UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

PERMEABILITY AND PORE-FLUID CHEMISTRY OF THE
BULLFROG TUFF IN A TEMPERATURE GRADIENT: SUMMARY OF RESULTS

By

J. Byerlee, C. Morrow, and D. Moore

Introduction

The permeability and fluid chemistry of a Nevada Test Site tuff is being studied under conditions simulating a nuclear waste repository environment. The purpose of this project is to investigate the changes that take place with time when groundwater comes in contact with heated rock, and to determine the ease with which potential radionuclide-bearing groundwater could be carried into the environment.

Sample Description

Samples of the Bullfrog Member of the Crater Flat Tuff were collected from the southwest end of Yucca Mountain, just outside the boundaries of the Nevada Test Site. The Bullfrog at this location has four distinct layers. Going up-section they are: an air fall, a vitrophyre, a vapor-phase altered ash flow, and an unwelded ash flow. Our samples were collected exclusively from the vapor-phase altered ash flow. They are devitrified, non-zeolitized and moderately welded. Deformed elongated pumice fragments are visible in the matrix, as well as large elongated voids.

Procedure

The experimental technique is described briefly below; additional details are presented in Morrow et al. (1981) and Moore et al. (1983). The experimental assembly is shown in Figure 1. A cylindrical sample of the Bullfrog Tuff, 7.62 cm in diameter and 8.89 cm long, with a 1.27 cm diameter

borehole, was used in the experiment. The borehole contained a coiled resistance heater to produce a temperature gradient between the center and outside of the rock. Water flowed radially through the tuff from the high temperature borehole to the lower temperature outer edge in response to a small differential pore pressure gradient between the center and outside of the rock. Cores were drilled such that flow would be along the direction of bedding and of elongation of the voids. All exposed metal in the high temperature area was gold plated to reduce contamination of the fluids. Gold shims at the ends of the sample prevented water from leaking between the tuff and the fused silica cylinders that served as thermal insulators.

The experimental design necessitated the presence of a good thermal insulator on either side of the rock sample. Such insulating cylinders also need to be impermeable, so that water flows only through the rock sample. The fused silica cylinders used best satisfy both these requirements. Because the insulators are exposed to the inlet fluids, the possibility exists that the fluids will a_cquire excess silica from the insulating cylinders. However, there is some evidence that such effects, if present at all, are minimal. For one thing, the fused silica cylinders are not immediately adjacent to the heating coil; as a result, they will not be heated to the same degree as the tuff cylinders. In addition, the same insulating cylinders were used in several experiments without showing evidence of corrosion along the borehole. Finally, we have conducted experiments on two different granodiorites, quartzite, and tuff and have found that silica in solution varies with the rock type used. Thus, dissolved silica concentrations in the discharged fluids are not being controlled by the presence of the fused silica insulators.

A stainless steel mesh was wrapped around the outside of the sample to a total thickness of 0.63 mm, to allow drainage of the pore fluids that have

passed through the rock. In this way, the jacket for the sample assembly did not interfere with fluid flow, while still sealing the sample from the confining pressure fluid. Pore pressure and hydrostatic confining pressure were held constant by a computer-controlled servo-mechanism. Samples of the pore fluids were taken at intervals during the experiments to determine changes in water chemistry as a result of interaction with the heated tuffs. Fluid samples also were collected during initial, room-temperature permeability measurements.

Three experiments were conducted using the Bullfrog tuff; the conditions are summarized in Table 1. Experiments 1 and 2 both had a borehole temperature of 250°C; deionized water was used as pore fluid in the first experiment whereas a natural groundwater (J13) from the Nevada Test Site was used in the second. The third experiment was conducted at a 150°C borehole temperature, again using the J13 water whose composition, as determined by our analysis, is presented in Table 2. We attempted to maintain a pore pressure differential of around 2.5 bars in all experiments. However, it was not possible to maintain that high a pressure differential during experiment 2 without making the flow rate unreasonably high. As a result, a 1.4 bar differential was used in experiment 2.

Permeability

The variation in permeability with time was determined from measured changes in the mass flow rate over the constant pore pressure differential. The radial flow form of Darcy's Law was solved for permeability and integrated over the radius from the inner borehole (r_1) to the outer edge of the sample (r_2), as follows:

$$k = \frac{Q_m}{2\pi\ell\Delta P} \int_{r_1}^{r_2} \frac{\nu(r)}{r}\, dr$$

Q_m is the mass flow rate, ℓ the length of the sample, k permeability, r the sample radius, and dP/dr the fluid pressure gradient between the center and outside of the sample. For the calculations, dP/dr is assumed to be constant. ν is the dynamic viscosity of water, which is a function of temperature and therefore of radius in these experiments. Values of ν used in the calculations were obtained from published steam tables. The permeabilities so calculated describe the bulk permeability properties of the rock cylinders.

Figure 2 plots the changes in permeability of the tuff cylinders with time. The initial, room temperature permeabilities of the three samples varied between 0.5 and 8.5 μda. The higher starting permeabilities of the tuffs in experiments 1 and 2 may be a function of differences in the size and degree of interconnection of void spaces in individual rock cylinders. The temperature in the borehole was raised to the desired value over a space of about 15 minutes, and a time-stationary temperature gradient was established across the tuff cylinders approximately an hour after initial heating. Some transient permeability increases accompanied the temperature increase, probably related to thermal cracking in the tuffs. The cylinders in the 250°C experiments showed marked permeability increases followed by equally rapid decreases in the first 6 hours of the heated experiment. Thereafter, the permeability of cylinder 2 continued to decrease slowly to approximately 70% of the pre-heated value. However, about 8 days elapsed before the permeability of cylinder 1 had completely returned to its initial value, and no further changes were measured. In the third experiment, at 150°C borehole

temperature, only a slight permeability increase was observed upon heating, but the permeability remained at that higher value throughout the experiment.

Fluid Chemistry

Sample Collection and Analytical Techniques. 1.5-ml samples of the fluids discharged at the low-temperature, outer edges of the tuff cylinders were collected at intervals during the experiments. Immediately upon collection, each sample was passed through a 0.45 μm filter and a 0.25 ml sample was separated for SiO_2 analysis. Room-temperature pH measurements were then made on the remaining fluid samples.

