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9519 Biotite Granodiorite Reacted in a
Temperature Gradient

University of California

LOS ALAMOS SCIENTIFIC LABORATORY

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G. K. Bayhurst

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9519 BIOTITE GRANODIORITE REACTED IN A TEMPERATURE GRADIENT

by

R. W. Charles and G. K. Bayhurst

ABSTRACT

A biotite granodiorite from the Fenton Hill Hot Dry Rock (HDR) geothermal system was reacted in a controlled temperature gradient with initially distilled water for 60d. Polished rock prisms were located in the gradient at 72, 119, 161, 209, 270, and 310°C. Scanning electron microscope and microprobe analyses show the appearance of secondary phases: Ca-montmorillonite at 72°C and 119°C; zeolite, either stilbite or heulandite, at 161°C; and another zeolite, thomsonite, at higher temperatures. Solution analyses show a steady state equilibrium exists between solution and overgrowths after about 2 weeks of reaction.

The chemographic relations for the system are explored in some detail indicating the divariant assemblages may be placed in a reasonable sequence in intensive variable space. These relations predict high and low temperature effects not directly observed experimentally as well as relevant univariant equilibria.

Solution chemistry indicates the Na-Ca-K geothermometer more adequately predicts temperature in this system than does the silica geothermometer.

I. INTRODUCTION

The Fenton Hill Hot Dry Rock project involves circulation of an aqueous fluid at depth in a hot, relatively dry, impermeable rock reservoir. After a circulation system is established at depth, working fluid will enter the rock reservoir from the wellbore, extract energy in the form of heat, and return to the surface through another wellbore. A temperature gradient will be imposed upon the rock reservoir as a result of this heat extraction. Once

circulation is initiated, the working fluid will enter a relatively cool rock fracture and move up the temperature gradient toward the second well bore. This temperature gradient as well as dynamic (flowing) conditions will cause a host of different rock alterations to appear along the fracture. An experimental circulation system has been developed with an imposed temperature gradient as an attempt to identify these rock-fluid reactions. While fixed temperature reactions in a closed system are important for defining the final equilibrium assemblages, circulation systems help define the transient states and mass transport the rock will encounter as it evolves with time.

Circulation systems with a temperature gradient have application in other fields of investigation. When placed in a rock repository, radioactive waste forms will induce a temperature gradient in the surrounding rock. Leaching selected elements from depth in a system similar to a HDR system will also create a temperature gradient.

II. EXPERIMENTAL PROCEDURE

Figure 1 and Plate 1 exhibit the controlled gradient circulation system. Flow is clockwise. Six polished rock prisms (2.5 cm x 0.6 cm x 0.6 cm) are attached to a tantalum rod which, when emplaced in the pressure vessel, spaces the prisms along the axis of the vessel. The reaction vessel, fashioned of A-286, is 102 cm long and 3.8 cm in diameter with a bore 1.3 cm in diameter. The bore was drilled and honed centered on the long axis of the vessel. The cone seals are also of A-286 while the caps and thrust washers are of 4340E. Only 1/3 of the vessel is heated. The other end is cooled by wrapping copper coils about the vessel and circulating cooling fluid with a Forma Scientific (model 2095) refrigerating unit. By adjusting the coolant temperature, the number and spacing of cooling coils, and the addition of asbestos insulation, a smooth temperature gradient is obtained inside the vessel under run conditions. Figure 2 depicts the calibration for this particular run.

Temperature is monitored using a Lindberg Hevi-Duty model 55031A clam-shell furnace. Temperature control is effected by a Love Instruments model 71 controller. Continual monitoring of temperature is done with a Honeywell 24 channel strip chart recorder.

The remainder of the system is constructed of standard 1/4 inch high pressure valves, tubing and fittings. Capillary tubing (0.16 cm O.D. x 0.08 cm I.D.) connects the circulation pump, Scientific Systems model C-239, and the

Fig. 1. The controlled temperature gradient circulation system.

Haskel pump, model MCP-188, to the line. The Haskel pump initially pressurizes the system and maintains pressure during sampling.

Provisions are made to sample solutions at two points in the system. The portion of the system from the hot end of the pressure vessel to the hot sampler is maintained at run temperature. At this point temperature is dropped to room temperature by radiative cooling. The cool sample is taken downstream to determine the precipitation in the line. A ballast tank is usually added to the system to adjust the rock fluid ratio. Total volume for the system with a 500 ml ballast volume is about 700 ml. Solution is drawn into the system by vacuum.

