

Experimental investigation of clogging of fissures and pores in granite

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ABSTRACT. Fluid flow through a fractured granite core and leaching experiments on granite powder (at constant temperatures of 50 and 100 °C and during cooling from 100 to 50 °C) indicate that the dissolved silica content of the fluids originates from the dissolution of feldspars and phyllosilicates. The dissolution of quartz is not ruled out but it should be a minor phenomenon. The precipitation of quartz may control the dissolved Si content during constant temperature leaching. During cooling from 100 to 50 °C chalcedony, aluminosilicates, and chlorite are all capable of precipitation, possibly leading to some clogging or sealing of fissures.

KEYWORDS: granite, fluids, fissures, silica.

STORAGE in geological formations is presently considered to be one of the most realistic means of disposal of radioactive wastes. Many questions remain, however, concerning the long-term fate of radionuclides once stored in repositories. For example the groundwater present around or near the storage site could carry away radionuclides in the event of the failure of the engineered barriers. Thus, low permeability is one of the most important qualities sought in a rock formation to be selected for the 'far field' containment of the wastes.

The heat produced by the presence of radioactive wastes will not only disturb or create groundwater flow (by convection) but also modify the geochemical interactions between water and rock. Most minerals dissolve when the temperature increases and subsequently precipitate when the fluid cools down as it moves away from the heat source. This hydrothermal cycle could thus modify the porosity and the permeability of the host rock by depositing freshly formed minerals in pores and fissures. This might be especially beneficial in helping to seal the cracks and fractures which are likely to be abundant close to the repository because of mechanical stress during construction of the storage site.

Granite has been investigated as a host repository. It is formed mostly of quartz, feldspar, and phyllosilicates, all of which might show increased solubility under higher temperature conditions

created by the storage of radioactive wastes. Ribstein and Ledoux (1983) recently presented a hydrodynamic simulation calculation of the sealing of a theoretical granite fracture by precipitation of silica due to hydrothermal processes expected in the vicinity of radioactive waste repositories. As observed by Reed (1982), major limitations of theoretical models are: (1) the limited existence and quality of thermodynamic and kinetic data; (2) the question of validity of the assumed geochemical process(es) considered; and (3) the assumption of equilibrium or steady-state conditions.

The present paper reports an attempt to monitor the changes in silica and aluminium content of a fluid flowing through a fractured granite core as well as more elaborate leaching experiments performed on batch samples. To our knowledge, this is the first report of such water-granite interactions for small temperature gradients (50 to 100 °C).

Other workers (e.g. recently Morrow *et al.*, 1981 and Moore *et al.*, 1983) studied the leaching of silica, alkaline metals and several minor cations and anions, and a reduction in permeability in both unfractured and fractured granite samples was observed. This they related to the deposition of minerals (quartz and feldspar) dissolved beforehand at higher temperature (200–310 °C). We are interested here in investigating the same phenomena but at temperatures representative of other technical options ($T < 100$ °C) for the storage of radioactive wastes.

Materials and methods

The sample investigated is Fanay granite from the Saint Sylvestre massif (20 km north of Limoges, France). Granite from this area was described by Leroy (1971). A petrographic study confirmed that the sample used is a two-mica granite belonging to a leucogranitic suite. It is a light coloured rock of large to medium grain size with main mineral components quartz, orthoclase, albite, plagioclase, muscovite and a more or less chloritized biotite. Its chemical composition is given in Table I.

Two sets of experiments were performed:

(1) Distilled water was passed through a column packed with Fanay granite powder ($< 125 \mu\text{m}$) maintained at 80°C in order to dissolve a reasonable quantity of silica. The fluid was then circulated through a granite core (fig. 1). This cylinder had first been fractured by

inserting a teflon rod dipped in liquid nitrogen into a hole in its middle. The fissure was caused by the rod being brought back to room temperature. Two water flow rates were used: 0.3095 l/day for 18 days and 0.605 l/day for an additional 12 days (fig. 2).

