

## Chemical reactions accompanying fluid flow through granite held in a temperature gradient

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**Abstract**—Distilled water was passed at a low rate down a temperature gradient through cylinders of Barre and Westerly Granite. Temperatures ranged from 80–100°C at the outer edges of the cylinders to 250–300°C in central, drilled holes which housed the heating coils. The measured permeabilities of the granite cylinders decreased by as much as two orders of magnitude in experiments of 1–3 weeks' duration. The amount of permeability decrease varied directly with temperature and inversely with the rate of fluid flow. The compositions of the fluids discharged from the granites were functions of temperature and flow rate as well as mineral composition, with dissolved silica concentrations showing trends different from those of the other analyzed species. Fluids from experiments run at higher temperatures but at much lower initial rates of fluid flow had higher concentrations of most ions but substantially lower dissolved silica contents. In contrast, an increase in temperature at similar rates of fluid flow resulted in higher silica concentrations. In the experiments, the distilled water acquired enough dissolved materials at high temperatures to become supersaturated with respect to several minerals at the low-temperature edges of the cylinders. Some of this material, particularly silica, was deposited along grain boundaries and microfractures, causing the observed permeability decreases. The very low rates of fluid flow in some high-temperature experiments significantly increased the rates of SiO<sub>2</sub> precipitation and reduced dissolved silica concentrations relative to other species in the discharged fluids.

### INTRODUCTION

A SERIES OF permeability experiments has been conducted which model the flow of groundwater away from canisters heated by radioactive decay at deep-burial nuclear waste disposal sites in granitic rock. The work was performed to determine the effectiveness of the geologic barrier in containing radionuclides in the event of canister leakage. The results of some early experiments are summarized in MORROW *et al.* (1981), who found that the permeabilities of both intact and fractured granite samples decreased as a result of several days of slow fluid flow. Additional experiments were conducted subsequently, in which the low-temperature fluids discharged from the granite cylinders were collected for chemical analysis. 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 purposes of this paper are: (1) to determine the origin of the contrasting behavior of silica with the other species in solution; (2) to describe the relationships between fluid composition and permeability change in the experiments; and (3) to discuss the significance of the results with respect to nuclear waste disposal siting and geothermal systems. The potential of the experimental apparatus for the study of diagenetic processes is also discussed.

### EXPERIMENTAL CONDITIONS

The experimental design is shown in Fig. 1. Cylindrical samples of granitic rock, 7.62 cm in diameter and 8.89 cm long, contained a 1.27 cm diameter borehole in which a coiled resistance heater produced a temperature gradient

between the core and outer surface. Distilled water flowed radially through the granite cylinders from the high-temperature borehole to the low-temperature outer edge. Gold shims were placed at the ends of the granite cylinders to seal them from the adjoining impermeable, fused silica cylinders that served as thermal insulators. Exposed metal in the high-temperature borehole area, such as the heating coil, was gold-plated to reduce contamination of the fluids. The sample assembly was separated from the containing Cu-Ni plated jacket by a stainless steel mesh that allowed drainage of the discharged, low-temperature fluids away from the rock cylinder. The mesh and jacket potentially could react with the low-temperature discharged fluids, although no visual evidence of reaction was observed on the samples or the metal.

Cylinders of Barre and Westerly Granite were used in the experiments. Sixteen thin sections of the two rock types were examined petrographically and with electron microprobe (Table 1); the results are consistent with previous descriptions made by MAYNARD (1934), CHAYES (1950, 1952), and MURTHY (1957). Igneous minerals in both rock types consist of plagioclase, quartz, potash feldspar, biotite and muscovite with accessory magnetite, ilmenite, apatite, zircon, and tourmaline. Plagioclase in the two rocks is compositionally zoned, and both the cores and rims of plagioclase from Barre are enriched in sodium compared to those in Westerly (Table 1). Minor calcite, chlorite, epidote/clinozoisite, and sphene occur as natural alteration minerals in both rocks; Westerly also contains fluorite and Barre fine-grained albite (An<sub>2</sub>) as alteration minerals. Biotite and the chlorite replacing it in Westerly are enriched in Mg compared to the same minerals in Barre (Table 1).

Conditions of the experiments conducted are listed in Table 2. Temperatures in the central boreholes of the cylinders were 250°, 275°, and 300°C in different experiments, and those at the outer edges were 80°–100°C. In the experiments at 250° and 275°C, confining pressures were 300 bars and outlet pore pressures 100 bars; pore pressures within the borehole were maintained at 105 bars, producing a low rate of fluid flow through the cylinders. Confining pressures of 600 bars, outlet pore pressures of 200 bars, and inlet pore pressures of 210 bars were used in the experiments

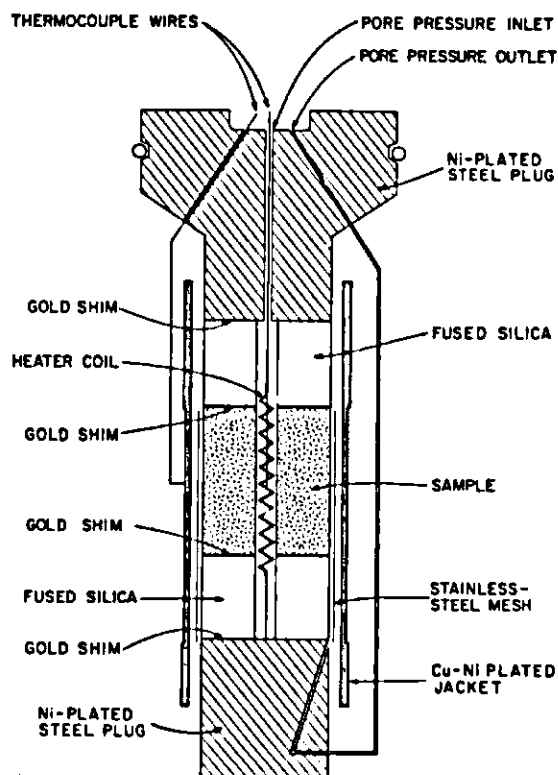


FIG. 1. Schematic sample assembly.

run at 300°C borehole temperature. Deionized and distilled water was the starting fluid; the water was degassed in a vacuum chamber immediately prior to use.