Selected samples were analyzed for up to 12 dissolved species. The fluids reserved for silica analysis were digested overnight in a 1N NaOH solution and then analyzed by standard spectrophotometric techniques, using the molybdate blue method (ASTM, 1974, pp. 401-2). From the larger fluid sample, the cations Na, Ca, K, and Mg were determined using atomic absorption techniques, and the total dissolved inorganic carbon content was determined with a carbon analyzer. The anions Cl, F, SO_4, NO_3 and, where present, NO_2 and PO_4, were determined using ion chromatography. The results of these analyses are listed in Table 3, and the variations in pH and Na and SiO_2 concentrations with time during the heated experiments are plotted in Figures 3-5.

In near-neutral solutions, dissolved silica is not significantly ionized, and inorganic carbon in solution exists principally as bicarbonate ion. However, the solutions discharged from the tuffs have relatively high pH

values, which lead to ionization of a large proportion of the silica content and formation of carbonate at the expense of bicarbonate ion. In order to estimate the extent of such ionization reactions, the fluid compositions were analyzed with the SOLMNEQ computer program (Kharaka and Barnes, 1973; modified by Mariner, personal communication, 1982), for temperatures of 25°C. These determinations, along with the calculated OH concentrations , are listed in Table 4.

Cation-anion balances determined from the combined values of Tables 3 and 4 are good for some samples but not others. Possible reasons for some of the poor balances include: (1) The calculations were made at 25°C, but the solution concentrations may still reflect the higher-temperature conditions of the experiments. Unfortunately, the large temperature gradient in the experiments makes it difficult to choose a more appropriate temperature for the SOLMNEQ calculations. (2) For these high-pH solutions, slight errors in pH can have a significant effect on the calculated ionic concentrations in Table 4. We are looking into the possibility of adding an on-line pH electrode to the experimental assembly, which might provide a better estimate of the pH of the pressurized fluids discharged from the tuffs. At the present time, the calculated values in Table 4 should be viewed only as approximations of the true values; but we are continuing to investigate ways to improve the calculations.

Room-Temperature Fluids. The fluids collected during the preliminary, room-temperature permeability measurements acquired considerable amounts of dissolved species (Tables 3 and 4). After 2 or 3 days' pumping, however, the ionic concentrations began to decrease fairly rapidly. The sequence of increasing and then decreasing ionic concentrations is shown for experiment 1

in Tables 3 and 4. Before heating the tuffs, we continued pumping until the conductivity of the discharged fluids was about 10 to 20 percent of the highest measured value; this was done in order to reduce the amount of such adhered and pore species in the heated run.

The room-temperature fluids were characterized by high pH, high Na contents relative to other cations, and relatively high SiO_2 contents (Tables 3 and 4). The principal anions in the early-collected, high-conductivity samples were Cl, SO_4, NO_3, HCO_3, and CO_3. Trace amounts of NO_2 and PO_4 were present in some samples. Some Mg and Ca concentrations in room-temperature fluids from experiments 2 and 3 were unusual in being lower than the starting J13 fluid used in the experiments.

Heated Fluids. The concentrations of dissolved species in the discharged fluids increased rapidly upon initial heating and then gradually decreased again (Tables 3 and 4). The maximum concentrations reached in experiments 1 and 3 were similar to each other and somewhat higher than those of the second experiment. Total silica contents (Fig. 5) and pH values (Fig. 3) generally increased over the first few days, and then gradually dropped; the exception was in experiment 2, where silica rose to 220-240 ppm (as mg/l SiO_2) and then remained constant (Fig. 5). Because the ratio of bicarbonate to carbonate and the amount of dissociation of silica in the solutions (Table 4) vary directly with pH, the concentrations of CO_3, H_3SiO_4, and H_2SiO_4 rose and fell with the pH.

By the end of the experiments, species such as Na (Fig. 4), total SiO_2 (Fig. 5), and carbonate + bicarbonate had settled out to concentrations well above those of the starting fluids, and they dominated the final solutions.

Ions such as Cl, SO_4, and F decreased rapidly to near zero concentrations in experiment 1 and to near the initial J13 values in 2 and 3. In the first and second experiments, measurable NO_2 concentrations were found some time after the start of the heated run. This NO_2 may possibly have been derived from the alteration of NO_3 in solution. The final concentrations of both NO_3 and NO_2 together were lower than for the starting J13 groundwater in experiments 2 and 3. In addition, all Mg concentrations and some Ca and K concentrations were below J13 values.

Discussion of Fluid Compositions

Room-Temperature Fluids. Mineral-fluid interactions seem insufficient to account for the high concentrations of dissolved material contained in the room-temperature fluids. The rapid decrease in the concentrations of many of the dissolved species with time (Table 3) also suggests the removal of a finite amount of readily leached material, rather than continuous mineral reaction. In addition, some species in the fluids, such as NO_3, PO_4, Cl, and SO_4 do not come from minerals in the tuff. Instead, they probably were derived principally from materials that were loosely adhered onto mineral surfaces or deposited on vug walls. Some of the species, such as Cl or S, could have had a magmatic origin, being concentrated in intercrystalline spaces because few of the minerals replacing glass in the tuffs could accommodate them (Ellis and Mahon, 1964). Species such as NO_3 and PO_4, which may have had an organic source (T.S. Presser, personal communication, 1982), are found in the J13 groundwater and may have been deposited along cavities in the tuff by evaporating groundwaters. In support

of this possibility, the tuff samples were collected from the sides of an intermittent stream, where they would be continually subjected to alternating wet and dry conditions.

The loss of Mg and, in some cases, Ca from the J13 waters does suggest that some kind of mineral-water interaction was taking place. However, the low temperatures and relatively rapid flow rates would seem to argue against mineral growth in the short time available. Instead, some simple ion-exchange process, perhaps in clay minerals, may be responsible for the observed decreases. Such exchange reactions would readily occur at low temperatures.

High-Temperature Fluids. Several competing factors may be important in controlling the heated fluid compositions, among them (1) the removal of additional adhered materials from mineral surfaces, (2) the presence of a temperature gradient, (3) the effects of flow rate, and (4) the complicated mineralogy of the tuffs. As a result, it is difficult to determine the principal controls of the final, relatively stable solution compositions in the three experiments. However, a few tentative conclusions can be drawn.