(2) The composition of the fluid (originally 30 ml of

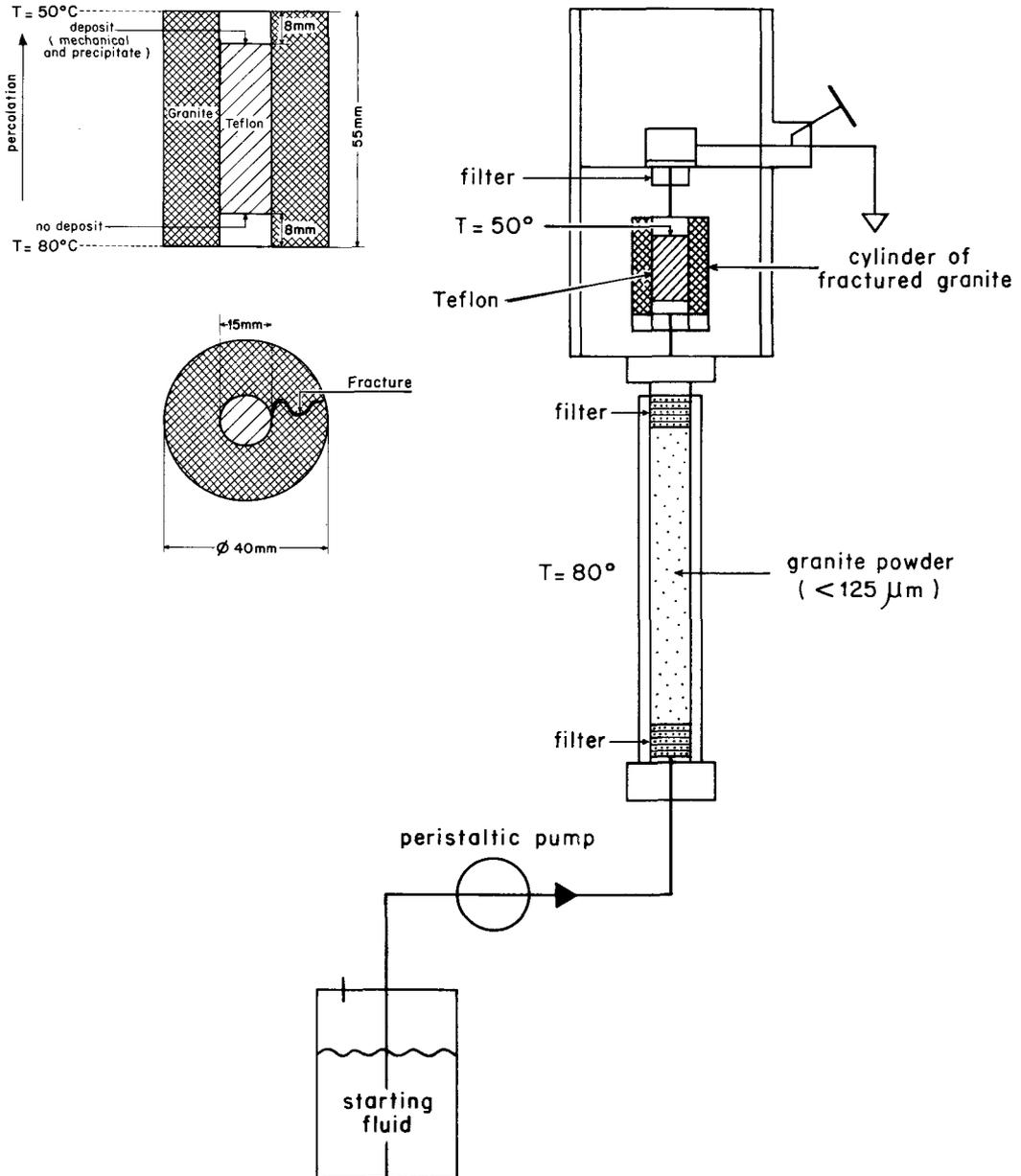


FIG. 1. Schematic diagram of the experimental assembly.

Table I. Chemical composition of the Fanay granite

Element	Content %
Loss on ignition	3.05
SiO ₂	61.40
Al ₂ O ₃	16.10
FeO	3.60
Fe ₂ O ₃	1.90
CaO	0.78
MgO	3.70
Na ₂ O	3.70
K ₂ O	4.40
TiO ₂	0.85
P ₂ O ₅	0.34
MnO	0.08
Total	99.90

Millipore Milli-Q deionized water), reacted with 1.5 g of ground granite, was monitored against time on batch samples in 50 ml autoclaves. The granite was lightly

ground and separated into three size fractions by sieving (< 125, 125–250, and 250–500 μm). Four separate series were run (Table II). Series A (Fanay 125A, 250A, and 500A) and B (Fanay 125B, 250B, and 500B) were carried out at 50 and 100 °C, respectively. Series C (Fanay 125C, 250C, and 500C) was kept at 100 °C for a given period of time, and cooled to 50 °C for a week. Series C (Fanay 125D) was kept at 100 °C for 2 weeks, cooled to 50 °C and subsequently monitored for up to 8 weeks.

The fluid samples were filtered at the end of each experiment. Dissolved silica was measured by molybdenum blue spectrophotometry (Charlot, 1961). Dissolved Al and Fe were determined by flameless atomic absorption. The major cations and the anions were measured by ion chromatography. Total bicarbonate was estimated by electrical charge balance. Fluid pH was measured, but since the liquid was cooling down during the measurement, values used in the thermodynamic calculations described below were calculated by mass balance on protonated species. With the exception of the 100 °C leaching of the smallest size fraction (series 125B), pH does not vary greatly between calculated and measured values, but small differences in the range investigated may

