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REPORT**

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**Chemical interactions between
the bentonite and the natural
solutions from the granite near a
repository for spent nuclear fuel**

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Géologie, France)

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THE NATURAL SOLUTIONS FROM THE GRANITE NEAR A
REPOSITORY FOR SPENT NUCLEAR FUEL

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ABSTRACT

The chemical evolution of a bentonite in contact with two different aqueous solutions from Swedish granitic massifs has been studied by geochemical modelling of mass transfers.

The initial solutions are natural solutions from drillholes, one shallow diluted groundwater and one more saline solution from a deep aquifer in the granite. In order to model the behavior of bentonite in a repository for spent nuclear fuel (SKB project, Stockholm), the clay/solution ratio was taken very high (4 kg/kg or 10 moles of bentonite/kg H₂O). The solubility product of the reacting bentonite has been estimated from 25 to 200°C using a solid solution model.

With these data the calculations showed that the bentonite does not remain stable with respect to the solutions along the heating curve (25 to 100°C). The alteration of the bentonite may change a lot the chemistry of the solutions and produce a secondary clay (smectite) and calcite, zeolite (laumontite) and amorphous silica. The mass transfer is always less important for the most saline water.

However, these mass transfers and chemical evolutions of the solutions correspond to an overall limited degradation of the bentonite phase because of an internal self buffering effect due to a high clay/water ratio. In particular no evolution to an illite type clay has been detected with no evidence for a potassium uptake in the exchangeable sites in a closed clay + water system.

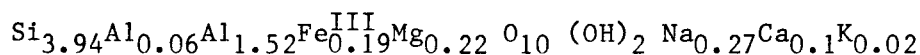
INTRODUCTION

The stability of a bentonite (Wyoming-type) with respect to the natural waters from a Swedish granitic massif has been studied between 25 and 100°C. First, the solubility product of the Wyoming bentonite taken as representative from the bentonites which will be used as physico-chemical barrier in a storage site, has been estimated over the temperature range of interest. Then the bentonite dissolution, in two typical waters from the Swedish granites was calculated at 25°C in order to define an initial equilibrium point for the bentonite + solution mixture along the heating curve. This mixture was then heated by simulation, along the temperature increase, up to 100°C, with different options for the possible secondary minerals. Finally the solutions obtained at 100°C by these successive calculations were tested for saturation with respect to the granite-forming minerals.

1

ESTIMATION OF THE SOLUBILITY PRODUCT OF THE BENTONITE FROM 0 TO 200°C

The selected bentonite is a Wyoming montmorillonite introduced in the previous report (Fritz et al., 1984):



The program CISSFIT calculates for this composition of the clay the distribution of the theoretical end-members (mole fractions X_i = activities A_i) constituting this clay in an ideal solid solution (Tardy and Fritz, 1981; Fritz, 1985). For each end-member the Mass-Action Law is written:

$$K_i = Q_i/A_i = Q_i/X_i \text{ (ideal)}$$

with 27 end-members (3 pyrophyllite-type, 12 micas-type and 12 celadonite-type). The resolution of this system of equations gives all values of Q_i and X_i . The solubility product K^* of the total phase can then be determined by:

$$K^* = \prod_i (K_i X_i)$$

and

$$\log K^* = \sum_i X_i \log K_i + \sum_i X_i \log X_i$$

The values of interest in this study are the following:

at 0 °C, $\log K^* = 5.441$; at 25° C, $\log K^* = 3.654$;
at 60°C, $\log K^* = 1.736$; at 100°C, $\log K^* = 0.330$.

These values were used in the program DISSOL and have been fitted by a polynomial function (Chebishev's method; polynomial degree = 4) for the calculation versus temperature in the program THERMAL. All these data allow us to introduce the bentonite as a defined compound, reactant in the simulations.

2 DISSOLUTION OF THE BENTONITE IN THE GRANITE SOLUTIONS AT 25°C

2.1 THE INITIAL REACTING SOLUTIONS

Two solutions were selected for these tests in order to cover the salinity range expected in the granite solutions on the field:

- the Finnsjön (mean well solution), called here FI, still used in the previous researches (Fritz et al., 1983, 1984) with a salinity of 0.36 g/l of TDS,
- the Stripa VI water also considered in previous reports with a salinity of about 1.22 g/l (TDS).

The composition of these solutions at 25°C had been previously calculated with the program THERMAL from 10°C up to 25°C and more. In these two solutions at 25°C, the bentonite is not stable and may be dissolved irreversibly. The major chemical characteristics of these solutions at 25°C can be found in the Tables I to VI (first lines).

2.2 DISSOLUTION OF BENTONITE AT 25°C

The ideal modelling would have required a combined dissolution and heating calculation. However, the two programs DISSOL and THERMAL can only simulate successive but separate processes. The program DISSOL can only be used at 0, 25, 60 and 100°C in the temperature range of interest here. For these reasons we did the successive simulations as following:

- heating of the solutions from field temperature (about 10°C) to 25°C;
- dissolution of bentonite until equilibrium at 25°C;

Table I: Sequence of events in the simulated dissolution of the bentonite, at 25°C, in the Finnsjön dilute water (program DISSOL). Option A.

log ξ	n*	Mineralogical events	pH	log pCO ₂	Eh (mV)	logQ bentonite
-12.81	ϵ	goethite precipitates	7.40	-2.11	119.9	1.629
-11.62	ϵ	kaolinite precipitates	7.40	-2.11	119.9	1.671
-6.51	0.031	calcite precipitates	7.45	-2.16	117.1	2.059
-6.48	0.034	2:1 clay precipitates	7.45	-2.16	117.1	2.080
-6.47	0.034	calcite has been redissolved	7.45	-2.16	117.4	2.081
-6.37	0.043	goethite has been redissolved	7.43	-2.14	118.6	2.093
-6.25	0.056	calcite precipitates	7.45	-2.16	117.6	2.179
-6.24	0.058	kaolinite has been redissolved	7.42	-2.13	119.6	2.153
-4.34	4.560	bentonite becomes stable	8.01	-2.88	84.3	3.654

ξ = reaction progress variable in the simulation
n* = $\xi \cdot 10^5$ = number of millimoles of bentonite dissolved/kg H₂O
(available: 10 moles/kg H₂O or 4 kg/kg H₂O).