Fluid samplers are shown in Figure 3. These samplers allow extraction of fluid at constant temperature and pressure, preventing fractionation of the sampled fluid. The system is mounted vertically (the right side is up). Valves and fittings are standard 0.64 cm (1/4") high pressure tubing with

Plate 1. The controlled temperature gradient circulation system.

Fig. 2. Temperature calibration of the reaction vessel.

Fig. 3. Fluid sampler, A, B, D, E, and G = high pressure valves. A and B have high temperature modification for use with hot fluid. C = sample chamber, F = pressure gauge, H = Haskell gas pump, I = argon reservoir, J = high pressure metering valve, and K = water trap.

cone in cone seals. Valves A and B are modified with an extended valve stem and graphite asbestos packings when they are used to sample hot solution. C is the sample chamber made of 316ss, 2.54 cm O.D. x 9 cm long. The volume is about 35 cm³. H is a Haskell gas pump.

Initially the sampler is pumped up to run pressure with argon gas and heated to run temperature by heat tapes with valves A, E, and J closed. Valve A is opened. Valve E is opened. Valve J, a metering valve, is opened and argon is bled off through the water trap. Argon and H₂O were found to be immiscible when A is opened over a period of as long as 48 h. When H₂O appears in the trap, the sampler is full. Then valves A, B, and D are closed and the sampler is allowed to cool. The sample is contained at this point in C, except for a small amount in the 0.64 cm tubing which is of negligible volume. One merely has to open the sampler and analyze. No precipitates have been found thus far in the sampler.

This study reacted biotite granodiorite (9519) with initially distilled water for a period of 2 months at 1/3 kbar total pressure with a flow of 3 cc/min. Fluid was sampled at 1, 2, 5, 8, 14, 30, and 60d. All rock prisms were removed at the conclusion of the experiment. Rock prisms were centered at 72, 119, 161, 209, 270, and 310°C in the temperature gradient vessel.

Initial modal rock analysis is shown in Table I. Fourteen phases have been identified. Kspar (var. microcline, Or₉₃) is relatively fresh. Plagioclase shows a bimodal composition. The albite rich rims (Ab₈₉) surround a core of oligoclase (Ab₇₄). Biotite is commonly chloritized. Original biotite always shows a K deficiency and is too aluminous to be on the annite-phlogopite join. Sphene, apatite, magnetite, and zircon round out the primary mineral phases. In addition to chlorite, metamorphic alteration includes epidote, sericite, calcite, and a trace of prehnite. Changes in major phase composition were determined in two ways. The interior of each rock prism was examined as well as the surface. One half of each prism was dipped in epoxy as an attempt to preserve the delicate overgrowths. This half was then sectioned in order to determine chemical and morphological changes in the interior of the prism.

Solutions were analyzed by plasma emission spectrometry. Rock prisms were examined with a scanning electron microscope (SEM) with a nondispersive detector and an electron microprobe.

TABLE I^{*}

BIOTITE GRANODIORITE MODAL ANALYSES: 9519-1

Potassium Feldspar	15
Plagioclase	38
Quartz	25
Biotite	13
Chlorite	
Magnetite	1
Epidote	3
Sphene	2
Calcite	1
Apatite	1
Miscovite	1
Zircon	tr
Sericite	tr
Sulfide	tr
Prehnite	tr

^{*}From LA-6930-MS, A. W. Laughlin and A. Eddy.

∞ TABLE I (cont.)