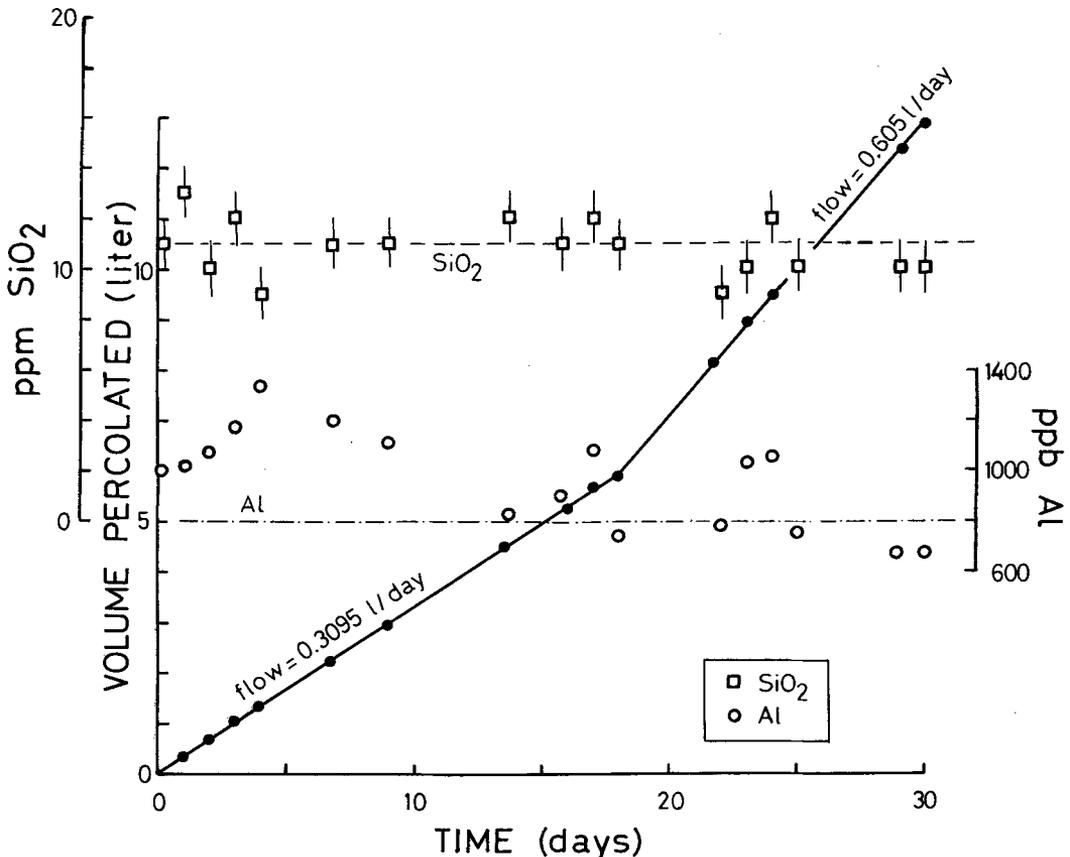


FIG. 2. Fluid flow of deionized water (previously passed through a fractured core of Fanay granite (see fig. 1). The broken lines represent the Al and SiO₂ concentrations measured between the column and the core.

Table II. Experimental conditions

Series	Grain size (μm)	Temperature of the 1st step ($^{\circ}\text{C}$)	Duration (days)	Temperature of the 2nd step ($^{\circ}\text{C}$)	Duration (days)
Fanay 125A	< 125	50	3 to 35	-*	-
Fanay 125B	< 125	100	3 to 35	-	-
Fanay 125C	< 125	100	3 to 35	50	7
Fanay 125D	< 125	100	14	50	0 to 57
Fanay 250A	125 to 250	50	3 to 35	-	-
Fanay 250B	125 to 250	100	3 to 35	-	-
Fanay 250C	125 to 250	100	3 to 35	50	7
Fanay 500A	250 to 500	50	3 to 35	-	-
Fanay 500B	250 to 500	100	3 to 35	-	-
Fanay 500C	250 to 500	100	3 to 28	50	7

* No second step

bring about significant variations in the calculations of the state of saturation of the leachate fluids with respect to most Si-containing minerals.

Results and discussion

Flow through a fractured granite core. The percolation of dionized water, initially put in contact with ground (< 125 μm) Fanay granite, through a fractured granite core indicates that for our low-temperature gradient (80 to 50 $^{\circ}\text{C}$) and for our,

unfortunately, related fast flow rates, there is no observable change in the dissolved silica content (fig. 2). After an initial increase from 1000 to 1300 ppb, dissolved Al follows a slowly decreasing trend to about 700 ppb. These results are difficult to interpret because the pH of the solutions was not measured.

If there were a pH variation with time it would probably be an increase which would in turn lower the dissolved Al concentration. A more likely

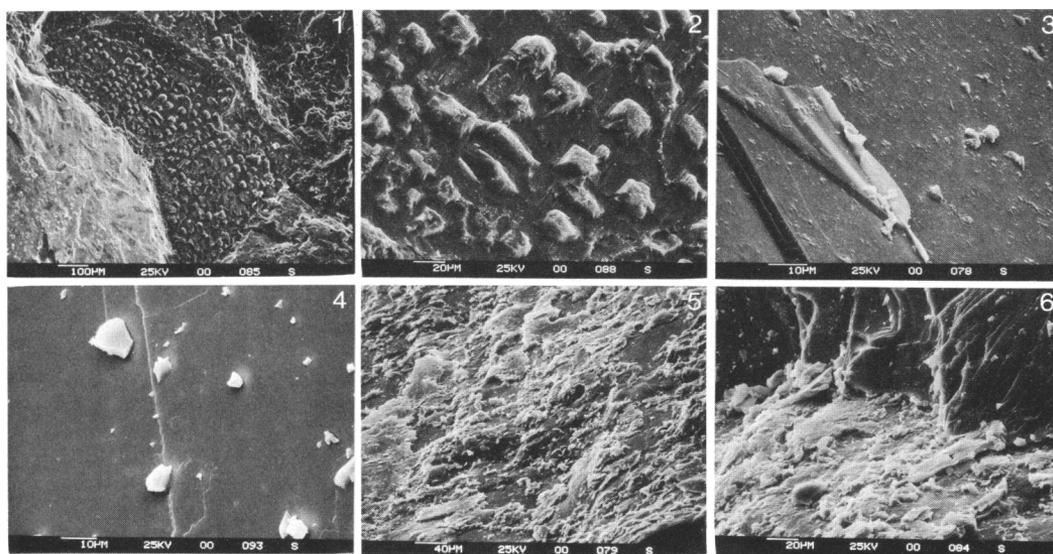


FIG. 3. SEM pictures: (1) leached feldspar in the fracture; (2) detail of (1) showing the selective alteration; (3) phyllosilicate in the fracture; (4) phyllosilicate in a fresh fracture (after the experiment) contrasting with the absence of deposit; (5) silicate coating on feldspar in the fracture; (6) deposit at the contact between two silicate minerals.

