quartz rather than some other silica species may be the crystallized phase, because the silica contents of the solutions continued to decrease to values below the solubilities of chalcedony and a-cristobalite. In addition, the final fluid samples of the 300°C Westerly Granite experiment (NWD22) were in equilibrium with quartz at the low-temperature, outer edge of the cylinder (Table 2).

The reduced dissolved silica concentrations in higher temperature and pressure experiments (Fig. 4) may be a function of the competing effects of temperature and flow rate on silica solution and redeposition. Rimstidt and Barnes (1980) have demonstrated the importance to quartz precipitation of the fluid volume and the relative interfacial area between solid and aqueous phases. With the very small channel size, large crystal surface areas, and low and progressively declining flow rates, the conditions of these experiments were highly favorable for quartz precipitation.

Thus, although the higher-T fluids will acquire greater amounts of dissolved silica near the borehole, the correspondingly decreased flow rates at the higher confining pressures will enhance reprecipitation of the silica at low temperatures in the granites.

Concluding Remarks As indicated by fluid chemistry and petrographic examination of fracture surfaces, quartz precipitation along grain boundaries and microfractures may have been the principal source of the observed permeability decreases in the granodiorites. The silica content of the discharged fluids is particularly sensitive to reductions in flow rate, in contrast to the other dissolved species. Other minerals, such as calcite and probably some aluminosilicates were also supersaturated in some of the fluids. These materials may have been deposited as well, but at low rates compared to quartz.

The effects of temperature and fluid volume on the rate of permeability decrease are explicable in terms of the amount of material transported from high to low temperatures across the granites. Increasing temperature raised the concentrations of the solutions around the borehole, thus increasing the amount of material that was transported and redeposited at low temperatures in the cylinders. However, decreasing flow rate reduced the amount of mass transfer in a given time; and if the fluid volume was sufficiently low, permeability decreases occurred at a lower rate despite increasing temperature.

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