Table II: Sequence of events in the simulated heating of the bentonite + solution system from 25°C to 100°C (program THERMAL) with the Finnsjön dilute water. Option A.

T°C	n*	Mineralogical events	pH	log pCO ₂	Eh (mV)
		bentonite, calcite and 2:1 clay initially at equilibrium			
25.09	ϵ		8.01	-2.88	84.0
42.25	0.667		7.92	-2.67	9.7
60.00	1.917		8.02	-2.68	-79.6
85.33	6.388		8.39	-2.99	-222.5
100.00	13.130		8.57	-3.36	-303.6

Table III: Chemical characteristics of the solution along the simulated dissolution of bentonite at 25°C, and heating from 25°C to 100°C with the initial Finnsjön dilute water. Option A.

T°C	pH	Al $\mu\text{M/kg H}_2\text{O}$	Fe $\text{nM/kg H}_2\text{O}$	K	Na	Ca	Mg $\text{mM/kg H}_2\text{O}$	Si	SO ₄	Alkalinity $\text{meq/kg H}_2\text{O}$
25.00	7.40	0.006	0.004	0.190	0.634	1.525	0.189	0.185	0.175	3.344
25.00	7.45	0.004	0.003	0.191	0.643	1.527	0.196	0.263	0.175	3.373
25.00	7.43	0.004	0.003	0.190	0.645	1.522	0.196	0.270	0.175	3.363
25.00	7.45	0.004	0.002	0.191	0.649	1.522	0.199	0.296	0.175	3.374
25.00	7.42	0.004	0.003	0.191	0.649	1.508	0.198	0.295	0.175	3.345
25.00	8.01	ϵ	ϵ	0.257	1.845	0.527	0.049	2.190	0.175	2.347
25.09	8.01	ϵ	ϵ	0.257	1.845	0.527	0.049	2.190	0.175	2.347
42.25	7.92	0.004	ϵ	0.263	2.020	0.397	0.020	2.497	0.175	2.210
60.00	8.02	0.044	0.002	0.240	2.337	0.208	0.003	3.129	0.175	2.092
85.33	8.39	1.108	0.005	0.099	3.379	0.064	ϵ	5.379	0.175	2.700
100.00	8.57	4.907	0.006	0.044	4.722	0.053	ϵ	8.405	0.175	3.978

Cl is constant (0.56 millimoles/kg H₂O).

Table IV: Sequence of events in the simulated dissolution of the bentonite, at 25°C, in the Stripa V1 water (program DISSOL). Option A.

log ξ	n*	Mineralogical events	pH	log pCO ₂	Eh (mV)	logQ bentonite
-14.02	ϵ	2:1 clay precipitates	8.95	-5.56	-116.1	2.247
-6.92	0.012		8.93	-5.55	-115.1	2.372
-5.92	0.122		8.75	-5.34	-104.2	2.979
-5.26	0.545	bentonite becomes stable	8.59	-5.16	-94.8	3.654

Table V: Sequence of events in the simulated heating of the bentonite + solution system from 25°C to 100°C (program THERMAL) with the Stripa V1 water. Option A.

T°C	n*	Mineralogical events	pH	log pCO ₂	Eh (mV)
		bentonite, calcite and 2:1 clay initially at equilibrium			
25.00	0.000		8.59	-5.16	-94.8
46.47	0.292		8.18	-4.56	-182.6
60.00	0.654		8.06	-4.33	-244.6
84.89	2.117	daphnite precipitates	8.08	-4.17	-373.1
86.06	2.166	calcite precipitates	8.10	-4.19	-380.4
90.71	2.712	pyrite precipitates	8.18	-4.36	-409.3
95.68	3.050	daphnite has been redissolved	8.57	-5.19	-465.8
97.49	3.446		8.62	-5.32	-480.0

Table VI: Chemical characteristics of the solution along the simulated dissolution of bentonite at 25°C, and heating from 25°C to 100°C with the initial Stripa V1 water. Option A.

T°C	pH	Al μM/kg H ₂ O	Fe nM/kg H ₂ O	K	Na	Ca	Mg mM/kg H ₂ O	Si	S	SO ₄	Alkalinity meq/kg H ₂ O
25.00	8.95	0.043	0.0009	0.031	12.048	4.291	0.008	0.216		1.062	0.102
25.00	8.59	0.004	0.0005	0.041	12.155	4.243	0.012	1.061		1.062	0.132
25.24	8.58	0.004	0.0006	0.041	12.155	4.243	0.012	1.061		1.062	0.132
46.47	8.18	0.030	0.022	0.046	12.217	4.223	0.012	1.468		1.062	0.158
60.00	8.06	0.108	0.133	0.050	12.292	4.214	0.007	1.869	ϵ	1.062	0.208
84.89	8.08	1.121	1.207	0.058	12.580	4.231	ϵ	3.211	ϵ	1.062	0.529
86.06	8.10	1.298	1.098	0.058	12.596	4.244	ϵ	3.311	ϵ	1.062	0.571
90.71	8.18	2.109	0.762	0.061	12.727	4.284	ϵ	3.896	0.001	1.061	0.789
95.68	8.57	7.528	0.253	0.047	12.644	4.219	ϵ	5.107	0.006	0.316	2.067
97.49	8.62	9.416	0.200	0.045	12.700	4.231	ϵ	5.660	0.009	0.138	2.507

Cl is constant (18.2 millimoles/kg H₂O).

- heating of the bentonite + solution systems at equilibrium from 25 to 100°C.

Three successive options were tested for these simulations, concerning the possible secondary minerals:

- option A: laumontite, wairakite, prehnite and amorphous silica were not allowed to precipitate even if they were stable,
- option B: laumontite, wairakite, prehnite were introduced as possible secondary minerals,
- option C: amorphous silica was finally allowed to precipitate in addition to these minerals.