Table IV. Ratios Si/R (R = Na, K, Al, Ca or Mg) for the leachate solutions^a

Series	Si/Na	Si/K	Si/Al	Si/Ca	Si/Mg
Fanay A	1.6±0.9 ^b (2.6-5.5) ^c	1.6±0.6(0.6-2.6)	17±17(2- 63)	3.0±2.8(0.1-8.4)	7.5±4.3(2-17)
Fanay B	3.6±1.0 (2.1-5.5)	5.7±2.1(3.1-11)	17±10(5- 45)	11 ±10 (1 -37)	51 ± 52 (6-190)
Fanay C	3.1±0.8 (1.6-4.1)	5.1±1.7(2.0-7.7)	42±28(13-100)	4.1±2.8(1.3-12)	34 ± 31 (8-137)
Fanay 125D	2.6±0.4 (1.9-3.0)	4.3±0.5(3.8-4.9)	50±19(23- 73)	24 ±10 (15-42)	71 ± 28 (52-125)

^a Ratios of concentrations (in mole/l)^b Standard deviation^c Range of values

explanation, however, is that the observed Al variation is caused by its participation in leaching and/or precipitation processes occurring in the granite fracture. Scanning electron microscope (SEM) observations of the fracture surface and of particles showed weathered features caused by the leaching action, as well as deposits due to the precipitation of newly formed minerals (fig. 3).

Leaching experiments. The detailed results of the variation in the composition of the various leachate series are presented in Table III. In no autoclave was there complete dissolution of the granite grains. On the contrary, flocculates were frequently observed on the filters. The following general trends can be observed.

For both the 50 and the 100 °C leaching experiments (series A and B) the fluid showed little varia-

tion after 2 to 3 weeks in its Si, Na, and K composition (fig. 4). Al, Fe, Ca, and, to a lesser extent, Mg behaved erratically. This is, however, quite plausible, as will be shown elsewhere (Oustrière *et al.*, in prep.) by computer simulations of mass transfer of the type developed by Helgeson (1979). These observations support the hypothesis that all of these elements are involved in mineral dissolution and precipitation. For the anions SO₄, NO₃, Cl, Br, and I, the concentrations have reached steady state at the first sampling (after only 3 days of reaction time). This is not surprising as they can come either from intergranular material (Moore *et al.*, 1983) or, for the halogens, from easily leachable surface sites of phyllosilicates (biotite, chlorite, muscovite) where they can replace hydroxyl groups. Both possibilities are consistent with the grain size dependence of the equilibrium concentrations.

Dissolved silica concentrations increased during the first 21 days of reaction time, after which they slowly decreased for all temperature conditions and grain sizes, with the possible exception of series D where they became somewhat constant (see figs. 5 and 6). It is interesting to note in fig. 6, where the evolution of dissolved SiO₂ is drawn on a single diagram for the < 125 μm grain size only, that cooling of the fluid to 50 °C, even after up to 6 weeks, resulted in values higher than those of the series A (50 °C) leaching experiment.

Dissolved silica can originate from the leaching of most of the granite-forming minerals. The average values of the ratios of Si/R (where R is Na, K, Al, Ca, or Mg), calculated for all leachate solutions, are shown in Table IV. They were compared to the corresponding stoichiometric ratios of granite minerals (orthoclase KAlSi₃O₈, albite NaAlSi₃O₈, biotite KFe₃AlSi₃O₁₀(OH)₂, muscovite KAl₃Si₃O₁₀(OH)₂, chlorite Mg₅Al₂Si₃O₁₀(OH)₈, and anorthite CaAl₂Si₂O₈) and possibly of newly formed minerals (kaolinite Al₂Si₂O₅(OH)₄ and other aluminosilicates such as montmorillonite, illite, or zeolites). There is another method of estimating magmatic rocks weathering budget

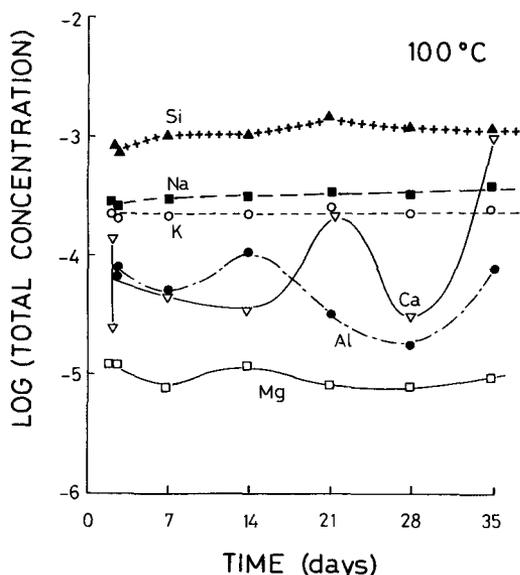


FIG. 4. Change in fluid composition with time (Series Fanay 125B).