Ions such as Cl, SO_4, and NO_3, which decreased rapidly from high initial values to 0 or J13 levels, probably comprise those intercrystalline species that were not removed during the room-temperature permeability measurements. The initial concentrations of Na, HCO_3 and CO_3, and SiO_2 also may have been augmented by materials leached from mineral surfaces; however, their final, relatively high concentrations probably are due to tuff- water interactions, as influenced by temperature and flow rate. As shown in Table 1, the third experiment had the lowest rates of fluid flow and the second experiment the highest. At the lower flow rates, more time was available for material to go into solution. As a result, solution

concentrations throughout experiments 1 and 3 were similar, despite the much lower temperatures of the third experiment. Although the first two experiments had similar temperature ranges, the higher flow rates of the second experiment caused solution concentrations to be concomitantly lower, despite the fact that the starting fluid in the first experiment was deionized water and that in the second experiment was J13 groundwater.

The use of deionized water or J13 groundwater in different experiments had little apparent effect on the permeability of the tuffs and no influence on the discharged solution compositions, except to raise the base level of some species. The lack of influence is probably due to the very dilute, near-neutral character of the J13 groundwater. The major importance in using J13 was in the observation that some elements were lost from the fluids as they flowed through the tuffs. Ion exchanges similar to those proposed for the room-temperature fluids may explain part of the observed decreases in Mg, Ca, and K contents. In addition, the growth of minerals such as smectite clays or zeolites in open spaces is more likely at elevated temperatures. From the solution compositions, it is impossible to tell whether mineral growth actually occurred; however, SEM examinations of the starting materials and run products is planned to see if any new-grown minerals can be identified.

The reduction of the NO_3 contents to values below those of J13 in experiment 3 may be a function of the instability of nitrate rather than the removal of NO_3 from solution by reaction with the tuff. The possible conversion of some NO_3 to NO_2 during parts of the experiments, described previously, suggests that NO_3 is relatively unstable; the loss of all NO_3 may be caused by vaporization of NO_3 to N_2 gas.

Significance of Results to Nuclear Waste Disposal

Despite the possibility of mineral growth during the heated runs, the permeability of the Bullfrog tuff cylinders did not show significant decreases in experiments of up to 5 weeks. The lack of permeability change in these experiments contrasts with our previous studies on granite (Morrow et al., 1981; Moore et al., 1983) and on quartzite (unpublished data). The granites and quartzite lacked any large voids, so that fluid flow was concentrated along microfractures and grain boundaries. Material such as silica that went into solution at high temperatures was redeposited at low temperatures in the granite and quartzite samples. Because of the narrow aperture sizes and low flow rates, which were more conducive to mineral reaction, permeability reductions of up to 2 orders of magnitude were measured in both rock types. Similar mineral deposition or growth may have occurred in the Bullfrog tuff samples; but because of the large initial pore and vug spaces, small decreases in their size caused by mineral growth would have little effect on permeability.

For proposed nuclear waste disposal in unsaturated zones of the Nevada Test Site, the lack of permeability decrease in the examined tuffs apparently is desirable, as it keeps downward-percolating groundwaters from accumulating around the canisters. However, it should be remembered that other tuff layers at the Nevada Test Site may not have such high porosities and permeabilities. As a result, their permeabilities potentially could be more drastically altered by mineral growth accompanying localized heating and fluid flow. In addition, the uptake of Mg, Ca, and some K from solution by the tuff may be

important when the materials used in constructing the nuclear waste repository are considered. The groundwaters are so dilute that any mineral growth resulting from such element uptake would have at best a minor influence on the permeability of tuff layers with large void spaces. However, some proposed backfills and cement grouts may provide a sufficient source of elements such as Ca and Mg to cause extensive mineral growth even in the tuffs considered here, with resulting crack-filling and permeability reductions. Such possibly deleterious interactions between site materials and the host tuff layers should be investigated.

The relatively high pH acquired by the waters flowing through the tuffs may make the solutions corrosive with respect to the canisters. The long-term importance of groundwater pH, if potentially corrosive, to a waste disposal site is unknown. For one thing, the pH of the discharged fluids did become slightly less basic with time (Fig. 3). In addition, the low rainfall at the Nevada Test Site would limit the amount of water reaching the level of the canisters, which also would limit the amount of possible corrosion.

References

American Society for Testing and Materials (1974) Annual Book of ASTM, Part 31 [water]. Philadelphia, PA, 902 pp.

Ellis, A.J. and Mahon, W.A.J. (1964) Natural hydrothermal systems and experimental hot-water/rock interactions. Geochim. Cosmochim. Acta 28, 1323-1357.

Kharaka, Y.K. and Barnes, I. (1973) SOLMNEQ: Solution-mineral equilibrium computations. NTIS, U.S. Dept. Commerce, PB-215 899, 81 pp.

Moore, D.E., Morrow, C.A., and Byerlee, J.D. (1983) Chemical reactions accompanying fluid flow through granite held in a temperature gradient, Geochim. Cosmochim. Acta 47, 445-453.

Morrow, C., Lockner, D., Moore, D., and Byerlee, J. (1981) Permeability of granite in a temperature gradient, J. Geophy. Res. 86, 3002-3008.

TABLE 1. Experimental Conditions

Experiment #	1	2	3
Confining Pressure, bars	300	300	300
Pore Pressure, bars	100	100	100
Differential Pore Pressure, bars	2.4	1.4	2.5
Borehole Temperature, °C	250	250	150
Jacket Temperature, °C	68	73	48
Pore Fluid	Deionized water	J13 groundwater	J13 groundwater
Average Daily Flow Rate	65ml	100ml	14.5 ml

TABLE 2. Composition of J13 Groundwater From the
Nevada Test Site

pH	7.69	
SiO_2	61	mg/ℓ
Na	44	mg/ℓ
K	4.5	mg/ℓ
Mg	1.9	mg/ℓ
Ca	12	mg/ℓ
HCO_3*	120	mg/ℓ
SO_4	17	mg/ℓ
NO_3	8.1	mg/ℓ
F	2.2	mg/ℓ
Cl	8.1	mg/ℓ
Cation Sum	2.784 meq/ℓ	
Anion Sum	2.796 meq/ℓ	
Balance	-0.4%	