#### CHEMICAL ANALYSES

Samples of the discharged, low-temperature fluids were collected at intervals of several hours to 3–4 days, depending on the rate of fluid flow through the granite cylinders. A total of 9 dissolved species were analyzed, and the results are shown in Table 3. Sample collection and analytical procedures evolved during the series of experiments. Room-temperature measurements of pH were made immediately upon collection, using pH paper in B250-1 and B275 and a pH meter in the other experiments. In B250-1, B275, and W250 the sample volume varied and not all species were analyzed in many samples; in addition, the fluids were not

filtered before analysis. However, in subsequent experiments, a 1.5 ml sample was passed through a 0.45  $\mu\text{m}$  filter immediately upon collection and a 0.25 ml sample separated for  $\text{SiO}_2$  analysis. Repeated experiments at 250°C were conducted on Barre Granite; the range of silica concentrations in the fluids from the two experiments partly overlapped, with some of the filtered samples in B250-2 having higher silica concentrations than any of the unfiltered samples of B250-1. The lack of filtration in the early experiments, therefore, apparently did not lead to anomalously high  $\text{SiO}_2$  concentrations.

The samples reserved for silica analysis were digested in a 1 N NaOH solution and then diluted to 25 ml for standard spectrophotometric analysis, using the molybdate blue method (ASTM, 1974; p. 401–2). From the larger fluid sample, the cations Ca, Na, K and Mg were determined using atomic absorption techniques. A 0.5 ml aliquot was diluted 1:50 to produce a 25 ml stock for duplicate analyses of the four cations. The bicarbonate content was determined from measurements of total inorganic carbon on undiluted samples of 0.05 ml size, made with a carbon analyzer. Three additional anions, Cl, F, and  $\text{SO}_4$ , were determined using ion chromatography, with the instrument adapted to a 0.5 ml sample loop. Dilutions of 1:10 or 1:5 were used in this last technique.

As reflected in the balances (Table 3), the equivalent concentrations of anions and cations in most samples are nearly equal and closely approximate the values calculated from the measured conductivities of the solutions. Thus, the determined ions are those that essentially comprise the solutions.

#### DISCUSSION OF RESULTS

##### 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:

$$\frac{Q_m}{2\pi l} = \frac{kr}{\nu} \frac{dP}{dr}$$

where  $Q_m$  is the mass flow rate,  $l$  the length of the sample,  $k$  permeability,  $r$  the sample radius, and  $dP/dr$  the pressure gradient between the center and outside of the sample.  $\nu$  is the dynamic viscosity of water, which is a function of temperature and therefore varies with radius in these experiments. Additional in-

Table 1. Compositions of Minerals in Westerly and Barre Granite\*\*

	Westerly				Barre			
	Plagioclase		Biotite	Chlorite	Plagioclase		Biotite	Chlorite
	Cores	Rims			Cores	Rims		
$\text{SiO}_2$	63.7	64.6	37.2	26.2	65.1	67.7	36.7	26.3
$\text{TiO}_2$			2.6	0.1			2.7	0.1
$\text{Al}_2\text{O}_3$	22.8	22.2	15.9	19.1	21.8	20.0	16.2	19.7
$\text{Fe}_2\text{O}_3^*$	0.1	0.1			0.1			
$\text{FeO}^*$			19.8	27.6			20.9	29.0
$\text{MgO}$			9.8	13.9			8.7	12.4
$\text{MnO}$				0.5				0.6
$\text{CaO}$	3.7	1.9	0.1	0.1	2.8	0.7		0.1
$\text{Na}_2\text{O}$	9.2	10.3	0.1		9.8	11.2	0.1	
$\text{K}_2\text{O}$	0.3	0.3	8.2	0.1	0.3	0.2	9.8	0.1
Anhydrous Total	99.8	99.4	93.7	87.6	99.9	99.8	95.1	88.3

\* Total iron reported as  $\text{Fe}_2\text{O}_3$  or  $\text{FeO}$

\*\* Analytical and refinement techniques after Moore and Liou (1979)

Table 2. Experimental Conditions and Permeability Changes

Experiment	Rock Type	Temp Grad. (°C)	Conf. Pr. (bars)	Pore Pr. (bars)	Diff. Pore Pr. (bars)	Duration of exp (days)	Fluid Vol. (ml)	Permeability, K (nda)		Final x 100 (%)
								Initial	Final	
B250-1	Barre	80-250	300	100	5	18	42	790	160	20.2
B275	Barre	104-275	300	100	5	13	32	49	17	34.7
W250	Westerly	84-250	300	100	5	12	134	740	47	6.4
W300	Westerly	92-300	600	200	10	13	34	240	9.3	3.9
B250-2	Barre	103-250	300	100	5	9	114	2,000	30	1.5
B300	Barre	94-300	600	200	10	20	24	74	7.6	10.3

formation on the permeability calculations is contained in MORROW *et al.* (1981).