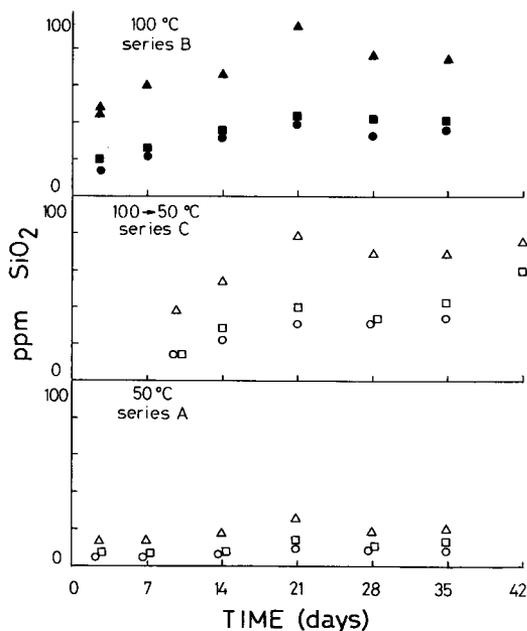


FIG. 5. Change in silica concentration with time (triangles, $< 125 \mu\text{m}$; squares, $125\text{--}250 \mu\text{m}$; circles, $250\text{--}500 \mu\text{m}$).

(Sarazin, 1978; Sarazin *et al.*, 1976) but it has not been used here.

First of all, although the observed dissolved SiO_2 values are compatible with published solubilities of quartz (Iler, 1979), none of the values of Si/R indicates that this mineral is a major contributor to the dissolved silica. The dissolution of quartz cannot, however, be ruled out since Bourrié (1978) has shown that about 10–20% of it could be leached under temperate climate weathering in granite of the Vosges and the Massif Central.

The 100 °C constant temperature leachate solutions (series B) have Si/R ratio values (Table IV) suggesting that albite and, to a lesser extent, a K-mineral (K-feldspar, biotite and/or muscovite) are leached from the granite. This is confirmed by the undersaturation of albite, adularia, and muscovite, in WATEQ* calculations. Anorthite is also undersaturated and should therefore be leached. The values of the ratios Si/Al, Si/Ca, and Si/Mg are very variable. They are all large, indicating the possible precipitation of low Si and high Al, Ca, and Mg minerals. WATEQ calculations of saturation

* Saturation indices [$\text{SI} = \log(\text{Ionic Activity Product})/(\text{Solubility Product})$] were calculated using the water speciation computer program WATEQ (Truesdell and Jones, 1974).

indices eliminate the possibility of formation of kaolinite (for Al) and chlorite (for Mg). The Ca (and possibly the Mg) behaviour might be due to the precipitation of calcite (and of a Mg carbonate) or to the adsorption on freshly formed surfaces such as kaolinite, montmorillonite or illite (all thermodynamically possible under the observed leachate fluid concentrations).

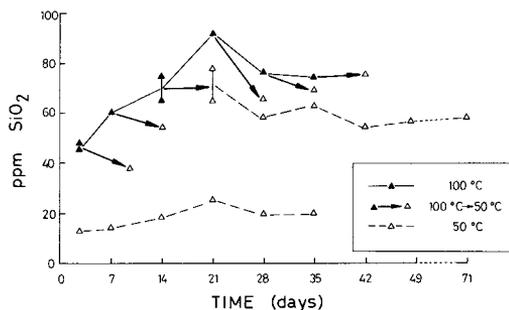


FIG. 6. Change in silica concentration with time (fraction $< 125 \mu\text{m}$).

The constant temperature leachate solutions (series A) present lower Si/R ratios at 50 than at 100 °C, with the exception of Si/Al where the values are similar, suggesting that some Si must precipitate, possibly as quartz as shown in fig. 7. The dissolution of albite, K-feldspar, and anorthite are here also substantiated by WATEQ computations. These thermodynamic calculations show a supersaturation of the fluid with respect to kaolinite, muscovite, Ca-montmorillonite, and (for Fanay 125A only) phlogopite.

When compared to the 100 °C leaching, the cooling experiments (series C and D) show a decrease in Si/Na and Si/K ratios, indicating some preferential precipitation of Si (possibly as chalcidony) with respect to Na and K. In contrast, the Si/Al ratio increases which, since gibbsite is undersaturated (fig. 8), could occur because of the precipitation of a high Al and/or low Si mineral such as muscovite, kaolinite, or, less likely, montmorillonite and illite, for all of which the fluid is in a state of supersaturation. A slow precipitation of chlorite could explain the high Si/Mg ratio for the series D. The solutions of the series 125D are found to be undersaturated with respect to anorthite throughout the 57 days of cooling.