This sequence was chosen in order to see the influence of zeolite precipitation. This is slightly different from the tests of Johnston and Miller (1984), who described also in their experimental and theoretical study other zeolites like leonhardite. The stability diagram for this last phase was taken from the book of Helgeson et al. (1969). After this publication, the same authors have rechecked all the data (Helgeson et al., 1978) and we have only considered here minerals for which the data were confirmed in this last publication.

2.3 BENTONITE - SOLUTION EQUILIBRATION AT 25°C (option A)

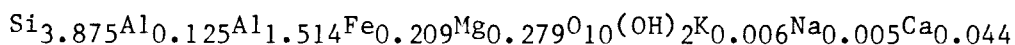
The minerals taken into account in this calculation were the following:

- goethite, pyrite, gibbsite and kaolinite,
- calcite and gypsum,
- a binary chlorite solid solution (clinochlore + daphnite),
- an ideal solid solution for 2:1 clays (molecular end-members, 3 pyrophyllite-type, 12 mica-type),
- the oversaturation with quartz was accept as a common phenomena in most of the natural waters at low temperatures (below 100°C).

With option A for zeolites and amorphous silica (no precipitation), the dissolution of bentonite with respect to the natural waters was calculated with the program DISSOL after verification of the unstability of the system bentonite + solution. The dissolution calculation gave two respective sequences of events given in Tables I (solution FI, dilute) and IV (solution VI, more saline).

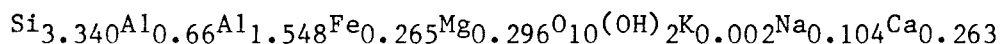
2.3.1 For FI (dilute), the secondary minerals are respectively:

- goethite (0.006 millimoles/kg H₂O, finally redissolved)
- kaolinite (0.026 " " " " " ")
- calcite (1.26 millimoles/kg H₂O)
- a 2/1 clay (4.09 " " ") showing a smectite formula



and the quantity of bentonite dissolved is 4.56 millimoles/kg H₂O.

2.3.2 For VI (saline), the only secondary phase is a 2:1 phyllosilicate less abundant, more substituted in the tetrahedral sites:



(0.390 millimoles/kg H₂O)

and the amount of bentonite dissolved before equilibration is also less important (0.545 millimoles/kg H₂O).

These calculations show clearly that the quantity of bentonite dissolved before reaching the equilibrium point with the solutions is less important with a more saline water (for quite the same initial silica content and different pH values): the salinity is 3.4 times higher in VI and the quantity of dissolved bentonite is 8.4 times lower), but the secondary clay produced during this dissolution is more substituted in the tetrahedral sites (still poor in potassium). However, in both solutions, the amount of mass transfer remains quite neglectable, in the solid phase, with respect of the available quantity of bentonite (several millimoles versus 10 moles/kg H₂O). At the contrary, these mass transfer between solid phase induce important changes in the water chemistry through a very strong buffering effect of the bentonite (see Table III beginning line and VI, beginning line):

- the pH increases for FI from 7.40 to 8.01,
- the pH decreases for VI from 8.95 to 8.59,
- the silica content increases significantly in both solutions from initial quite equivalent values (0.185 to 2.19 millimoles/kg H₂O for FI and 0.216 to 1.06 millimoles/kg H₂O for VI).

These equilibration process at 25°C require a larger mass transfer in the most diluted water, as normally expectable. In the FI solution, for example the silica content rises up, close to the saturation (Figure 1, initial part of the curve at 25°C.)

3

EFFECT OF THE HEATING (25 to 100°C) ON THE BENTONITE IN EQUILIBRIUM WITH THE SOLUTION (OPTION A)

The results of the calculation at 25°C were taken as starting data for the simulation of the temperature increase.

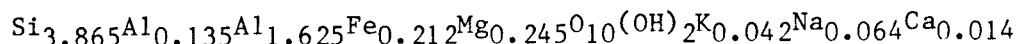
3.1 THE FINNSJÖN FI DILUTE WATER

All along the heating process, the equilibrium is maintained with the bentonite, the calcite and the secondary 2:1 phyllosilicate whose composition changes progressively.

At 100°C the heating process has induced the following transfers (Table II):

- dissolution of bentonite: 13.1 millimoles/kg H₂O;
- precipitation of calcite: 1.57 " " " ;
- precipitation of a 2:1 clay: 11.8 " " " ;

with a smectite-type composition:



The mass transfers are here several times more important than during the simple equilibration at 25°C, but must be compared again to the amount of available clay buffer (10 to 15 millimoles/kg H₂O versus 10 moles/kg H₂O).

During this heating process, the composition of the solution changed a lot for maintaining the equilibrium with the bentonite (Table II and III). One may particularly notice:

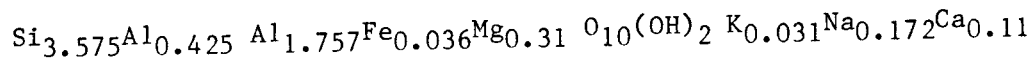
- an increase of the pH from 8.01 to 8.57,
- an important increase of the concentrations of Al, Na, Si,
- an important decrease of Ca and K concentrations,
- a slight increase of the alkalinity.

3.2 THE STRIPA VI WATER

With this solution the temperature increase gives a different sequence due to a reduction of more than 80% from the available sulphate and precipitation of ferrous minerals in the mineralogical sequence (Table V):

- bentonite and a 2:1 clay (solid solution) are initially at equilibrium, the bentonite being partially dissolved and transformed into the secondary clay;
- a ferrous chlorite (daphnite) is precipitated and redissolved after pyrite precipitation (maximum amount of chlorite = 0.055 millimoles/kg H₂O);
- calcite is precipitated (0.040 millimoles/kg H₂O);
- pyrite is precipitated over 90°C.

At 97.5°C the amount of dissolved bentonite is again less important than for the FI solution (3.45 millimoles/kg H₂O) like the amount of secondary clay (2.52 millimoles/kg H₂O) whose composition is still that of a swelling clay:



In the solution the chemical changes are also significant:

- a small increase of pH from 8.59 to 8.62 (very comparable to the value obtained with FI : 8.57);
- an important increase of Al, Si again;
- a stable Ca concentration at the high initial value, and this very different from the FI solution (important activity coefficients effects on Ca and CO₃ in the calcite equilibration condition);
- a decrease of the K concentration (uptake in the clay);
- an important increase of the alkalinity due to the sulphate reduction (87% of the initial content);
- the initial high Na concentration increases only slightly due to the bentonite dissolution.