The initial and final measured permeabilities are listed in Table 2. Initial permeabilities ranged from 49 to 2,000 nanodarcies and final values 7.6 to 160 nanodarcies. In all cases, permeability decreased during the experiments; the most significant reduction occurred in experiment B250-2, in which the final measured permeability was 1.5 percent of the starting value. The changes in permeability with time for the experiments normalized to their initial values are shown in Fig. 2. The permeabilities of the Barre cylinders in B250-1 and B275 showed roughly linear rates of decrease throughout the experiments (Fig. 2a). In the other four experiments, the major permeability drop was accomplished in the first 1-2 days, with more modest reductions thereafter (Figs. 2b and c).

As examples of the changes in flow rate accompanying the permeability decreases, 20-30 ml of water flowed through the granite cylinders in the first day of experiments W250 and B250-2. By the end of these two experiments, only 3-4 ml fluid per day was flowing through the granites. In the two 300°C experiments the effective pressure, that is the difference between confining and fluid pressure, was twice that of the other experiments (Table 2); this had the effect of decreasing crack widths. As a result, flow through the granites was lower throughout these two experiments, ranging from 3-4 ml in the first day to 0.5-1 ml at the time the experiments ended.

MORROW *et al.* (1981) reported that an increase in temperature at the same or reduced pressure conditions caused permeability to decrease more rapidly. Similar temperature effects were observed in these experiments and, in addition, a correlation was found between the rate of permeability change and the volume of fluid passed through the cylinders. In the two Barre experiments at 250°C, the initial permeability of the granite cylinder used in B250-1 was only 40 percent that of B250-2, and B250-1 showed correspondingly lower rates of both fluid flow and permeability decrease (Table 2). The 300°C experiments were conducted at the highest effective pressures, which correspondingly reduced the volume of fluid passed through the granites (Table 2). This decrease in fluid volume has the opposite effect of increased temperature on permeability change. As an example,

five times the amount of water was used in experiment B250-2 than in B300 (Table 2), and B300 shows a lesser rate of permeability change despite the temperature increase. The fluid volume of B300 was more nearly equal to that of both B250-1 and B275, and the rate of permeability reduction increased with temperature for these three experiments.

#### Sources of species in solution

Material going into solution during the experiments was derived both from mineral reaction and from intergranular materials such as pore fluids and ions adsorbed onto grain surfaces. The intergranular materials are readily removed from the granites, and the fluids discharged during the initial, room-temperature measurements of permeability contained a number of these dissolved species. Although diluted by the distilled water, the compositions of the discharged fluids indicate the kinds and relative proportions of species existing along and between the grain boundaries. Figure 3 compares samples of similar solution concentrations derived from the room-temperature permeability measurements. The fluids from Barre are distinctive from those of Westerly, particularly with respect to their much higher sulfate contents. Barre also has lower Cl concentrations relative to the other anions and higher Na/Ca ratios.

The species present in the intergranular spaces may have a number of different sources, among them residual igneous fluids that were concentrated in fluid inclusions and along grain boundaries, as described by ELLIS and MAHON (1964). The occurrence of hydrous alteration minerals such as chlorite and epidote attest to the introduction of hot water-rich fluids to both granites at some time in their history, perhaps related to deuteritic alteration. The relative enrichment of Na in the Barre intergranular fluids, corresponding to the more sodic plagioclase in Barre, may be a relic of the reaction of such high-temperature waters with plagioclase in the two granites. Circulating groundwaters derived from rain or snow would also react with the granite in an attempt to reach equilibrium (PACES, 1972).

The concentrations of dissolved species in the room-temperature fluids decreased with continued flushing. In the last four experiments listed in Table 3—W250, W300, B250-2 and B300—distilled water

Table 3. Compositions of Low-Temperature Fluids Discharged From the Granite Cylinders. Concentrations are in milligrams per liter; Balance = 100 (cations-anions)/1/2 (cations+anions).