The saturation index values of quartz calculated with the WATEQ speciation computer program indicate that for the constant temperature leaching (both for 100 and 50 °C) the dissolved silica (leached

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Table III. Leachate fluid composition (all concentrations in ppm)

Experiment	Duration (days)	measured pH ^a (at T °C)	pH ^b	SiO ₂	Na	K	Hg	Ca	Al	Fe	HCO ₃ ^c	SO ₄	NO ₃	Cl	Br	I
Faney 125A	3	8.35(38)	8.20	13	3.60	5.65	0.80	3.65	0.987	0.140	25.6	1.48	0.28	1.56	0.48	1.57
	7	8.6 (45)	8.53	14	13.9	8.60	0.65	2.45	0.983	0.447	52.3	1.83	0.73	1.99	0.43	1.69
	14	8.5 (45)	8.43	18	4.70	6.70	1.20	6.40	0.968	0.390	40.1	1.92	0.39	1.70	0.43	1.81
	21	7.91(30)	7.74	25	6.15	7.95	1.50	10.6	0.178	0.036	20.8	ND ^f	ND	0.89	-	-
	28	8.35(38)	8.17	19	4.55	6.40	0.45	1.65	0.409	0.068	16.8	1.92	5.30	1.62	0.48	1.94
35	8.4 (39)	8.24	20	5.30	6.60	0.50	1.65	0.238	0.040	24.4	2.01	0.85	1.86	0.48	1.69	
Faney 250A	3	7.00(38)	6.98	7	1.75	2.75	0.50	3.55	0.662	0.051	18.0	0.52	0.23	0.92	0.11	0.60
	7	7.5 (45)	7.49	7	25.4	4.40	0.60	2.80	1.02	0.543	79.8	0.52	2.65	0.71	0.11	0.60
	14	7.8 (45)	7.79	8	5.40	6.90	0.60	21.2	0.275	0.132	89.5	0.70	0.39	0.78 ^f	0.11	0.60
	21	7.7 (47)	7.69	13	4.95	8.50	0.40	1.20	0.116	0.026	27.3	1.48	0.45	1.06	0.11	0.60
	28	7.8 (38)	7.73	11	1.95	3.20	0.50	1.90	0.704	0.007	14.3	0.61	0.22	0.64	0.11	0.84
35	7.5 (39)	7.46	12	2.35	3.30	0.45	1.15	0.273	0.537	15.1	0.70	0.11	0.69	0.05	0.73	
Faney 500A	3	7.15(38)	7.13	5	1.30	2.55	0.60	38.2	0.359	0.056	124	0.44	0.28	0.53	-	0.24
	7	7.3 (45)	7.29	4	1.85	4.20	0.80	7.20	0.781	0.216	33.4	0.44	1.07	0.57	-	0.24
	14	7.55(45)	7.54	6	1.65	3.70	0.80	8.15	0.380	0.170	36.8	0.52	-	0.57	-	-
	21	7.12(39)	7.10	9	1.50	2.75	1.00	4.60	0.176	0.020	23.9	0.52	0.45	1.06	-	0.24
	28	7.15(38)	7.13	9	1.10	2.25	0.70	8.40	0.888	0.512	32.5	0.52	0.28	0.59	0.05	0.24
35	7.25(39)	7.23	8	0.85	2.20	0.40	1.30	0.147	0.020	9.3	0.70	0.17	0.60	-	-	
Faney 125B	3	8.45(34)	7.72	45	6.60	8.20	0.30	1.05	2.46	0.219	22.5	2.09	0.44	1.81	0.44	1.94
	3 ^d	8.16(60)	7.83	48	6.40	8.30	0.30	6.30	1.83	0.135	38.8	2.50	0.53	1.77	0.44	1.81
	7	8.1 (50)	7.67	60	7.40	8.20	0.20	1.90	1.41	0.077	28.7	2.50	0.35	1.58	0.44	1.94
	14	8.3 (45)	7.74	65	7.80	8.75	0.30	1.45	2.85	1.34	28.4	2.67	0.35	2.02	0.40	1.69
	21	7.65(38)	7.43	92	7.25	10.10	0.20	9.30	0.924	0.072	53.1	2.59	0.53	2.54	0.36	1.69
28	8.1 (45)	7.60	76	7.30	7.95	0.28	1.40	0.499	0.028	27.8	2.92	0.44	1.72	0.40	1.57	
35	8.5 (45)	8.02	74	9.55	9.70	0.50	50.3	2.20	0.438	182	3.92	0.40	2.15	0.40	2.06	
Faney 250B	3	7.20(34)	7.19	20	2.85	4.15	0.40	1.15	1.62	0.462	14.1	0.40	0.40	0.90	0.05	0.60
	7	7.9 (50)	7.62	25	2.35	3.10	0.40	4.05	0.856	0.028	19.8	0.70	0.80	1.00	0.11	0.60
	14	7.6 (45)	7.48	36	4.45	4.15	0.70	5.75	1.14	0.468	34.0	0.50	0.30	1.40	0.11	0.73
	21	7.78(40)	7.41	44	3.10	2.50	0.40	2.60	0.84	0.048	14.6	1.10	0.80	1.80	0.11	0.60
	28	7.95(45)	7.62	42	3.80	3.70	0.70	4.55	1.22	3.61	34.3	0.90	0.70	1.00	0.16	0.73
35	7.97(45)	7.61	41	5.15	5.40	0.30	3.95	0.671	0.032	29.1	1.30	0.30	1.60	0.16	0.60	
Faney 500B	3	7.25(38)	7.33	15	1.20	2.30	3.05	41.4	1.11	0.140	144	0.61	0.45	0.55	-	-
	7	7.8 (48)	7.55	22	1.95	3.35	0.40	1.30	0.569	0.246	13.2	0.61	0.45	0.64	-	0.12
	14	7.7 (45)	7.57	32	5.75	4.25	0.40	1.60	0.517	0.025	24.8	0.52	0.51	0.87	-	0.36
	21	7.35(39)	7.19	39	2.70	2.95	0.40	1.55	2.14	0.264	10.1	0.79	0.51	1.51	-	0.12
	28	8.05(38)	7.54	33	2.70	2.30	0.40	1.65	0.520	0.024	13.7	0.79	0.39	0.82	0.05	0.24
35	6.8 (45)	6.89	36	5.55	4.70	0.80	9.80	0.955	0.360	51.7	1.05	0.34	0.89	0.11	0.36	
Faney 125C	3+ 7	8.2 (45)	8.13	38	6.90	4.55	0.40	3.45	0.704	0.054	27.9	2.54	0.57	2.01	0.49	1.88
	7+ 7	8.3 (40)	8.18	54	8.45	10.40	1.00	15.0	1.78	0.308	77.3	2.67	0.40	2.30	0.44	1.57
	14+ 7	6.9 (30)	6.85	78	7.75	7.95	0.45	4.20	0.521	0.041	35.7	3.09	1.77	2.60	0.40	1.69
	21+ 7	8.05(35)	7.88	66	8.20	8.25	0.20	7.30	0.462	0.148	48.3	2.46	0.54	2.05	0.44	1.69
	28+ 7	8.15(39)	8.03	69	8.80	9.95	0.60	21.8	1.00	0.267	97.8	2.69	0.60	2.13	0.48	1.81
35+ 7	7.90(45)	7.86	75	8.50	8.65	0.70	28.0	1.06	0.237	114	2.76	0.40	2.11	0.53	1.81	
Faney 250C	3+ 7	7.6 (45)	7.59	14	3.20	4.55	0.70	4.65	0.252	0.072	28.7	1.16	0.44	1.07	0.09	0.73
	7+ 7	7.3 (40)	7.28	28	4.20	4.75	0.70	10.3	0.473	0.090	48.0	0.75	1.46	1.04	0.27	0.36
	14+ 7	7.7 (48)	7.69	40	3.70	4.15	0.50	4.55	0.424	0.072	27.2	ND	0.62	1.18	0.09	ND
	21+ 7	7.8 (35)	7.70	34	4.45	5.70	0.40	3.85	0.195	0.054	30.8	0.83	0.31	0.92	0.09	0.60
	28+ 7	8.2 (39)	8.05	42	4.05	3.55	0.70	5.70	0.715	0.207	32.6	0.83	0.44	0.84	0.09	0.73
35+ 7	5.61(45)	5.60	60	7.00	5.05	1.10	7.95	0.803	0.020	31.5	14.2	0.35	2.43	0.45	0.60	
Faney 500C	3+ 7	7.3 (45)	7.29	14	3.40	3.30	0.60	7.40	0.208	0.060	36.9	0.58	0.09	0.82	0.09	0.24
	7+ 7	7.5 (40)	7.47	22	3.25	4.25	0.70	3.40	0.537	0.106	24.7	0.75	0.22	1.21	0.05	-
	14+ 7	6.95(45)	6.94	30	3.05	3.40	0.70	14.8	0.135	0.112	58.6	0.67	0.75	0.99	-	0.24
	21+ 7	7.7 (35)	7.62	32	3.35	3.30	0.50	5.75	0.147	0.050	30.6	0.75	0.58	1.01	-	-
	28+ 7	7.75(39)	7.70	34	3.35	3.25	0.60	13.7	1.18	0.025	52.8	0.92	0.53	0.85	0.05	0.24
Faney 125D	14+ 0	ND	7.74	75	9.69	10.1	0.24	1.20	1.43	0.037	34.3	2.88	0.62	2.02	0.48	1.57
	14+ 7	7.7 (39)	7.62	65	9.07	8.60	0.40	1.83	0.882	0.037	34.6	2.62	0.56	1.95	0.59	1.69
	14+14	7.95(42)	7.86	59	8.25	8.13	0.45	1.73	0.431	0.026	31.5	2.88	0.62	2.40	0.59	1.81
	14+21	ND		63	9.51	8.22	0.37	1.60	0.861	0.100	35.0	2.56	0.34	1.90	0.53	1.57
	14+28	8.15(39)	8.01	54	11.1	9.21	0.39	2.34	0.605	0.069	43.9	2.44	0.34	1.78	0.48	1.69
	14+34	7.90(38)	7.78	57	8.40	9.74	0.36	1.82	0.363	0.043	33.9	2.88	1.69	2.04	0.53	1.94
	14+57	7.90(38)	7.77	58	7.40	7.83	0.38	2.12	0.424	0.035	29.1	ND	ND	ND	ND	ND