3.3 OVERSATURATION WITH RESPECT TO LAUMONTITE, PREHNITE OR AMORPHOUS SILICA

The sequences obtained with the option A for secondary minerals are consistent with the hypothesis that zeolite or amorphous silica would not control the chemistry of the solution below 100°C. However, the high silica and aluminium contents with this option gave a supersaturation with respect to laumontite (Figure 2) and prehnite (Figure 3), even below 100°C.

The heating process, at the contrary prevents the solutions FI and VI from the oversaturation with respect to amorphous silica if these minerals are not precipitated (Figure 1).

For these reasons, the simulations were repeated with an option B, allowing laumontite, wairakite (even less stable than laumontite below 100°C, see Figure 2), or prehnite to precipitate. With this option the laumontite appears as the most stable of these discussed minerals all along the sequence, but the precipitation of laumontite was followed by an increase of the silica content which gave an oversaturation with respect to amorphous silica over about 50°C (Figure 4). The complete results of these B-sequences will not be described here: the precipitation of amorphous silica was considered, at least, as favoured kinetically than the zeolite formations. The complete results will now be discussed for the option C where all these minerals will be allowed to precipitate if their saturation states are respectively reached in the solutions.

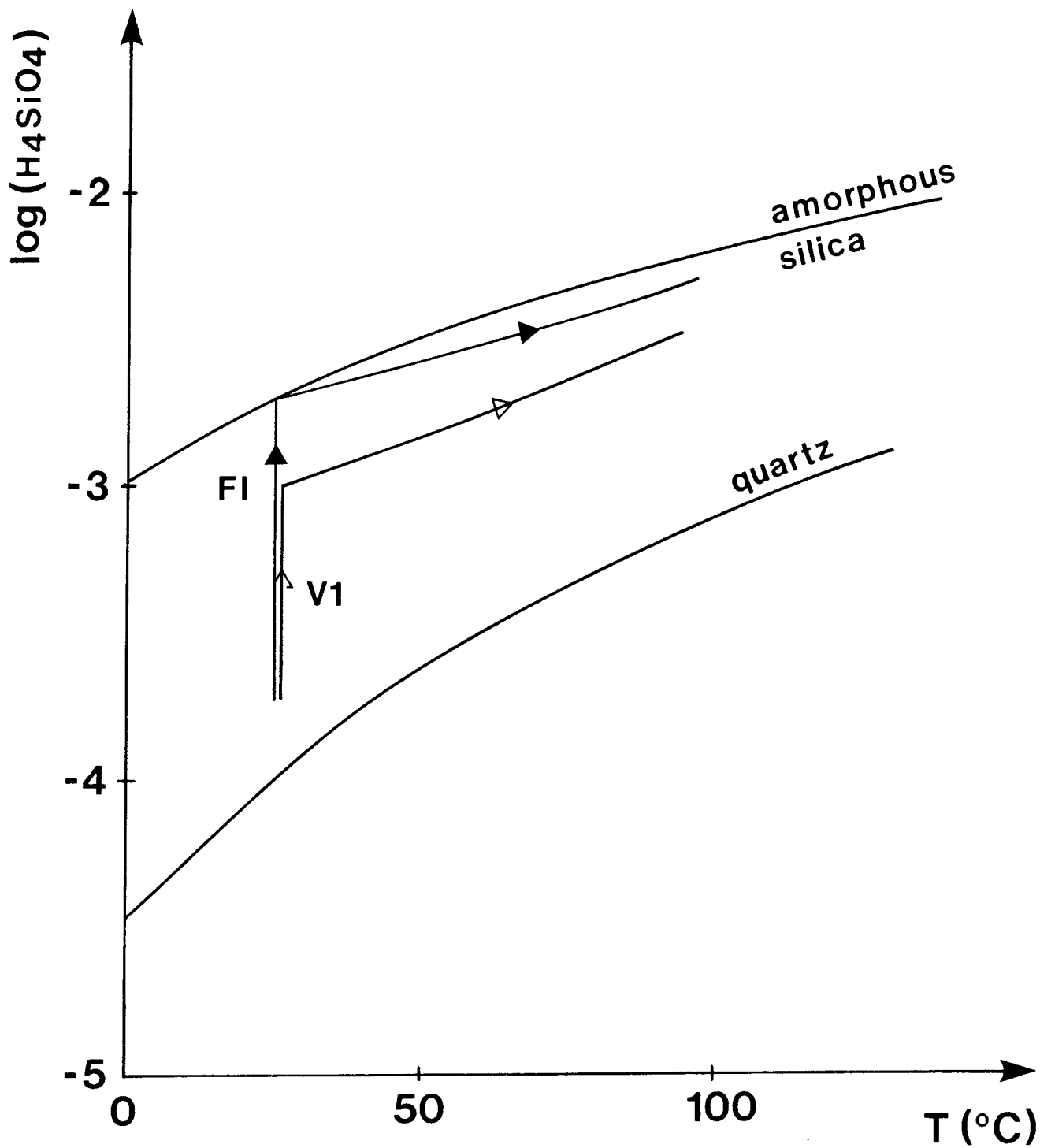


Figure 1. Evolution of the silica activity versus temperature along the bentonite - solution equilibrium (Option A).

V1: Stripa V1 water.

FI: Finnsjön dilute water.