MAJOR AND MINOR PHASE COMPOSITION

Potassium Feldspar (microcline)	Na 0.07±.01	K 0.93±.01	Al 1.02±.01	Si 2.98±.01	O 8			
Plagioclase								
Core	Na _{0.74±.01}	K _{0.01±.01}	Ca _{0.26±.01}	Al _{1.28±.01}	Si _{2.72±.01}	O ₈		
rim	Na _{0.89±.01}	K _{0.02±.01}	Ca _{0.09±.01}	Al _{1.13±.01}	Si _{2.87±.01}	O ₈		
Biotite	K _{0.88±.02}	Mg _{1.37±.02}	Fe ⁺² _{1.21±.01}	Mn _{0.04±.01}	Ti _{0.09±.01}	Al _{1.41±.01}	Si _{2.81±.01}	O _{10(OH)2}
Chlorite	Mg _{2.50±.02}	Al _{2.49±.02}	Fe ⁺² _{2.18±.01}	Mn _{0.08±.01}	Si _{2.73±.01}	O _{10(OH)8}		
Epidote	Ca _{1.99±.02}	Fe ⁺³ _{0.77±.05}	Al _{2.24±.04}	Si _{3.11±.01}	O _{12(OH)}			
Sphene	Ca _{1.00±.02}	Al _{0.09±.01}	Fe ⁺² _{0.06±.01}	Ti _{0.87±.01}	Si _{1.03±.01}	O ₅		
Sericite	Na _{0.03±.01}	K _{0.89±.01}	Mg _{0.13±.03}	Fe ⁺³ _{0.24±.04}	Al _{2.60±.07}	Si _{3.17±.02}	O _{10(OH)2}	
Prehnite	Ca _{1.92±.01}	Al _{1.99±.01}	Si _{3.02±.01}	O _{10(OH)2}				

III. RESULTS

A. Weight Change

All prisms showed a measurable change in weight after drying in a vacuum overnight (Table II, Figure 4). Prisms at 72°C and 119°C showed a net weight increase of a few tenths of a percent corresponding to an accreted phase covering the entire surface of the rock. Weight change becomes negative at 161°C and increases to 23.8% at 310°C.

B. Morphological Changes

Plates 2-7 show portions of the reacted rock surfaces at 72°C through 310°C. Both the 72°C and 119°C prisms show botryoidal precipitates. There is also a more or less uniform coating of the same material covering all of the original minerals. The material looks mostly amorphous. At 161°C, all mineral phases are coated with a mossy precipitate. At this temperature the overgrowth appears entirely crystalline.

At 209°C the habit of the precipitate changes sharply. Overgrowths no longer blanket the entire surface. These are confined primarily to the plagioclase feldspar and are prismatic in habit (see Plate 5). Large cavities appear (2 o'clock) where quartz has been dissolved. Two resistant apatite grains are seen at 8 o'clock in this cavity. Surrounding the cavity is resistant chloritized biotite. In the northwest corner of the plate the plagioclase shows chemical alteration with secondary precipitation. In the southwest (7 o'clock) is an etched microcline grain with secondary overgrowth of the same composition as that which grows as a template on the plagioclase.

This description holds at 270°C and 310°C with little change other than greater dissolution of quartz and microcline. The 270°C (Plate 6) photomosaic concentrates primarily on an altered plagioclase grain. Biotite at 11 o'clock is resistant. At 310°C complete quartz removal is observed. The microcline (at 3 o'clock and 7 o'clock) shows etching. Plagioclase (10 o'clock) is altered and the biotite at 6 and 12 o'clock remains resistant.

C. Chemical Changes

Both the fresh rock surface and thin sections were analysed. Results from these two approaches are presented in Tables III and IV. Table V lists secondary phase compositions.

TABLE II
WEIGHT CHANGE

Prism #	Temperature (°C)	Original Weight (g)	Final Weight (g)	Weight Change (g)	Change (%)
1	72	2.8433	2.8470	+0.0037	+ 0.1
2	119	2.8350	2.8460	+0.0110	+ 0.4
3	161	2.8425	2.8320	-0.105	- 0.4
4	209	2.8615	2.7458	-.1157	- 4.0
5	270	2.8938	2.3805	-.5133	-17.7
6	310	2.8621	2.1811	-.6810	-23.8
		17.1382	Total weight loss	1.3058

Fig. 4. Weight change for the reacted granodiorite prisms.

Plate 2. Scanning electron microscope photomosaic of a portion of the prism at 72°C.

Plate 3. Scanning electron microscope photomosaic of a portion of the prism at 119°C.

Plate 4. Scanning electron microscope photomosaic of a portion of the prism at 161°C

209°C

Plate 5. Scanning electron microscope photomosaic of a portion of the prism at 209°C.

Plate 6. Scanning electron microscope photomosaic of a portion of the prism at 270°C.

Plate 7. Scanning electron microscope photomosaic of a portion of the prism at 310°C.