Experiment	Time (days)	pH	SiO <sub>2</sub>	Na	Ca	K	Mg	Cl	F	SO <sub>4</sub>	HCO <sub>3</sub>	Balance (%)
<b>B250-1</b>												
	2.1	7	94	190	224	46	5.3	730	10	80		
	3.2	7		170	160	37	2.7	490	11	53	140	- 7.3
	4.0	7		150	110	29	1.6	360	11	38	130	- 5.8
	5.0	7		140	88	20	1.0	280	11	32	120	- 0.3
	6.0	7	140	120	64	17	1.3	250	14	29	120	-14.5
	7.0	7		110	46	14	0.6	170	11	19	120	- 3.3
	8.0	7	150	100	38	12	0.3	150	14	20	110	- 8.8
	9.2	7		92	28	10	0.3	120	12	16	110	- 9.5
	10.1	7	150	85	24	10	0.2	100	13	13	100	- 4.6
	11.0	7		81	26	9.4	0.6	91	12	12	97	1.4
	13.0	7		75	19	8.4	0.2	73	11	10	94	1.2
	15.2	7		67	19	6.6	0.1	66	12	9	99	- 5.3
	18.0	7	160	64	18	6.8	0.4	61	11	11	97	- 5.8
<b>B275</b>												
	1.0	7	150	140	96	36	0.6	220	11	110	100	10.1
	2.0	7	160	140	77	29	0.4					
	2.9	7	170	150	70	26	0.3	160	15	81	78	7.4
	3.9	7	170	120	51	16	0.3					
	6.9	7	220	100	30	11	0.1	100	21	40	130	-11.6
	8.0	7	200	99	27	11	0.1	80	19	31		
	9.9	7	180	90	24	8.0	0.05				110	
	11.2	7	210	84	20	7.2	0.1	75	15	26		
	12.9	7	160	84	21	9.0	0.1	70	20	23	110	- 7.2
<b>M250</b>												
	1.0	6.8		34	53	13	3.9	82	3.5	18		
	1.1	7.3	210					85	3.1	18	110	
	1.9	7.1	210					61	3.4	17	130	
	2.1	6.9		35	49	12	3.6	62	3.6	15		
	2.2	7.0	210					61	3.3	13	140	
	3.1	7.0	230					48	2.9	12	120	
	3.3	6.7		32	38	11	2.9	49	3.0	12		
	4.0	6.8	230					43	2.7	10	110	
	4.1	7.7		30	36	9.6	2.5	40	2.8	8		
	5.0	7.6	250	27	33	9.0	2.1	36	2.6	9		
	6.0	7.3	230					29	3.2	8	110	
	6.2	7.7		28	32	8.0	2.6	30	3.2	10		
	6.9	6.9	230					28	3.3	7	110	
	7.3	7.6		27	33	8.0	1.9	26	3.2	6		
	8.9	7.2	180	28	31	7.6	1.9	21	3.2	7		
	10.0	7.2	180					21	3.5	8	130	
	11.0	7.6		32	33	9.7	2.1	22	3.8	7	130	11.1
	11.9	7.7	180					19	3.7	7	140	
<b>M300</b>												
	1.0	7.6	47	62	82	32	4.4	91	3.8	36	300	- 5.6
	3.1	7.6	59	76	99	33	6.4	87	3.6	66	340	0.2
	3.9	7.2	58	81	72	36	6.1	77	3.3	66	320	- 4.9
	4.9	7.0	69	81	98	37	7.5	73	3.5	70	350	5.6
	8.0	7.6	34	78	78	41	6.8	64	3.4	60	320	4.8
<b>B250-2</b>												
	0.2	7.4	220	35	27	23	1.1	25	1.6	49	94	5.8
	0.9	7.6	320	26	23	16	0.6	17	1.4	21	84	14.5
	2.2	7.6	220	35	25	20	0.6	17	2.5	23	110	14.0
	4.1	7.9	180	46	21	16	0.4	13	3.9	22	150	0.1
	4.9	7.6	180	48	22	12	0.2	14	4.6	22	160	- 5.8
	6.0	7.4	180	51	23	18	0.3	17	5.0	20	160	1.8
	7.0	7.5	130	51	21	15	0.5	17	5.2	18	160	- 2.3
<b>B300</b>												
	2.0	7.1	71	120	93	45	4.0	81	10.0	190	310	- 4.4
	4.0	7.2	82	140	84	43	1.2	67	4.8	180	320	3.1
	6.0	7.6	56	150	73	44	0.8	64	5.0	170	310	6.1
	10.2	7.6	93	140	60	33	0.4	54	5.4	140	280	6.7
	13.3	7.7	120	140	54	28	0.4	46	5.5	140	280	4.7
	18.0	7.3	110	140	49	32	0.4	47	9.8	100	280	9.8
	19.9	7.4	88	110	48	24	0.6	46	3.9	110	240	1.5

was passed through the granite cylinders for 3 to 5 days prior to heating in order to remove much of this material. However, experiments B250-1 and B275 were run without a protracted period of cold-water flushing. As a result, little intergranular material was removed, and the early-sampled heated fluids contain a large contribution from the pore species (Table 3). The solution concentrations decreased rapidly with time, and by the end of experiment B250-1, most of the ionic concentrations except F and HCO<sub>3</sub> had decreased to 10 to 12 percent of their initial values.

Cold water was run through the cylinder in B275 for several hours longer than for B250-1, and the initial solutions correspondingly are less concentrated.

Fluoride and bicarbonate concentrations did not decrease along with the other ions in B250-1 and B275; and dissolved silica concentrations actually increased with time (Table 3). The contents of these three dissolved species in solution may have been controlled by mineral reaction during the first two experiments. The relatively uniform compositions reached in the last few days of experiments B250-1