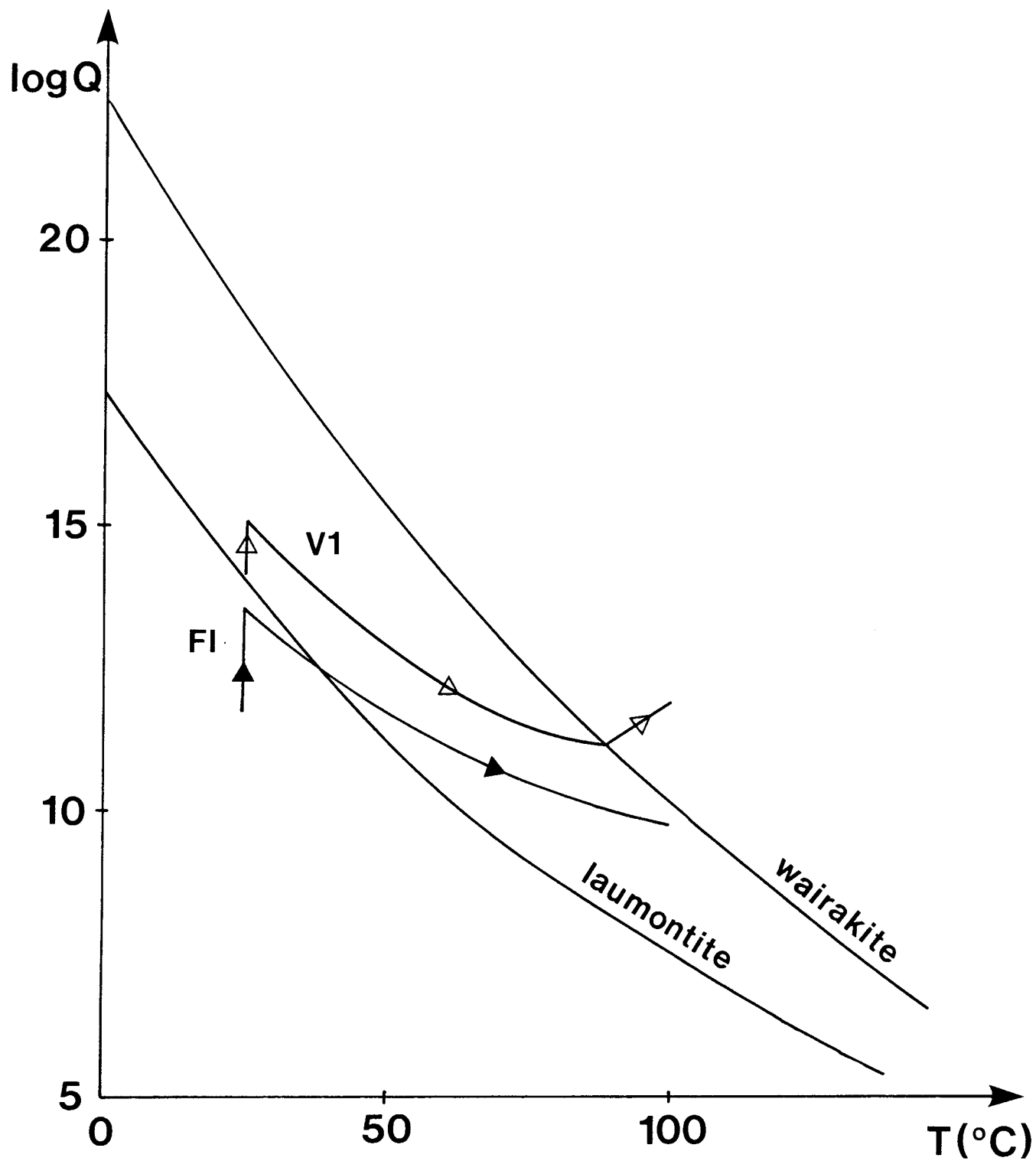
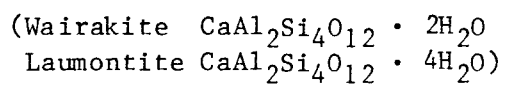


Figure 2. Evolution of the ion activity product (Q) of wairakite and laumontite in the solutions in equilibria with the bentonite from 25°C o 100°C. Option A.



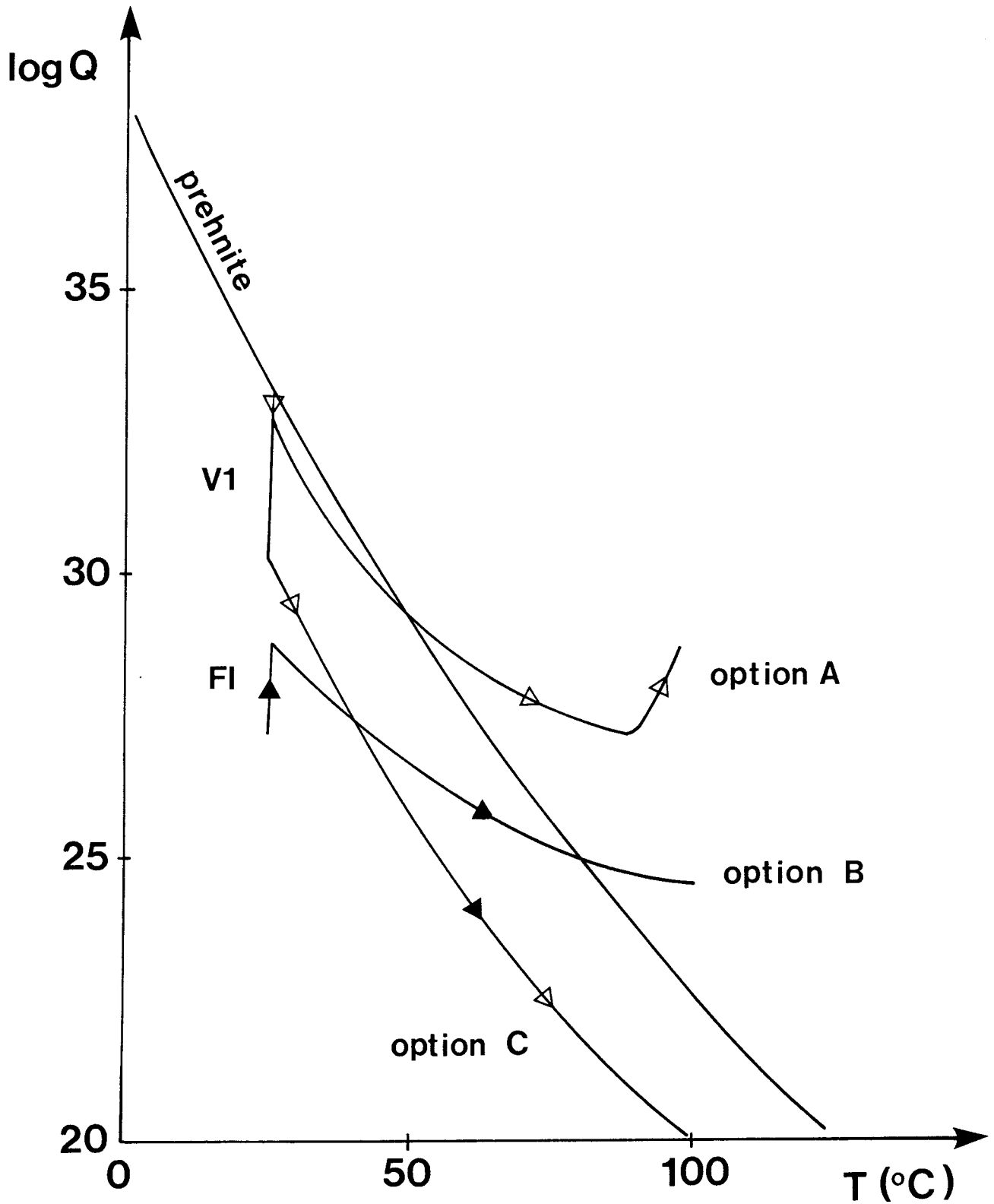
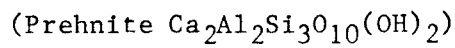