^a See text ^b See text ^c See text ^d Duplicate ^e Not determined ^f Below detection limit

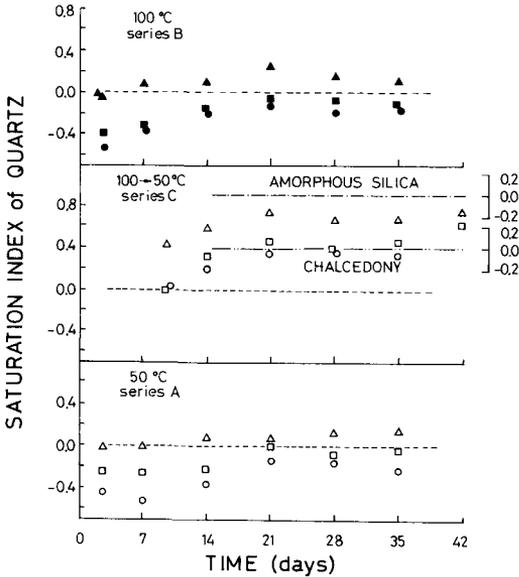


FIG. 7. Saturation index of quartz. The saturation indexes of amorphous silica and chalcedony are superimposed. (triangles, < 125 μm ; squares, 125-250 μm ; circles, 250-500 μm).

tion, which indicates a slower dissolution rate. This agrees with the observations of Iler (1979) of the greater extent of dissolution of smaller particles of amorphous silica and of Bares (1968) of the presence on quartz grains of an external layer more reactive to leaching.