* Determined by both carbon analyzer and titration methods

TABLE 3. Chemical Analyses (mg/ℓ) of Collected Fluids

Experiment	Sample	Days	pH (@25°C)	Na^+	K^+	Ca^{++}	Mg^{++}	$SO_4^=$	NO_2^-	NO_3^-	F^-	Cl^-	$PO_4^{\equiv}$	SiO_2	Total C
Room-Temperature (1)	139	--	9.49	480	12	7.5	0.9	200	--	390	6.9	280	--	22	44
	142	--	9.72	530	10	7.1	0.8	190	--	400	5.6	310	--	32	30
	145	--	9.59	610	12	5.4	0.6	220	--	460	0.9	330	--	40	43
	149	--	10.18	860	16	7.6	0.8	300	--	530	3.4	390	Tr	NA	100
	151	--	10.33	460	9	1.6	0.2	120	--	200	2.0	140	Tr	160	56
Heated Run	152	0.2	10.12	690	19	1.5	0.2	210	--	310	5.3	240	Tr	380	78
	153	1.0	10.33	640	17	1.3	0.2	130	--	220	7.0	150	--	610	62
	154	1.2	10.34	590	14	0.5	0.2	110	--	180	6.0	110	Tr	700	55
	155	1.5	10.26	520	12	1.0	0.1	66	--	120	4.6	100	Tr	590	52
	156	2.0	10.29	440	11	0.7	0.2	39	--	68	3.2	68	Tr	590	54
	157	2.2	10.11	390	8.5	0.5	0.1	30	--	50	2.6	42	Tr	600	53
	159	2.9	10.19	360	8.3	2	0.1	23	--	57	2.4	32	Tr	560	55
	161	3.9	10.04	310	7.1	1	0.1	15	--	24	1.8	21	Tr	500	60
	166	6.1	9.95	230	5.8	0.5	0.1	9	--	12	1.2	17	Tr	410	46
	167	6.9	9.95	220	7.1	1.0	0.1	7	--	8	1.2	16	Tr	400	43
	169	8.2	9.72	230	7.1	--	0.02	15	5.9	15	1.4	20	Tr	370	56
	171	9.0	9.62	250	10	2	0.1	36	17	9.3	1.7	48	--	330	60
	173	10.0	9.77	200	5.9	1.9	--	9	4.9	6.4	1.5	15	Tr	330	44
	174	10.9	9.14	190	12	1.1	0.3	6.6	--	4.7	1.1	10	Tr	300	74
	178	12.9	9.60	160	5.2	--	0.1	3.9	--	3.4	0.8	6.8	Tr	310	44
	180	13.9	9.70	150	4.4	--	0.1	3.6	--	2.3	0.8	5.5	Tr	300	38

TABLE 3. Chemical Analyses (mg/ℓ) of Collected Fluids (Continued)

Experiment	Sample	Days	pH (@25°C)	Na^+	K^+	Ca^{++}	Mg^{++}	$SO_4^=$	NO_2^-	NO_3^-	F^-	Cl^-	$PO_4^{\equiv}$	SiO_2	Total C
(2) Room-Temperature	186	--	8.67	630	15	93	2.1	590	--	340	5.7	230	Tr	41	66
	195	--	9.46	160	5.9	22	0.22	97	2.7	5.7	3.3	13	Tr	71	60
Heated Run	196	0.3	8.87	400	22	34	0.17	250	--	160	8.8	110	Tr	160	59
	197	0.5	8.94	370	20	24	0.07	250	--	140	11	98	Tr	130	64
	198	0.9	9.07	310	16	18	0.06	190	0.62	81	9.6	59	Tr	200	55
	199	2.3	9.14	220	14	11	0.06	120	11	21	7.6	26	Tr	230	65
	201	3.0	9.12	180	11	10	0.16	87	14	7.5	6.5	22	Tr	200	65
	203	4.0	9.07	170	11	9.1	0.09	68	14	2.4	6	17	Tr	240	62
	207	6.0	9.12	150	9.6	8.1	0.02	58	9.6	1.4	5.4	13	Tr	240	44
	209	7.0	9.07	140	9.8	6.1	0.04	45	5.2	1.5	4.9	11	Tr	220	50
	211	8.0	9.01	130	10	6.4	0.23	41	5.1	1.6	4.4	11	Tr	240	44
	215	10.0	8.76	110	9.8	6	0.05	35	4.2	1.0	4.0	9.6	Tr	240	41
	219	12.0	8.82	110	9.0	7.3	0.06	35	5.6	--	4.2	10	--	230	52
	223	14.0	8.86	110	9.8	9.8	0.12	36	5.0	--	4.1	10	Tr	220	46
	226	15.5	8.87	110	9.5	8.8	0.05	32	4.4	--	3.8	9.4	Tr	240	42
	229	17.0	8.69	100	9.6	9.2	0.04	31	5.4	--	3.8	8.8	Tr	230	43
	233	19.0	8.67	100	9.4	9.3	0.05	30	3.8	--	3.5	9.2	Tr	230	41
	238	21.2	8.53	90	9.7	9.4	0.06	27	3.3	--	3.3	8.7	Tr	230	43

TABLE 3. Chemical Analyses (mg/ℓ) of Collected Fluids (Continued)