Figure 3. Evolution of the ion activity product (Q) of prehnite in the solutions in equilibria with the bentonite between 25°C and 100°C. Option A and C.



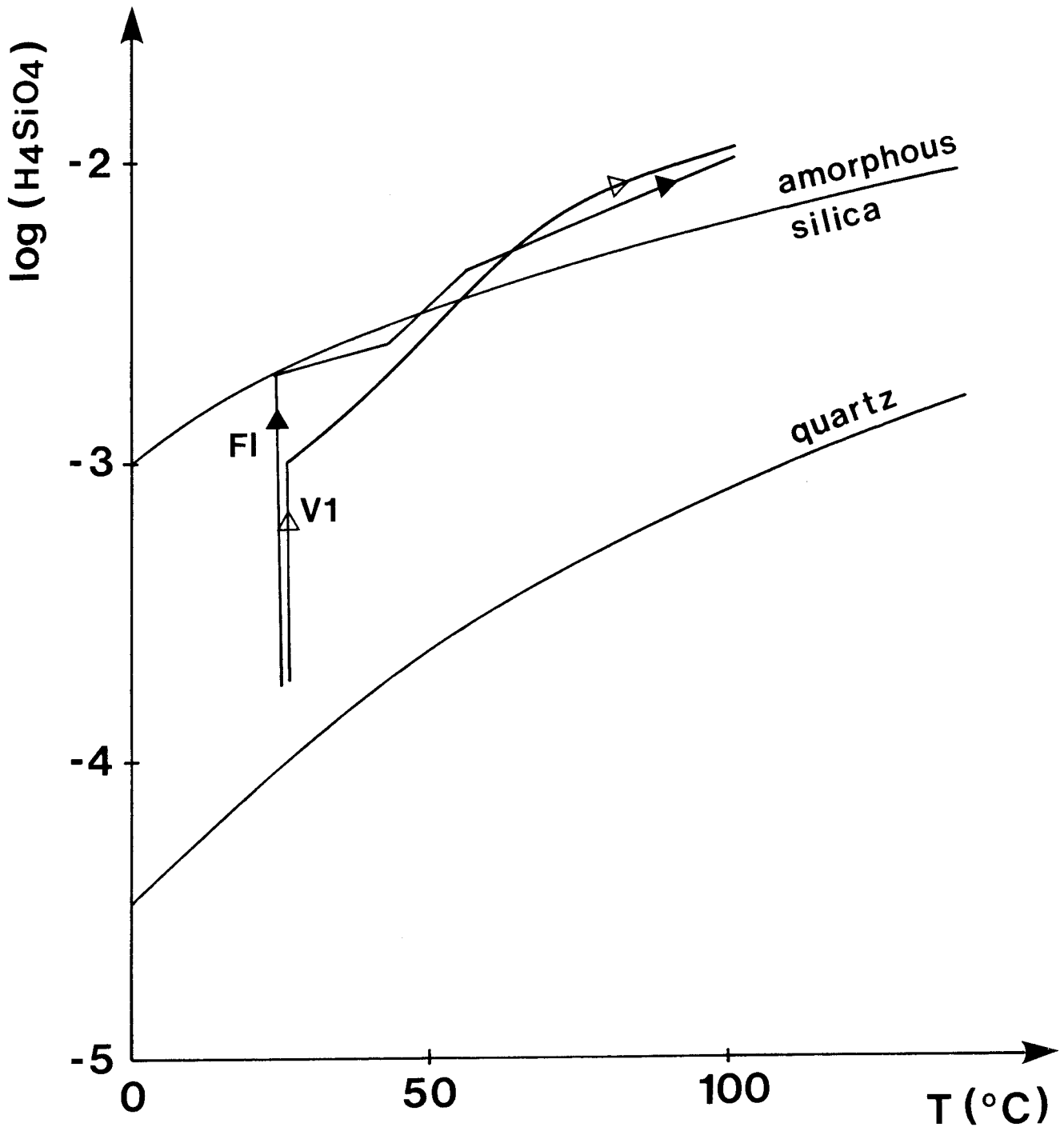


Figure 4. Evolution of the silica activity versus temperature along the bentonite solution equilibrium. Option B.

4 EFFECT OF THE HEATING (25 to 100°C) ON THE BENTONITE IN EQUILIBRIUM WITH THE SOLUTION (OPTION C)

The initial solutions for this series of calculations were taken in the previous sequences calculated at 25°C, but just before the first saturation state expectable for amorphous silica, or laumontite and prehnite (see Figure 2, 3 and 4). Then all the calculations made with option A and B were repeated with two major differences in the results: the laumontite and amorphous silica precipitate and change the chemical evolution of the solutions.