TABLE III
SURFACE ANALYSES

Surface Analyses of primary phases at 72°, 119°, and 161°C are omitted because they are masked by a covering of secondary phases.

On Microcline (8 oxygens)											
	Na	K	Ca	Al	Si	O					
Fresh (19 Analyses)	0.07±.01	0.93±.01	0.00	1.02±.01	2.98±.01	8					
209° (10 Analyses)	0.06±0.1	0.84±.03	0.00	1.06±.02	2.97±.02	8					
270°C (13 Analyses)	0.04±.01	0.89±.04	0.00	1.01±.01	3.00±.02	8					
310°C (10 Analyses)	0.06±.02	0.93±.01	0.03±.01	1.05±.01	2.95±.02	8					
On Plagioclase (8 oxygens)											
	Na	K	Ca	Al	Si	O					
Fresh Core (12 Analyses)	0.74±.01	0.01±.01	0.26±.01	1.28±.01	2.72±.01	8					
Rim (24 Analyses)	0.89±.01	0.02±.01	0.09±.01	1.13±.01	2.87±.01	8					
209°C (12 Analyses)	0.14±.01	0.10±.02	0.76±.04	1.81±.02	2.20±.01	8					
270°C (14 Analyses)	0.12±.01	0.14±.03	0.74±.04	1.79±.01	2.20±.01	8					
310°C (13 Analyses)	0.12±.01	0.07±.02	0.78±.04	1.85±.02	2.16±.02	8					
On Biotite (12(O,OH))											
Fresh (9 Analyses)	K	Na	Ca	Mg	Fe ⁺²	Mn	Ti	Al	Si	O	OH
209° (7 Analyses)	0.62±.06	0.08±.01	0.51±.04	0.85±.04	0.70±.04	0.02±.01	0.08±.01	1.72±.06	2.75±.03	10	2
270°C (8 Analyses)	0.74±.04	0.02±.01	0.01±.01	1.31±.06	1.05±.02	0.03±.01	0.08±.01	1.36±.03	3.00±.04	10	2
310°C (11 Analyses)	0.56±.11	0.02±.01	0.21±.07	1.18±.12	0.84±.08	0.03±.01	0.06±.01	1.72±.08	2.86±.05	10	2

TABLE IV
ANALYSES OF PRINCIPAL MINERALS FROM THIN SECTIONS

Microcline (8 oxygens)						
	<u>K</u>	<u>Na</u>	<u>Al</u>	<u>Si</u>	<u>O</u>	
Fresh (19 Analyses)	0.93±0.1	0.07±.01	1.02±0.1	2.98±.01	8	
72° (3 Analyses)	0.91±.02	0.06±.01	1.01±.02	2.99±.02	8	
119°C (2 Analyses)	0.95±.01	0.04±.01	1.02±.04	2.99.03	8	
161°C (1 Analysis)	0.96	0.04	1.05	2.95	8	
209°C (1 Analysis)	0.93	0.04	1.02	2.98	8	
270°C (1 Analysis)	0.96	0.03	1.01	2.99	8	
310°C (2 Analyses)	0.94±.01	0.04±.01	1.12±.08	2.91±.06	8	
Plagioclase (8 oxygens)						
	<u>Na</u>	<u>K</u>	<u>Ca</u>	<u>Al</u>	<u>Si</u>	<u>O</u>
Fresh						
Core (12 Analyses)	0.74±.01	0.01±0.1	0.26±.01	1.28±.01	2.72±.01	8
Rim (24 Analyses)	0.89±.01	0.02±.01	0.09±.01	1.13±.01	2.87±.01	8
72°C (9 Analyses)	0.86±.02	0.01±.01	0.06±.02	1.09±.02	2.93±.02	8
119°C (3 Analyses)	0.77±.05	0.04±.02	0.05±.02	1.16±.06	2.90±.05	8
161°C (11 Analyses)	0.83±.03	0.01±.01	0.03±.01	1.09±.02	2.94±.02	8
209°C (8 Analyses)	0.81±.03	0.01±.01	0.04±.01	1.07±.02	2.97±.02	8
270°C (3 Analyses)	0.84±.05	0.00	0.11±.05	1.13±.06	2.88±.08	8
310°C (3 Analyses)	0.81±.01	0.00	0.15±.04	1.18±.03	2.83±.04	8

TABLE IV (Cont.)