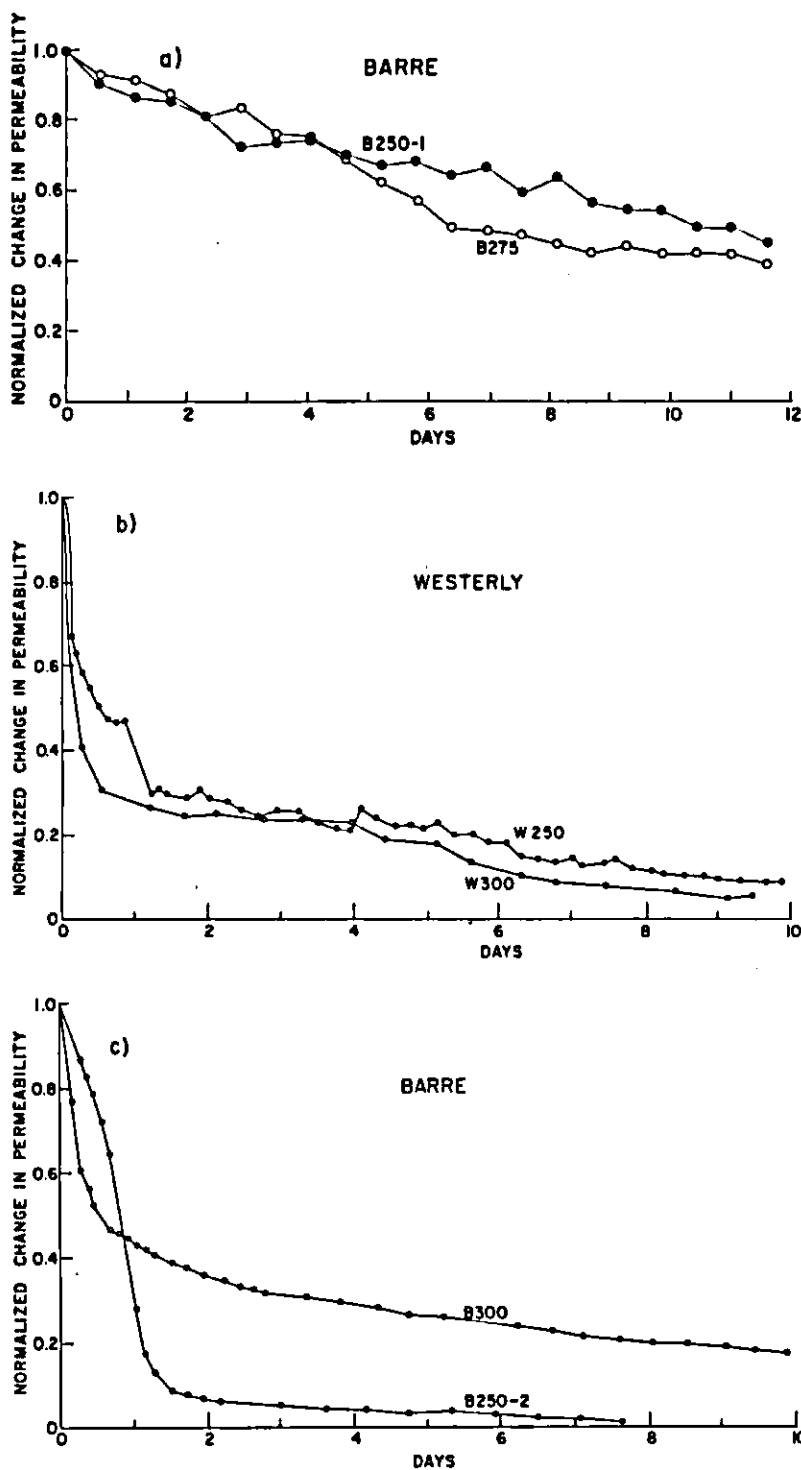


FIG. 2. Changes in permeability with time of: (a) experiments B250-1 and B275; (b) W250 and W300; (c) B250-2 and B300. Permeabilities are normalized to the initial value in a given experiment, to facilitate comparison of the rates of change in different experiments. Actual values of initial and final permeabilities are contained in Table 2.

and B275 and throughout the other experiments also may reflect control of solution composition by mineral reaction. However, the Cl and  $\text{SO}_4$  in solution in all experiments must be derived from the intergranular materials, for they have no mineral source.

Chloride may be a minor component of accessory apatite, yet apatite is one of the minerals most resistant to alteration by hydrothermal fluids (CHARLES, 1978). No sulfide minerals were observed in Barre or Westerly either in this or previous studies (MAY-

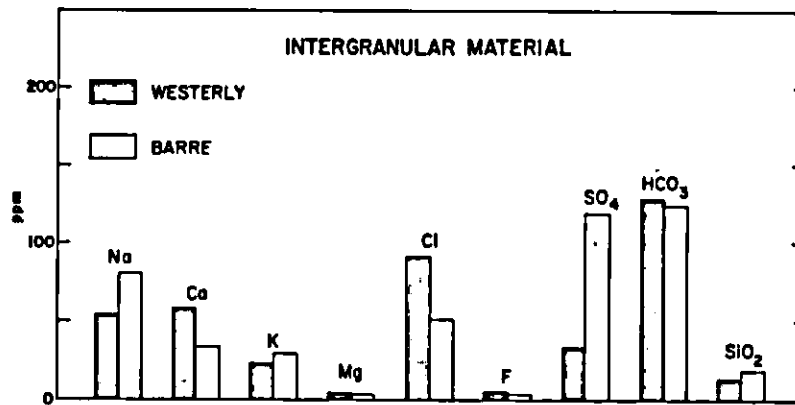


FIG. 3. Compositions of fluids of similar concentrations that were discharged from Barre and Westerly granite cylinders during room-temperature permeability measurements. The relative proportions rather than actual concentrations of species in a given solution are of significance, because of dilution by distilled water.

NARD, 1934; CHAYES, 1950, 1952; MURTHY, 1957) to provide a source for sulfate in solution.

Some textural evidence of high-temperature mineral reaction, observed in thin section, was found in concentric zones surrounding the boreholes of some granite cylinders. There, the calcite that partly replaces plagioclase showed a much more pronounced etching along cleavage and fracture traces than was observed in fresh specimens. MORROW *et al.* (1981) reported that sericitic alteration minerals in plagioclase near the borehole of a Westerly cylinder had changed color from grayish-green to a bright yellowish-brown.