4.1 EQUILIBRATION AT 25°C

For this initial step the two solutions behave differently.

4.1.1 The Finnsjön water FI

The sequence of minerals obtained (Table VII) follows the sequence obtained previously at the point where all the kaolinite has been redissolved (Table I). Here amorphous silica becomes stable and forms, just before the saturation point with bentonite.

Table VII: Sequence of events in the simulated dissolution of the bentonite, at 25°C, in the Finnsjön dilute water (program DISSOL). Option C.

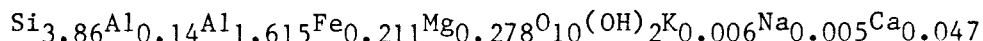
log ξ	n*	Mineralogical events	pH	log pCO ₂	Eh (mV)	logQ bentonite
*						
-6.24	0.058	kaolinite has been redissolved	7.42	-2.13	119.6	2.153
-4.41	3.873	amorphous silica precipitated	7.91	-2.75	90.6	3.591
-4.33	4.681	bentonite becomes stable	8.05	-2.92	82.4	3.654

* Follows Table I.

The cumulate mass transfers before the saturation point are now the following:

- dissolution of bentonite : 4.68 millimoles/kg H₂O
- precipitation of calcite : 0.139 " " "
- precipitation of amorphous silica : 0.340 " " "
- precipitation of a 2:1 clay : 4.212 " " "

with a smectite formula:

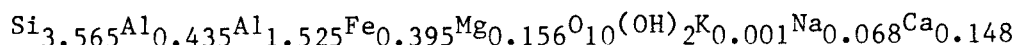


These mass transfers are only slightly different from those obtained with the A option, but the equilibrium point with bentonite is reached now without oversaturations (laumontite etc.) and at equilibrium with amorphous silica. The aqueous solution is also very similar with a slightly higher pH (8.05 instead of 8.01) and of course, a lower silica content (2.02 instead of 2.19 millimoles/kg H₂O).

4.1.2 The Stripa water VI

With this water the amorphous silica saturation is not reached at 25°C, but the laumontite appears very early in the sequence (Table X) and the complete sequence becomes:

- dissolution of bentonite : 0.991 millimoles/kg H₂O
- precipitation of laumontite: 0.314 millimoles/kg H₂O
- precipitation of a 2:1 clay: 0.478 millimoles/kg H₂O
poor in potassium but more substituted in the tetrahedric sites:



The major differences with the previous calculation (Table XII) concern the pH value (7.96 instead of 8.59) and the corresponding alkalinity (0.072 instead of 0.132 meq/l).

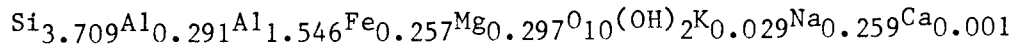
4.2 HEATING FROM 25 TO 100°C

The heating curve was again followed from 25 to near 100°C for the two solutions with the additional stabilities of amorphous silica (FI water) of laumontite (VI water).

4.2.1 The Finnsjön water FI (Tables VIII and IX)

The sequence of mineralogical events is given in Table VIII and shows only a new saturation point with respect to amorphous silica at 56°C. The total mass transfers are respectively:

- dissolution of bentonite : 172 millimoles/kg H₂O
- precipitation of:
 - calcite : redissolved later (1.44 mmoles/kg H₂O)
 - laumontite : 18.8 millimoles/kg H₂O
 - amorphous silica : 114 " " " "
 - a 2:1 clay phase : 127 " " " "



These mass transfers are about ten times more important than previously because of the pH increase (Table IX) which gives an important silica increase in solution (alkaline H₃SiO₄- balanced by an increase of sodium). The secondary clay remains rich in sodium in the exchangeable sites, like the bentonite. With the important evolution of the aqueous chemistry, the total mass transfer corresponds to less than 2% of the total initial bentonite. This is the maximum of bentonite alteration that we have found. It remains still reasonable.

Table VIII: Sequence of events in the simulated heating of the bentonite + solution system from 25°C to 100°C (program THERMAL) with the Finnsjön water. Option C.

T°C	n*	Mineralogical events	pH	log pCO ₂	Eh (mV)
28.74	ε	2:1 clay, bentonite, calcite and amorphous silica initially at equilibrium	7.99	-2.83	68.2
32.24	0.340	amorphous silica has been redissolved	7.94	-2.75	52.3
39.80	0.570	laumontite precipitated	7.88	-2.64	20.7
44.59	1.631	amorphous silica precipitated	7.80	-2.48	3.1
53.52	6.882		7.71	-2.15	-34.7
70.58	11.154		8.02	-2.32	-133.8
96.24	171.615		9.07	-3.21	-335.9

Table IX: Chemical characteristics of the solution along the simulated dissolution of bentonite at 25°C, and heating from 25°C to 100°C with the initial Finnsjön dilute water. Option C.

T°C	pH	Al nM/kg H ₂ O	Fe nM/kg H ₂ O	K	Na	Ca mM/kg H ₂ O	Mg	Si	Alkalinity meq/kg H ₂ O
*									
25.00	7.42	0.396	0.003	0.191	0.649	1.508	0.198	0.295	3.345
25.00	7.91	0.389	ε	0.249	1.667	0.640	0.093	2.022	2.475
25.00	8.05	0.515	ε	0.260	1.879	0.494	0.049	2.032	2.317
28.74	7.99	0.708	ε	0.260	1.879	0.494	0.049	2.207	2.317
32.24	7.94	0.975	ε	0.261	1.884	0.441	0.044	2.377	2.316
39.80	7.88	2.692	ε	0.263	1.945	0.455	0.029	2.472	2.268
44.59	7.80	3.290	0.001	0.275	2.226	0.428	0.026	2.909	2.499
53.52	7.71	7.213	0.005	0.303	3.591	0.297	0.019	3.416	3.618
70.58	8.02	79.185	0.009	0.230	4.637	0.019	0.001	4.737	4.000
96.24	9.07	75.251	0.002	0.034	15.280	ε	ε	15.859	14.429

Cl is constant (0.56 millimoles/kg H₂O).