	Biotite (12(O,OH))								
	<u>K</u>	<u>Mg</u>	<u>Fe</u>	<u>Mn</u>	<u>Ti</u>	<u>Al</u>	<u>Si</u>	<u>O</u>	<u>OH</u>
Fresh (9 Analyses)	0.88±.02	1.37±.02	1.21±.01	0.04±.01	0.09±.01	1.41±.01	2.81±.01	10	2
72°C (3 Analyses)	0.93±.01	1.39±.01	1.18±.01	0.03±.01	0.07±.01	1.40±.03	2.84±.01	10	2
119°C (3 Analyses)	0.77±.18	1.44±.19	1.31±.05	0.03±.01	0.07±.01	1.40±.03	2.84±.01	10	2
161°C (1 Analysis)	0.95	1.35	1.20	0.04	0.09	1.45	2.78	10	2
209°C (1 Analysis)	0.90	1.42	1.18	0.03	0.07	1.43	2.81	10	2
270°C (3 Analyses)	0.77±.15	1.50±.14	1.24±.01	0.03±.01	0.07±.01	1.43±.04	2.76±.09	10	2
310°C (3 Analyses)	0.93±.01	1.29±.01	1.24±.01	0.05±.01	0.11±.01	1.41±.02	2.81±.01	10	2

TABLE V
OVERGROWTHS AND SECONDARIES

Surface									
72°C "Beidellite" (19 Analyses)	K _{0.44±.09}	Ca _{0.47±.03}	Na _{0.06±.03}	Mg _{0.06±.03}	Fe ⁺³ _{0.58±.03}	Al _{4.46±.03}	Si _{6.96±.06}	O ₁₀	(OH) ₄ ·nH ₂ O
119°C "Beidellite" (17 Analyses)	K _{0.25±.03}	Ca _{0.41±.03}	Na _{0.06±.03}	Mg _{0.06±.02}	Fe ⁺³ _{0.36±.06}	Al _{4.40±.03}	Si _{7.18±.03}	O ₂₀	(OH) ₄ ·nH ₂ O
161°C "Stilbite" (25 Analyses)	Ca _{0.27±.04}	Na _{0.52±.08}	K _{0.72±.10}	Al _{2.14±.02}	Si _{6.93±.02}	O ₁₈ ·6 H ₂ O			
209°C "Thomsonite" (12 Analyses)	Na _{0.30±.02}	K _{0.25±.05}	Ca _{1.90±.10}	Al _{4.53±.03}	Si _{5.50±.02}	O ₂₀ ·6 H ₂ O			
270°C "Thomsonite" (14 Analyses)	Na _{0.30±.02}	K _{0.35±.08}	Ca _{1.85±.10}	Al _{4.48±.02}	Si _{5.50±.05}	O ₂₀ ·6 H ₂ O			
310°C "Thomsonite" (13 Analyses)	Na _{0.30±.02}	K _{0.18±.07}	Ca _{1.95±.10}	Al _{4.63±.05}	Si _{5.40±.05}	O ₂₀ ·6 H ₂ O			
Interior									
None observed for 72°, 119°, 161°, and 209°C									
270°C "Thomsonite" (4 Analyses)	Na _{0.33±.02}	K _{0.03±.01}	Ca _{2.15±.09}	Al _{4.58±.05}	Si _{5.40±.05}	O ₂₀ ·6 H ₂ O			
310°C "Thomsonite" (7 Analyses)	Na _{0.43±.05}	K _{0.04±.02}	Ca _{2.03±.05}	Al _{4.53±.05}	Si _{5.48±.05}	O ₂₀ ·6 H ₂ O			

Surface analyses show the first three prisms are completely blanketed by secondary phases which mask the original feldspar, quartz, and biotite substrate. At 72°C and 119°C the prism is covered with a Ca, K, Fe aluminosilicate with Si/Al = 1.6. At 161°C composition as well as morphology of the secondary changes to a K, Na, Ca aluminosilicate with Si/Al = 3.2. Surface analyses of the higher temperature prisms show a different Ca, Na, K aluminosilicate with Si/Al = 1.2. This grows as discrete clusters of crystals usually growing on a plagioclase substrate, although scattered clusters are found on the other primary phases. This third phase remains relatively constant in composition at 209°C, 270°C, and 310°C (see Table V).