Experiment	Sample	Days	pH (@25°C)	Na^+	K^+	Ca^{++}	Mg^{++}	$SO_4^=$	NO_2^-	NO_3^-	F^-	Cl^-	$PO_4^{\equiv}$	SiO_2	Total C
(3) Room-Temperature	244	--	9.85	390	4.4	1.2	0.06	70	19	34	4.5	130	7.5	150	84
Heated Run	246	1.3	10.27	660	11	1.9	0.06	89	32	40	7.5	180	16	350	110
	248	2.2	10.27	680	11	--	0.02	84	36	31	8.2	180	11	370	100
	249	4.0	10.42	660	7.0	--	0.09	69	27	30	8.2	140	7.7	500	100
	251	6.0	10.58	620	5.6	--	0.12	54	13	29	7.0	88	6.9	730	84
	253	8.0	10.64	540	5.4	1.9	0.12	40	6.8	20	5.7	51	5.8	660	63
	255	10.2	10.50	450	3.4	0.6	0.03	35	6.6	14	5.2	35	6.0	500	62
	256	11.4	10.54	440	3.6	--	0.14	34	3.0	12	5.0	30	5.7	590	52
	258	13.0	10.51	410	3.3	--	0.06	30	2.4	8.6	4.4	24	5.4	560	51
	260	15.0	10.44	390	6.4	3.1	0.06	28	1.5	6.2	4.1	22	7.1	460	52
	262	17.1	10.35	360	4.9	--	0.09	28	2	4.4	4.0	23	6.8	520	51
	264	19.0	10.24	320	3.7	--	--	27	2	3.3	3.9	20	5.0	450	51
	266	21.0	10.24	270	3.6	2.5	0.12	24	1.7	3.2	3.8	17	6.6	410	46
	268	23.0	10.10	240	2.9	1.2	0.15	24	1.6	2.1	3.7	16	6.5	240	47
	270	25.1	10.03	220	3.6	--	0.02	23	0.3	1.5	3.6	17	6.3	320	48
	272	27.0	10.03	200	3.4	1.9	0.06	21	--	0.5	3.4	15	6.7	310	47
	274	30.3	9.93	200	3.4	1.9	--	22	--	--	3.5	16	7.3	240	51
	276	33.0	9.89	180	6.0	--	0.09	19	--	0.1	3.3	14	6.5	250	50
	278	35.0	9.86	170	3.8	--	--	19	--	0.1	3.4	15	7.9	210	46
	280	37.0	9.77	160	3.3	--	--	18	--	0.1	3.3	13	7.2	210	42

19

TABLE 4. Dissolved Species (mg/ℓ) in Collected Fluids, Calculated From Measured Values With SOLMNEQ Computer Program

Experiment	Sample	OH^-	$H_4SiO_4^\circ$	$H_3SiO_4^-$	$H_2SiO_4^=$	HCO_3^-	$CO_3^=$
(1) Room-Temperature	139	0.61	19	16	0.15	170	48
	142	1.0	21	30	0.47	110	52
	145	0.78	31	33	0.39	160	59
	149	3.1	N.A.	N.A.	N.A.	190	310
	151	4.2	35	200	13	98	180
Heated Run	152	2.7	130	460	19	170	210
	153	4.3	130	780	53	100	210
	154	4.4	150	900	61	92	180
	155	3.6	150	740	41	100	160
	156	3.8	140	750	43	100	160
	157	2.5	210	720	26	130	140
	159	3.0	170	690	31	120	150
	161	2.1	200	580	18	170	140
	166	1.7	190	450	11	140	92
	167	1.7	190	440	10	130	84
	169	1.0	250	340	4.8	200	75
	171	0.79	250	270	3.1	230	72
	173	1.1	210	310	4.9	150	63
	174	0.26	350	120	0.45	340	33
	178	0.74	240	250	2.5	170	45
	180	0.93	210	260	3.4	140	46
(2) Room-Temperature	186	0.10	58	7.6	--	310	22
	195	0.54	65	48	0.37	220	51
Heated Run	196	0.15	210	42	0.09	280	22
	197	0.17	170	40	0.10	300	25
	198	0.23	240	76	0.25	250	26
	199	0.26	270	97	0.36	270	30
	201	0.25	240	81	0.28	270	27
	203	0.22	290	89	0.27	240	25
	207	0.25	290	96	0.33	190	18
	209	0.22	270	81	0.24	190	16
	211	0.19	300	79	0.20	210	15
	215	0.11	330	49	0.07	200	7.8
	219	0.12	310	53	0.09	220	10
	223	0.13	300	54	0.10	220	11
	226	0.11	330	50	0.07	200	8.5
	229	0.09	330	40	0.05	210	7.3
	233	0.09	330	39	0.05	200	6.7
	238	0.06	340	29	0.02	210	5.1

TABLE 4. Dissolved Species (mg/ℓ) in Collected Fluids, Calculated From Measured Values With SOLMNEQ Computer Program (Continued)

Experiment	Sample	OH^-	$H_4SiO_4^o$	$H_3SiO_4^-$	$H_2SiO_4^=$	HCO_3^-	$CO_3^=$
(3) Room-Temperature	244	1.4	82	160	3.2	270	150
Heated Run	246	3.8	85	440	26	200	360
	248	3.8	90	470	27	190	330
	249	5.3	89	650	54	140	350
	251	7.7	90	950	110	81	290
	253	8.7	72	860	120	64	250
	255	6.2	76	650	61	86	230
	256	6.8	83	780	80	67	190
	258	6.3	84	730	70	70	190
	260	5.4	80	590	48	80	180
	262	4.4	110	670	43	92	160
	264	3.4	120	560	27	150	110
	266	3.3	110	510	25	110	130
	268	2.4	85	280	9.6	120	110
	270	2.0	130	370	11	140	100
	272	2.0	130	350	10	130	100
	274	1.6	120	260	5.9	160	96
	276	1.5	130	260	5.4	160	87
	278	1.4	120	220	4.1	160	76
	280	1.1	130	200	3.1	150	60