* Follows Table III.

4.2.2 The Stripa V1 water (Tables X to XII)

The mass transfers calculated with the option C for V1 are also enhanced by the precipitation of amorphous silica and laumontite:

- dissolution of bentonite : 66.1 millimoles/kg H₂O

- precipitation of:

laumontite : 10.6 " " " "

amorphous silica : 27.5 " " " "

a 2:1 clay phase : 48.5 " " " "

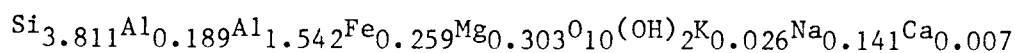


Table X: Sequence of events in the simulated dissolution of bentonite, at 25°C, in the Stripa V1 water (program DISSOL). Option C.

log ξ	n*	Mineralogical events	pH	log pCO ₂	Eh (mV)	logQ bentonite
-14.02	ε	2:1 clay precipitated	8.95	-5.56	-116.1	2.247
-10.86	ε	laumontite precipitated	8.95	-5.56	-116.1	2.254
- 6.74	0.018		8.75	-5.48	-111.2	2.381
- 5.26	0.556		8.04	-4.60	-62.2	3.478
- 5.00	0.991	bentonite becomes stable	7.96	-4.51	-57.1	3.654

Table XI: Sequence of events in the simulated heating of the bentonite + solution system from 25°C to 100°C (program THERMAL) with the Stripa VI water. Option C.

T°C	n*	Mineralogical events	pH	log pCO ₂	Eh (mV)
		2:1 clay, bentonite and laumontite initially at equilibrium			
25.11	ε		7.95	-4.51	-57.5
36.73	0.476		7.60	-4.05	-95.5
56.38	6.030	amorphous silica precipitated	7.18	-3.50	-170.8
60.00	13.322		7.18	-3.48	-189.4
70.48	15.775		7.39	-3.57	-255.2
91.86	52.795		8.51	-4.52	-441.9

Table XII: Chemical characteristics of the solution along the simulated dissolution of bentonite at 25°C, and heating from 25°C to 100°C with the initial Stripa VI water. Option C.

T°C	pH	Al μM/kg H ₂ O	Fe nM/kg H ₂ O	K	Na	Ca	Mg mM/kg H ₂ O	Si	S	SO ₄	Alkalinity meq/kg H ₂ O
25.00	8.95	0.043	0.0008	0.031	12.048	4.291	0.008	0.216		1.062	0.102
25.00	7.96	0.001	0.011	0.050	12.283	4.006	0.151	1.160		1.062	0.072
25.11	7.95	0.001	ε	0.050	12.283	0.040	0.151	1.062		1.062	0.072
36.73	7.59	0.002	0.138	0.059	12.403	3.869	0.223	1.546		1.062	0.071
56.38	7.18	0.003	3.273	0.160	13.847	3.125	0.200	3.515		1.062	0.082
60.00	7.18	0.004	4.124	0.268	15.715	2.198	0.143	3.745	ε	1.062	0.089
70.48	7.39	0.019	4.465	0.350	19.530	0.399	0.025	4.447	ε	1.062	0.152
91.86	8.51	1.555	0.462	0.095	23.289	ε	ε	8.388	0.003	1.059	2.821

Cl is constant (18.2 millimoles/kg H₂O).

The chemical evolution of the solution VI is also very important (Table XII) with a pH increase followed by an increase of the sodium and silica concentrations. These variations are a little less important than for solution FI, but calcium and magnesium are also completely extracted from the solution. This is probably the major effect on the solution chemistry from the combined precipitation of laumontite, amorphous silica and a secondary clay phase.

5 SATURATION STATE OF THE SOLUTION FROM THE BENTONITE ZONE WITH RESPECT TO THE MINERALS FROM THE GRANITE

After a complete reaction with the bentonite, the solutions VI and FI are highly transformed in their composition near 100°C. If they leave the bentonite zone and join again the granitic matrix they will react with the granite with an initial composition completely different from what it was before the reaction.

The saturation tests show that these solutions are saturated with respect to the minerals from the granite except anorthite and biotite (for FI). This means that the interaction with the granite will proceed in the part of the alteration sequences where the volumic balance gives a clear excess of volume in favour of the secondary minerals: the porosity may only decrease in the microfractures (see Fritz et al., 1984). Another effect must be recalled here. The solution leaving the repository zone will also follow a decreasing temperature gradient. This has not yet been simulated but will induce, particularly if the silica content is as high as expected, a precipitation of amorphous silica in addition to the clay minerals.

CONCLUSION

A large number of computer runs were conducted in order to underline progressively the effect of the different possible minerals that may precipitate from the solution interacting with the bentonite. The first result of all these calculations was to show how important the buffering effect of the bentonite is on the system. Even very important evolutions in the solutions correspond here to a very limited evolution of the clay phase because of the high clay/water ratio (4 kg/kg or 10 moles of bentonite per kg of water).

If the clay phase transforms slightly without chemical control on the solution by laumontite, the solutions (diluted or not) remain undersaturated with respect to amorphous silica but supersaturated with respect to quartz (whose formation was supposed negligible here below 100°C). However, if the laumontite equilibrium is maintained by precipitation of this mineral, the silica content of the solution increases and the amorphous silica may form. Here again the kinetic control, which is not included in the calculation (see discussion, part I) may modulate the mass transfers with time, but the resulting alteration will give an intermediate result between the two options of calculation (A and C) and the quantity of bentonite dissolved will not be very important. Finally another approximation which has been made for these simulations can be discussed: the total mass of bentonite reacts with the solution only through the dissolved part of this clay. The effect on the water chemistry is therefore partially underestimated and the quantity of bentonite dissolved, necessary to reach the equilibrium, is consequently overestimated. A next step in the precision of the calculation will need a new version of the computer models. However, it is important to know that the calculation presented here, even if they correspond to a certain overestimation of the bentonite evolution in a closed bentonite + solution system, predicts a limited degradation of this clay, particularly in its swelling properties: the evolution to an illite-type clay has not at all been detected, and there is no evidence for a potassium uptake in the exchangeable sites.

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