Surface analyses of the primary phases are only possible for the 209°C, 270°C, and 310°C prisms. Microcline is essentially congruently dissolved from all three prisms. Biotite, naturally chloritized, is partially covered with experimental secondary phases. This observation makes biotite reaction difficult to interpret from the surface analyses alone. The surface of plagioclase grains undergoes extensive recrystallization and is host to the major amount of Ca, Na, K aluminosilicate (Si/Al = 1.2). Quartz is extensively etched and entirely dissolved at 310°C.

The thin sections provide chemical information not available in the surface analyses. Quartz is extensively etched above 161°C. Almost no quartz remained in the 310°C prism. Microcline and biotite show no change in composition (see Table IV). Plagioclase in thin section shows a drop in An content for the lower temperature prisms compared with fresh plagioclase (see Figure 5). Clearly, reaction is not confined to the surface of the prisms. Ca, Na, K aluminosilicate (Si/Al = 1.2) appears within the plagioclase. Composition is very similar to that found in the surface analyses except it is much lower in K.

In neither the surface analyses or the thin section analyses were any of the other primary phases seen to react anyway but congruently with the exception of plagioclase. Other phases appear resistant.

D. Solutions

Solution analyses are shown in Table VI and Figure 6. Precision is about 5%. With only one exception hot sampled solutions (310°C) yielded higher solution burdens than cold sampled solutions (room temperature). All analysed cations reach a steady state after about 14d. Na, K, and Al, and to some extent Ca and Fe show an initial high concentration spike. Concentration

Fig. 5. Anorthite content of reacted plagioclase.

TABLE VI

SOLUTION ANALYSES. h = HOT SAMPLE, c = COLD SAMPLE

Mg was not detected

Sample	SiO ₂		Na		K		Ca		Fe		Al		Total	
	h	c	h	c	h	c	h	c	h	c	h	c	h	c
1d	267	46	8.2	2.2	14.2	2.6	0.20	0.10	0.08	0	9.3	1.6	299	52
2	373	249	11.7	6.9	13.8	10.0	0.20	0.20	0.04	0.04	9.7	7.2	408	274
4	390	289	7.7	7.3	7.2	6.5	0.20	0.10	0.08	0.04	8.7	6.6	414	309
7	515	349	7.4	9.2	7.2	6.2	0.60	0.20	0.10	0.02	9.3	7.3	539	372
14	556	362	6.8	5.7	7.7	5.7	0.40	0.30	0.20	0.10	7.1	5.6	578	379
30	542	483	13.5	12.1	8.0	6.7	0.17	0.08	0.02	0	6.6	5.4	570	507
60	565	467	15.5	12.8	7.9	6.9	0.24	0.14	0	0	5.3	4.0	594	491

Fig. 6. Solution analyses (SiO₂).

Fig. 6. Solution analyses (Ca).

Fig. 6. Solution analyses (Na).

Fig. 6. Solution analyses (K).

Fig. 6. Solution analyses (Fe).

Fig. 6. Solution analyses (Al).

Fig. 6. Solution analyses (Total burden).

spikes for the cold solution lagged behind that of the hot solution. SiO_2 rises smoothly to a steady state well below quartz saturation at 310°C . Fe concentration drops below detection after 30d.

IV. DISCUSSION

A. Weight Change

The major portion of the weight loss can be explained simply as quartz removal. The following calculation proves this point. The estimated rock density of 2.76 g/cm^3 is derived from the mineralogy (see Table VII). Mineral densities are taken from Robie, *et al.* (1979). If we assume all weight loss is due to quartz, the percent loss for prism 6 (310°C) would be 24.0% which approximates the observed loss (23.8%). Of course, this calculation ignores the reactivity of the other principal phases. Dissolution of some of the other primary phases is compensated by precipitation of secondary phases. These secondary precipitates can amount to a few tenths of a percent of the original prism weight.