THERMOCOUPLE WIRES

PORE PRESSURE INLET

PORE PRESSURE OUTLET

Ni-PLATED STEEL PLUG

GOLD SHIM

FUSED SILICA

HEATER COIL

GOLD SHIM

GOLD SHIM

SAMPLE

FUSED SILICA

STAINLESS-STEEL MESH

GOLD SHIM

Ni-PLATED STEEL PLUG
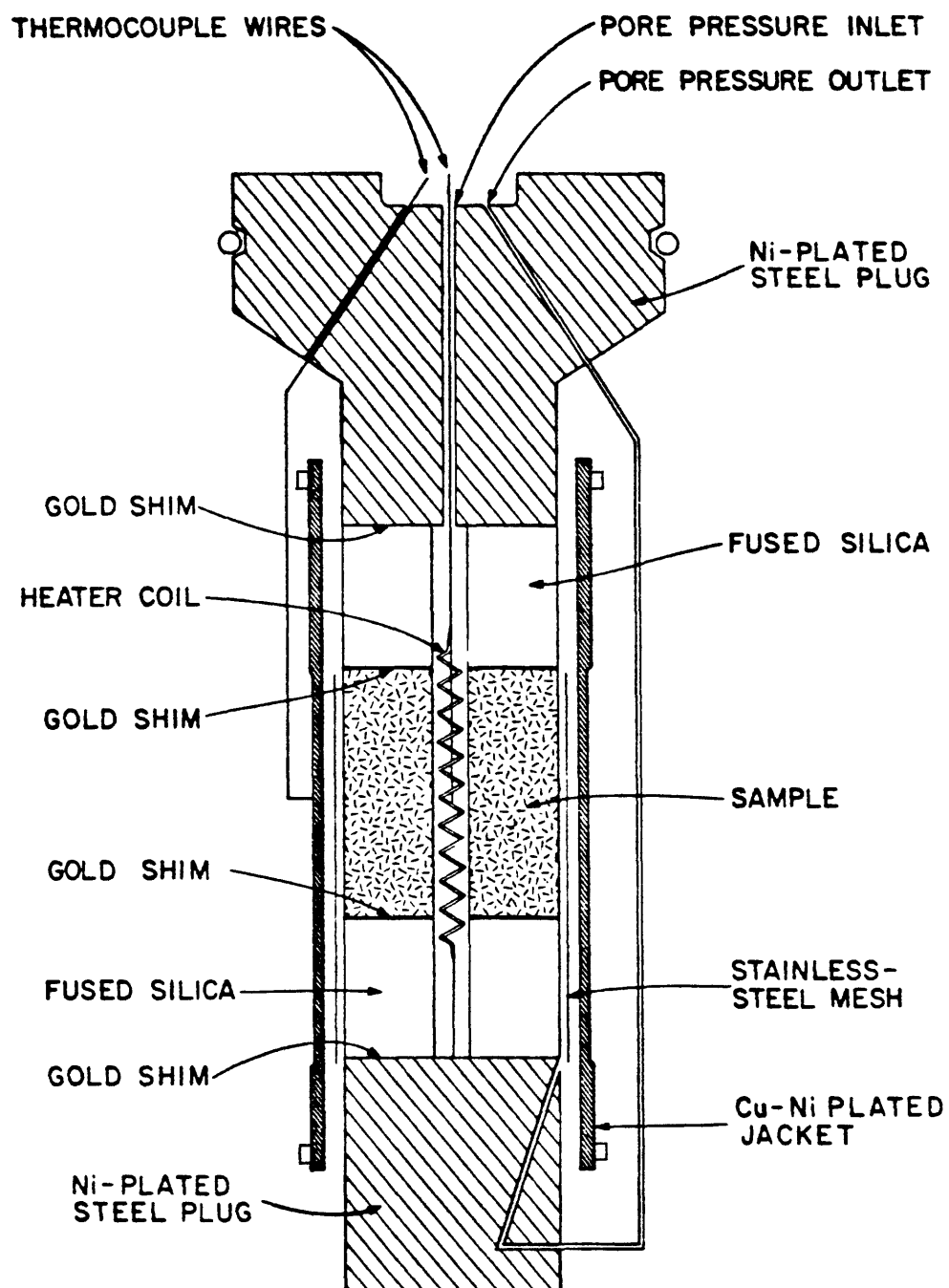
Cu-Ni PLATED JACKET