#### Variations in fluid composition

Fluids collected during the last four experiments shown in Table 3, in which the interference from the intergranular species was minimized, show some variations in composition with changing experimental conditions. In part, the solutions reflect the compositions of minerals in the two granites. Fluids discharged from Westerly are slightly enriched in Mg compared to those from Barre; this correlates with the higher Mg contents of biotite and chlorite in Westerly (Table 1). As was observed with the room-temperature fluids (Fig. 3), Barre fluids have higher Na contents and Na/Ca ratios, consistent with plagioclase compositions in the two granites.

The discharged fluids from a given granite show differences in composition with changing pressure-temperature conditions. The concentrations of Na, Ca, K, HCO<sub>3</sub>, and sulfate in the 300°C experiments of both Barre and Westerly are two to three times their concentrations in the 250°C experiments. For example, bicarbonate at 250°C ranges from 94 to 160 ppm, whereas it ranges from 280 to 350 ppm at 300°C. Chloride, Mg, and F show an increase with pressure-temperature conditions in one but not both granites; in no case are their concentrations lower overall in the higher temperature experiments. In contrast, silica concentrations are lower throughout

both 300°C experiments. In W250, silica in solution varies between 180 and 250 ppm; in B250-2, the range is 130–320 ppm. In W300, dissolved silica concentrations are all below 70 ppm, and in B300 the highest silica content is 120 ppm. Both 300°C experiments also were conducted at higher effective pressures than the other experiments. In B275, the pressure conditions were the same as in the 250°C experiments, and silica concentrations were in the same range as those of B250-2 and higher overall than those in B250-1.

As permeability decreases during an experiment, so too does the rate of fluid flow through the cylinders. In the same way, some species in the discharged fluids change concentration with time, perhaps in response to the increased reaction time at all temperatures. The best-defined variation with time is shown by silica, which in general increases to a maximum value within 1 to 5 days, after which time concentrations more or less steadily decrease. Experiments W250, W300, and B250-2 show this trend most clearly (Table 3). Silica concentrations in B275 and B300 show secondary maxima, as well, that occur before or after the highest observed values. The partial exception to this trend is B250-1, in which the highest concentration is reached only at the end of the experiment. Some ions in solution show changes with time in some but not all experiments. In the 300°C experiments, for example, bicarbonate ion shows similar trends to silica, with concentrations rising to a maximum value after 4 to 5 days and decreasing thereafter. The bicarbonate contents show no well-defined trends in the 250°C experiments. In W250 and B300, calcium concentrations decreased to 50–60 percent of their initial amounts with time.

#### INTERPRETATIONS

The fluids passing from high to low temperatures through the granite cylinders are subjected to continually changing conditions and probably do not reach equilibrium with the rock at any point along

their path. The distilled water acquires solutes both from the limited supply of intergranular material and, more importantly, from continuous reaction with minerals. Although the solutions were probably undersaturated at the high, borehole temperatures, they could become sufficiently concentrated to become supersaturated with respect to some minerals at lower temperatures and thus would have the potential to deposit those minerals from solution.

Selected fluid compositions from the last four experiments were analyzed with the SOLMNEQ computer program (KHARAKA and BARNES, 1973), which computes the degree of saturation as a function of temperature. Positive values of  $\Delta G_R$  indicate that the solution is supersaturated with respect to the phase considered. The calculations were made at the lowest temperatures in the cylinders, and the results for selected minerals are listed in Table 4. The fluids reaching the low-temperature edge of the granites were supersaturated with respect to one or more of the six minerals listed in Table 4, among others. Because Al determinations were not made, no data were available for aluminosilicates such as feldspars, zeolites, or clays.

MORROW *et al.* (1981) found some textural evidence that minerals were being deposited by the fluids. Following experiments using samples with freshly made, through-going fractures, SEM examination of 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, but some Ca-rich fibers also grew across the cleaved surfaces of plagioclase crystals. The deposition of such minerals in pores and along microfractures is probably the principal cause of the measured permeability reductions.

In the experiments run at higher temperatures and pressures, the principal effect on the composition of the discharged fluids was the increase of most ionic concentrations (Table 3). Magnesium concentrations were not systematically higher; however, Mg-bearing minerals such as chlorite, which are contained in both rock types examined, do show slightly negative solubility relationships in the temperature range of the

experiments (ELLIS, 1971). CHARLES (1978) subjected granodiorite disks similar in major mineral proportions to Barre and Westerly to the flow of distilled water at 295°C and 330 bars pressure; he found that quartz was by far the most reactive mineral and dissolved silica the principal solution species. In these experiments, too, quartz may have been the major reacting mineral.

Because quartz shows increased solubility with both temperature and pressure, silica concentrations in the solutions from 300°C experiments were expected to increase along with Na, K, Ca, and other ions. That silica concentrations were actually lower in the 300°C experiments may be because silica was even more effectively removed from solution through low-temperature precipitation reactions. Deposition of an SiO<sub>2</sub>-polymorph rather than some other, more complex silicate mineral may be the controlling precipitation reaction, in part because SiO<sub>2</sub> was the predominant phase deposited on fracture walls. In addition, no analyzed cation showed a concomitant reduction with silica in the 300°C experiments. Because Al concentrations are unknown, the formation of an Si-Al mineral such as kaolinite cannot be precluded even though no supporting textural evidence was found for the growth of such minerals. It is possible that minute amounts of aluminosilicate minerals were deposited along microfractures in the granites, helping to reduce permeability even though present in undetectable amounts.