When cooled down to 50 °C the fluids are supersaturated with respect to quartz (fig. 7), but it is also very likely that the precipitation of quartz is in fact hindered by a kinetic barrier and that one or more other silica-containing minerals control the dissolved SiO_2 content. For example, minerals such as amorphous silica or chalcedony, which are more soluble but also more easily nucleated, could form during the cooling stage. According to figs. 7 and 8, chalcedony is the most probable. However, the slow precipitation of supersaturated minerals (such as kaolinite, muscovite, montmorillonite and/or illite) as suggested, for example, by fig. 3(5) is also very likely. These results are consistent with most of the *in situ* observations: (1) of Bourrié (1978) of the weathering of granite from two French massifs (low-temperature leaching of plagioclase but not of K-feldspar and muscovite, and precipitation of kaolinite, vermiculite, and montmorillonite); and (2) of Sarazin *et al.* (1976) of the transformation of primary minerals of granitic rocks into kaolinite or halloysite.

mostly from feldspar, plagioclase and muscovite) could well be controlled by the precipitation of quartz (fig. 7). One should note that the large-grained samples take more time to reach satura-

For larger temperature gradients Moore *et al.* (1983) suggested that the flow rate through a granite core, or in other words, the reaction time, could induce SiO_2 control by either quartz or

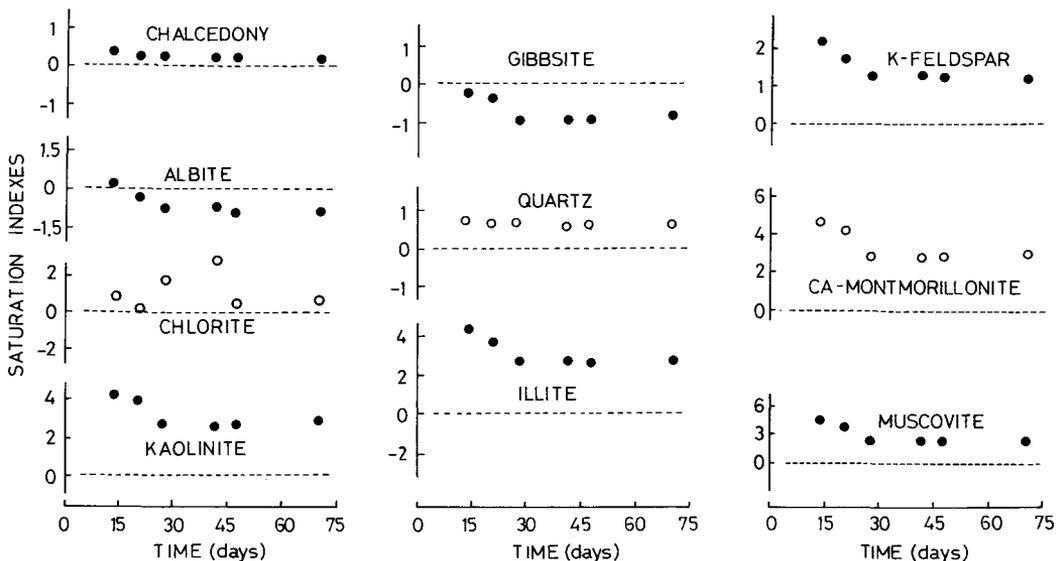


FIG. 8. Saturation indices of minerals during the long-term cooling experiment (Series Fanay 125D).

chalcedony. Like us, they observed a peak in dissolved SiO_2 which they attributed to variations in flow rate as permeability decreased with time.

Using our different experimental conditions (batch sample leaching rather than flow through a granite core) we would suggest that dissolved SiO_2 is regulated first by the dissolution of feldspar (and phyllosilicates) and during cooling by a competing precipitation (of chalcedony and alumin-, and phyllosilicates).

At the cool end (80 to 105 °C) of their granite cores Morrow *et al.* (1981) observed fibres of silica on exposed quartz grains and Ca-rich fibres on cleaved surfaces of plagioclase crystals. Mass transfer computer simulation indicated that kaolinite and Mg-chlorite could control the dissolved composition of a fluid cooled from 100 to 50 °C in contact with Fanay granite (Oustrière *et al.*, in prep.). Again quartz is calculated to precipitate but, as mentioned earlier, that might be prevented by a kinetic barrier. We need mineralogical confirmation of the ideas presented.

Conclusions

The present report helps in defining the geochemical processes involved in permeability changes during low-temperature-gradient thermal alteration. The precipitation of quartz may control the SiO_2 (dissolved mostly from feldspar and phyllosilicates) during the heating part of the thermal cycle but certainly not during the cooling part. Control by several other minerals was suggested although confirmation by scanning electron microscopy is needed.

Another paper will present quantitative speculations about kinetic measurements and their limitation in experiments using mixtures of minerals (such as granite) (Bourg *et al.*, 1983). Finally the present experimental results will be evaluated in terms of mass transfer computer simulations (Oustrière *et al.*, in prep.).

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