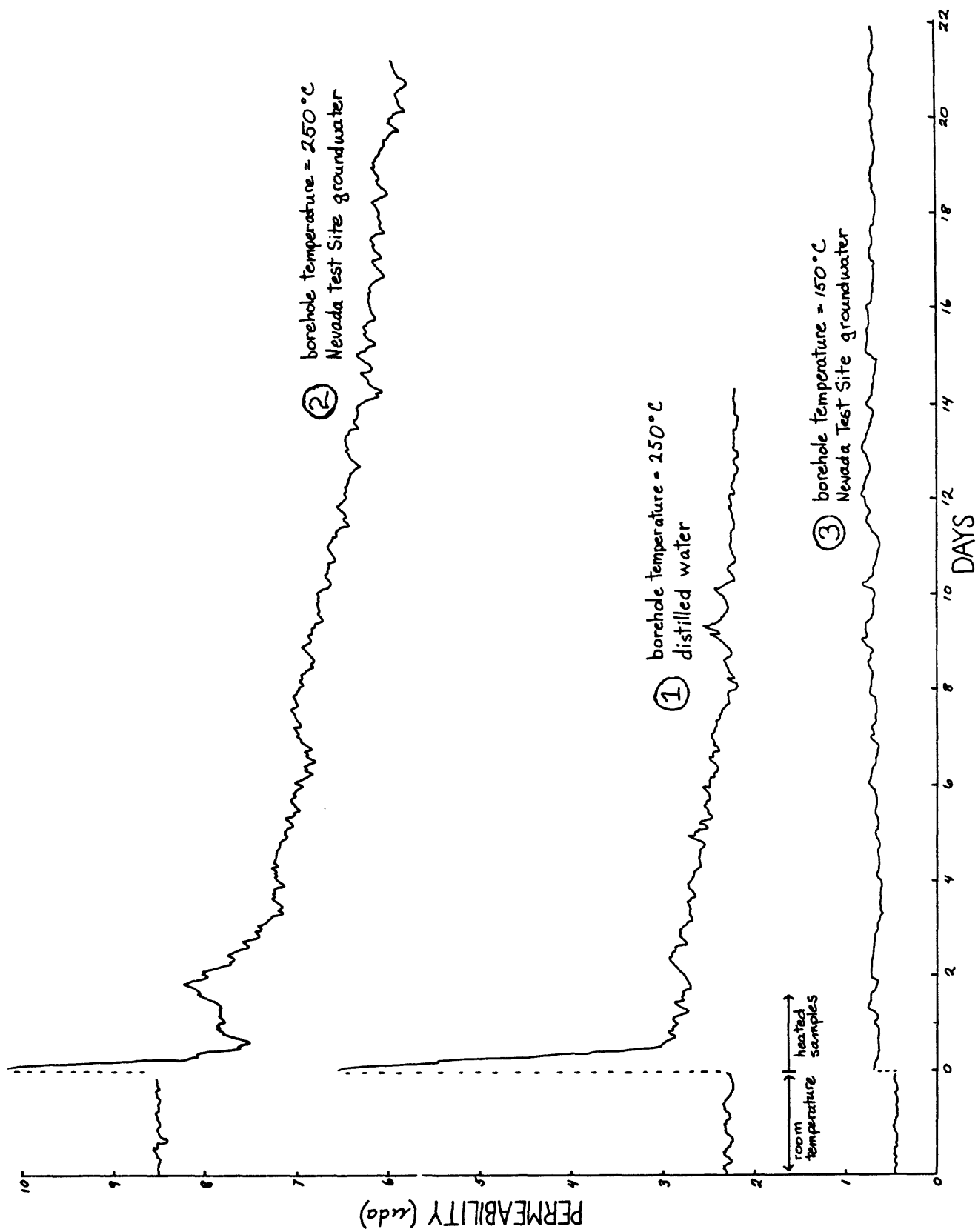Figure 1. Schematic sample assembly.
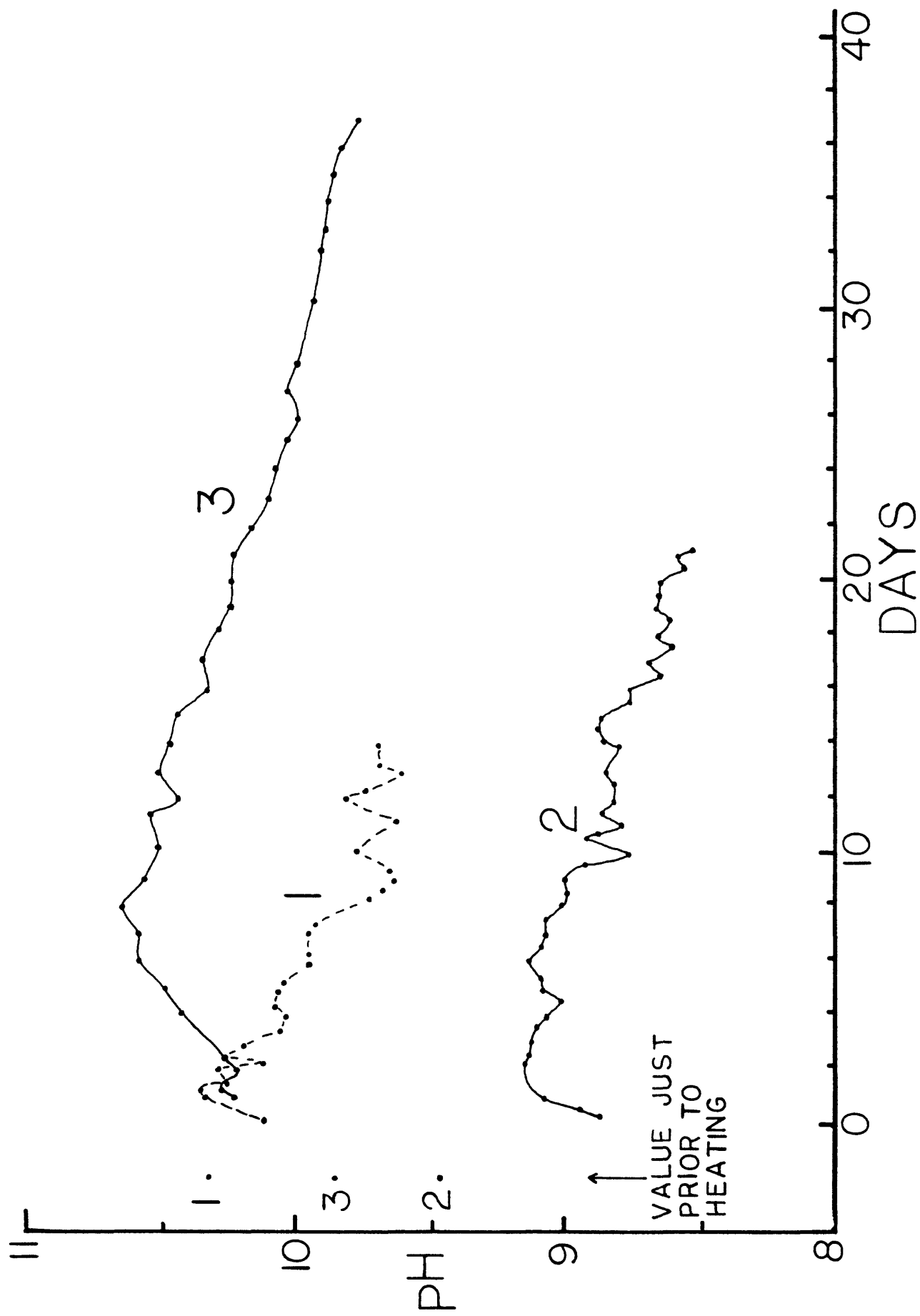
Figure 2. Changes in permeability of Bullfrog tuff as a function of time.