If deposition of an SiO<sub>2</sub> phase is the principal cause of reduced dissolved silica concentrations, then the solution compositions give some indication of which form of silica was being deposited. The 1.0-day sample from W250 (Table 4) was barely supersaturated with respect to amorphous silica ( $\Delta G_R = 0.02$ ) as well as the listed silica polymorphs at the outlet temperature; this sample contained 210 ppm SiO<sub>2</sub> in solution. Other fluid samples with similarly high SiO<sub>2</sub> concentrations would also be supersaturated with respect to amorphous silica at low temperatures. However, many other fluid samples, including the rest of those in Table 4, were undersaturated with amorphous silica. All of the discharged fluids in the 300°C experiments belong to this latter group and, as shown in Table 4, several of those fluid samples were unsaturated with respect to both chalcedony and  $\alpha$ -cristobalite as well. The final fluid samples of W300 were in equilibrium with quartz at the low-temperature outer edge of the sample (Table 4). It is possible, then, that quartz was the precipitated silica species.

The low silica concentrations in the highest temperature experiments probably result from their very low initial flow rates and correspondingly increased reaction times at low temperatures throughout those experiments. The variations in SiO<sub>2</sub> concentrations with time also may be a function of flow rate. As the progressively decreasing flow rates provide additional time for reaction, the solutions will interact more thoroughly with the granites at all temperatures. Because reactions are in general more rapid at higher

Table 4. Reaction States of Selected Fluid Samples at the Low-Temperature Sides of the Granite Cylinders. Positive Values of  $\Delta G_R$  Indicate Supersaturation.

Sample	T(°C)	pH(T)	$\Delta G_R$ (Kcal)					
			Quartz	Chalcedony	$\alpha$ -Cristobalite	Calcite	Fluorite	
W250								
1.0 days	84	6.7	1.3	0.8	0.5	-0.4	-0.3	
11.0 days	84	7.4	1.1	0.7	0.4	0.5	0.4	
W300								
3.1 days	92	7.4	0.1	-0.3	-0.6	1.8	-0.2	
8.0 days	92	7.4	0	-0.3	-0.7	1.7	-0.4	
B250-2								
0.2 days	84	7.2	1.3	0.9	0.6	-0.1	-1.8	
4.1 days	84	7.6	1.2	0.7	0.4	0.6	-0.8	
6.0 days	84	7.3	1.1	0.7	0.4	0.3	-0.4	
7.0 days	84	7.4	0.9	0.5	0.2	0.3	-0.4	
B300								
2.0 days	94	7.0	0.3	-0.1	-0.4	1.1	1.2	
6.0 days	94	7.4	0.1	-0.2	-0.6	1.6	0.2	
19.9 days	94	7.3	0.5	-0.1	-0.2	1.1	0	

temperatures than at low, the first effects of the reduced flow rates would be to increase the overall amount of  $\text{SiO}_2$  in the discharged fluids. Eventually, some upper limit may have been reached to the maximum silica concentration, perhaps corresponding to the saturation of the fluids with quartz at the borehole temperature. Attainment of this limit would correspond to the silica maximum in the discharged fluids. Then, as reaction time is further increased, concentrations on the high-temperature side are no longer raised but the rate of precipitation is increased, causing dissolved silica concentrations to decrease.

The effects of temperature and fluid volume on the rate of permeability decrease are explicable in terms of the amount of material—principally silica—transported from high to low temperatures across the granites. Increasing temperature raises the concentrations of the solutions, thereby increasing the amount of material that is transported and redeposited at low temperatures in the cylinders. Although with lower flow rates the fluids have more time to deposit minerals at low temperatures, the total amount of mass transfer in a given time is also reduced. If the fluid volume used in the experiment is sufficiently low, as for B300, permeability decreases occur at a lower rate despite increased temperatures (Fig. 2c). In the same way, the decreasing rates of permeability change with time, shown in Figure 2b and c, may also be the result of decreases in the amount of mass transfer with time. In B250-1 and B275 (Fig. 2a), the rates of permeability decrease were low and unchanging in the time of the experiments. For these two cases, enhanced precipitation at the lower flow rates may have balanced the reduction in fluid volume.

## APPLICATIONS

### *Nuclear waste disposal siting*

Many considerations are involved in selecting appropriate geologic repositories for nuclear waste isolation. Effective containment would be best provided by a rock body with low permeability and porosity, low hydraulic gradient, a high capacity for radionuclide adsorption in the case of leakage, and chemical and mechanical stability under the stress fields generated by radioactive heating (WITHERSPOON *et al.*, 1981). Granitic igneous terrains possess several of these favorable characteristics. For example, granites in the Illinois Basin have low intact permeabilities that decrease with increasing depth as a result of greater stresses that close fractures and pore apertures (HAIMSON and DOE, 1981). Groundwaters at 800 m depth in quartz monzonite in Sweden (WITHERSPOON *et al.*, 1981) are distinctly different in major and isotopic constituents from shallow waters, and the deep waters may be several thousands of years in age. These fluid characteristics suggest that natural groundwater flow in such rocks is very slow and that mixing of deep and shallow groundwaters is not extensive.

The effects of heat generation at the canister sites are of special importance, because thermally induced cracking and fluid migration could adversely affect the otherwise favorable characteristics of the granitic rock mass. The results of this work indicate that localized heating may actually enhance radioactive waste isolation in granitic rocks. Decreases in permeability were observed in both fractured (MORROW *et al.*, 1981) and intact granite samples as a result

of flow away from a heat source. Reactions involving silica may have been the most significant factor in the rapid self-sealing of the granite cylinders. Thus, quartz-rich rocks such as the granitic rocks examined or some gneisses and quartzites might be especially favorable geologic barriers for nuclear waste disposal.

The experimental conditions show a close correspondence to the situation at a nuclear waste repository, with high temperatures in the immediate area of the canisters and a rapid temperature drop across an area some tens of meters in width (WITHERSPOON *et al.*, 1980; p. 10). The actual size of the thermal aureole will depend on the amount of radioactive material placed within a canister and the spacing of canisters at a site.

Temperatures up to 300°C produced favorable permeability changes in the granites studied because the higher temperature water has the capacity to transport and deposit greater amounts of dissolved material in the surrounding rock. Thus, to some extent, high canister temperatures may enhance rather than inhibit nuclear waste isolation. However, other adverse effects to the rock mass may occur with long-term heating. In addition, high temperatures may be deleterious to the waste form, the canisters, and the backfill materials.

In the discussion of experimental results, all material transfer across the granite cylinders was attributed to fluid flow. However, the imposed temperature gradient itself will cause some migration of dissolved species in the pore fluids; this process of thermal diffusion is called the Soret effect (WALKER and DELONG, 1982). No attempt was made in this study to separate the contributions of thermal diffusion and fluid flow on mass transfer and resulting permeability changes in the granites. Nevertheless, such diffusive transfer may be an important process at a nuclear waste disposal site, where the rates of groundwater flow may be quite low compared to those of these experiments. Further studies are warranted to examine the effects of thermal diffusion on the permeability of nuclear waste repository host rocks.

### *Geothermal systems*

The "hot dry rock" concept of geothermal operations (HEIKEN *et al.*, 1981) was introduced to develop energy resources in areas which have large positive thermal anomalies but which lack a well-developed groundwater circulation system to transfer heat to the surface. In such places, a flow loop would be developed by drilling a deep injection well and a less deep production well, and then inducing fractures in the depth interval between the two wells. Water pumped down the injection well would rise along the fracture system to the production well, acquiring heat from the surrounding rock. The heat would be extracted from the water reaching the surface, and this water would then be recycled. Field tests in the hot dry rock program are being conducted in granodiorite very similar in mineral proportions (CHARLES, 1978) to the rock types of this study.

The factors that favor repository sealing for nuclear waste disposal may have marked adverse effects on the operation of such geothermal systems. These experiments illustrate the rapidity with which silica may be removed from high-temperature solutions when flowing at low rates through cooler rocks. If a temperature gradient exists along the induced fracture system, silica dissolved at depth may be redeposited at shallower levels of the fracture network; and the rate of deposition will increase with decreasing fracture width. Many of the narrow, subsidiary fractures could become completely sealed in a relatively short time, thus reducing the available surface area for heat transfer from the rock to the fluids. Extensive clogging would reduce the life of the plant, or at least make necessary the frequent refracturing of the rock at depth. The same rapid sealing processes are also operative in natural hydrothermal systems.

This study also illustrates some of the drawbacks to the use of the quartz geothermometer in determining reservoir



temperatures. Field sampling has shown that the best estimates are made from fluids discharged from large fissures with high flow rates. Through computer modelling, RIMSTIDT and BARNES (1980) demonstrated that decreasing the ascension rate and increasing the parameter  $A/M$  (= relative interfacial area between solid and aqueous phases/relative mass of water) will significantly enhance silica deposition and lower quartz-derived temperatures. In these experiments the low flow rates and narrow aperture size led to substantial amounts of silica precipitation in the rock samples. Decreasing the flow rate through pressure increase or permeability reduction led to even more effective removal of silica from solution, in agreement with RIMSTIDT and BARNES (1980).

#### Diagenesis

The rock types and temperature ranges used in this study are not directly applicable to interpreting diagenetic processes in clastic sediments. However, the parameters investigated, namely material transfer within a rock sample and its effect on permeability and porosity, are major factors in diagenesis; thus, suitable investigations could be conducted using this experimental apparatus. Many recent investigations have emphasized the importance of material transfer by bulk fluid flow to account for the observed dissolution and precipitation of minerals (HAYES, 1979; BLATT, 1979; SURDAM and BOLES, 1979; WOOD and SURDAM, 1979). The principal flow of fluids may be vertical rather than horizontal, with the fluids derived from the dewatering of sediments (HAYES, 1979). Thus, at least a slight  $T$  gradient may extend over the flow path, which could be modelled in experiments similar to those described here. SURDAM and BOLES (1979) and DAVIES *et al.* (1979), among others, have emphasized that fluid composition may be at least as important as temperature in controlling cementation reactions; the relative effects of fluid composition and temperature could readily be investigated.

#### SUMMARY

The permeability of granite was considerably reduced within several days by flow of water down a temperature gradient imposed on the samples. The cause of the permeability reductions appears to be the solution of minerals near the heat source and their redeposition at lower temperatures in the granite along grain boundaries and cracks. The rate of permeability change varied with temperature and flow rate, which controlled the amount of actual mass transfer from high to low temperatures in the granites. The available evidence suggests that a silica mineral, perhaps quartz, was the major precipitated phase during the experiments. The silica content of the discharged fluids was sensitive to reductions in flow rate which increased reaction times at all temperatures; the reactivity of the solutions with respect to silica deposition was enhanced because of the high ratio of channel surface area to fluid volume. The fluids were also supersaturated with respect to other minerals at low temperatures in the granite samples, but these minerals were deposited, if at all, at very low rates compared to silica. With additional time for reaction, these minerals might precipitate in increasing amounts; in addition, a greater degree of rock alteration might be observed.

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