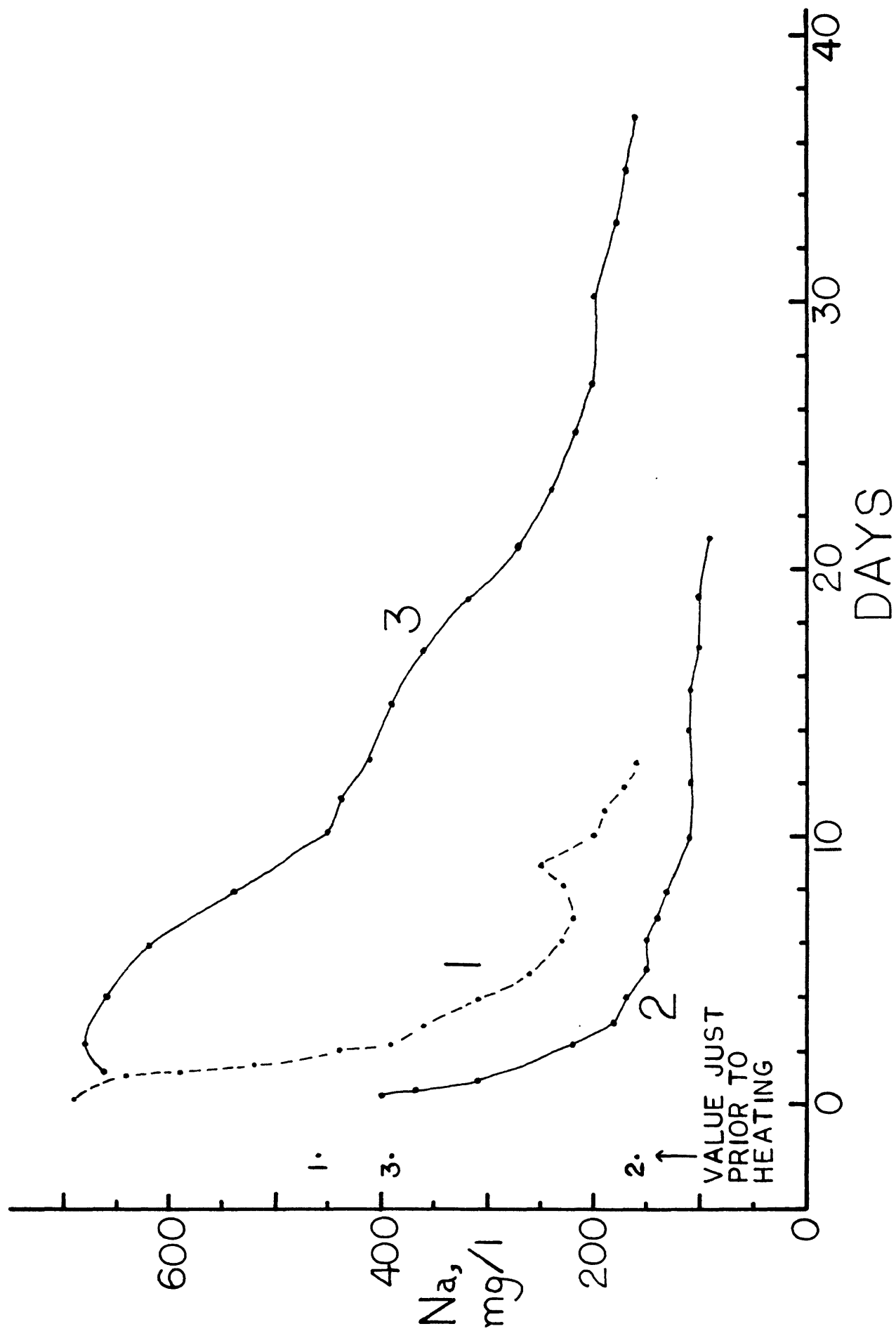Figure 3. Changes in pH with time of the fluids discharged from the Bullfrog tuff cylinders.

24

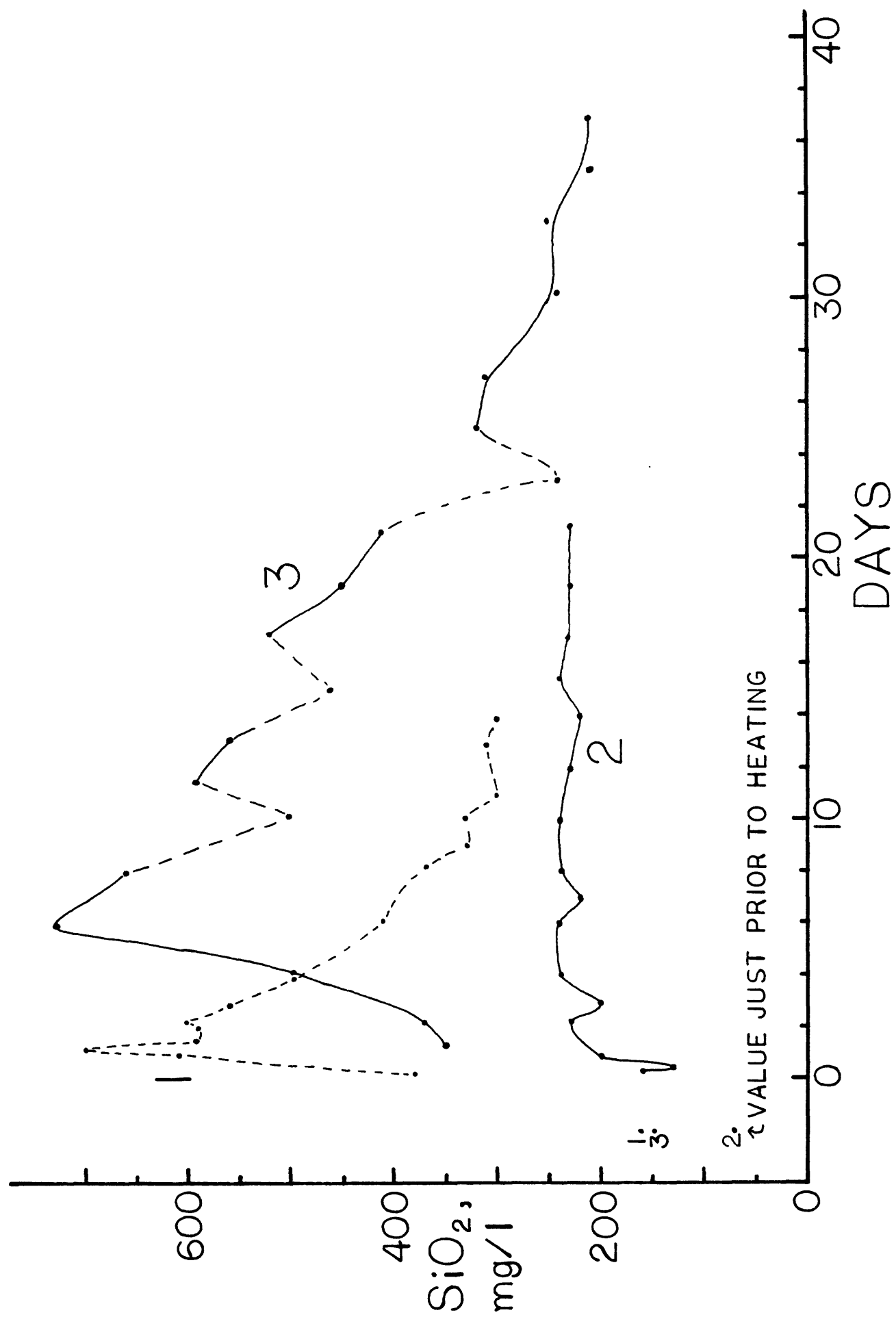Figure 4. Changes in Na content with time of the discharged fluids.

Figure 5. Changes in total dissolved silica content (as mg/l SiO_2) of the discharged fluids, as a function of time.