TABLE VII
ESTIMATED ROCK DENSITY

<u>Mineral</u>	<u>Volume (%)</u>	<u>Density (g/cm³)</u>	<u>Column 2 x Column 3 (g/cm³)</u>
Microcline	15	2.56	0.384
Plagioclase (Ab ₈₀ An ₂₀)	38	2.65	1.007
Quartz	25	2.65	0.663
Biotite	13	3.00	0.390
Epidote	3	3.50	0.105
Sphene	2	3.52	0.071
Calcite	1	2.71	0.027
Apatite	1	3.20	0.032
Magnetite	1	5.20	0.052
Muscovite	1	2.83	0.028
	<hr/> 100		<hr/> 2.76

B. Experimental Alterations and Natural Assemblages

The rock prisms react to yield major secondary phases. At 72°C and 119°C a Ca, K, Fe aluminosilicate (see Table V) grows with relatively uniform composition over the rock surface. In rare instances the material is platy, but usually it looks amorphous. Table VIII compares this composition with the dioctahedral montmorillonite, beidellite. Exact identification is difficult because no x-ray data is possible with this thin layer overgrowth. While the morphology indicates the secondary is at best cryptocrystalline, its composition compares favorably with a known clay. Not enough K or Al is present to call this phase illite. Presence of Fe and Mg shows possible solid solution with nontronite and common montmorillonite. This phase is an indicator of low temperatures and conditions of relatively high silica activity.

At 161°C a distinctly different aluminosilicate grows. The mossy texture under high magnification is really radiating sheaves of crystals.

TABLE VIII

COMPARISON OF OBSERVED SECONDARY PHASES WITH SAME END MEMBER COMPOSITIONS

72°C:	Ca _{0.47}	K _{0.44}	Na _{0.06}	[Al _{3.42}	Fe ⁺³ _{0.58}	Mg _{0.06}]	[Si _{6.96}	Al _{1.04}]	O ₂₀ (OH) ₄ ·n H ₂ O
119°C:	Ca _{0.41}	K _{0.25}	Na _{0.06}	[Al _{3.58}	Fe ⁺³ _{0.36}	Mg _{0.06}]	[Si _{7.18}	Al _{0.82}]	O ₂₀ (OH) ₄ ·n H ₂ O
	Beidellite	($\frac{1}{2}$ Ca, Na) _{0.66}		[Al ₄]	[Si _{7.34}	Al _{0.66}]			O ₂₀ (OH) ₄ ·n H ₂ O
161°C:	Ca _{0.27}	Na _{0.52}	K _{0.72}	Al _{2.14}	Si _{6.93}	O ₁₈ ·7H ₂ O			
	Stilbite (Ca, Na ₂ , K ₂)			Al ₂ Si ₇	O ₁₈ ·7H ₂ O				
	Heulandite (Ca, Na ₂ , K ₂)			Al ₂ Si ₇	O ₁₈ ·6H ₂ O				
209°C:	Na _{0.30}	K _{0.25}	Ca _{1.90}	Al _{4.53}	Si _{5.50}	O ₂₀ ·6H ₂ O			
270°C:	Surface:	Na _{0.30}	K _{0.35}	Ca _{1.85}	Al _{4.48}	Si _{5.50}	O ₂₀ ·6H ₂ O		
	Interior:	Na _{0.33}	K _{0.03}	Ca _{2.15}	Al _{4.58}	Si _{5.40}	O ₂₀ ·6H ₂ O		
310°C:									
	Surface:	Na _{0.30}	K _{0.18}	Ca _{1.95}	Al _{4.63}	Si _{5.40}	O ₂₀ ·6H ₂ O		
	Interior:	Na _{0.43}	K _{0.03}	Ca _{2.03}	Al _{4.53}	Si _{5.48}	O ₂₀ ·H ₂ O		
Thomsonite	Na Ca ₂	[(Al, Si) ₅] ₂				O ₂₀ ·6H ₂ O			

Table VII compares this phase with stilbite and heulandite. Without xray data the two are indistinguishable. The literature indicates both stilbite and heulandite may contain considerable K (Coombs, et al., 1959, and Deer, et al., 1963). Coombs, et al., (1959) gave the range in composition of stilbite as $(\text{Ca}, \text{Na}_2)\text{Al}_2\text{Si}_7\text{O}_{18} \cdot 7\text{H}_2\text{O}$ to $(\text{Ca}, \text{Na}_2)_{1.25}\text{Al}_{2.5}\text{Si}_{4.5}\text{O}_{18} \cdot 7\text{H}_2\text{O}$ and heulandite as $(\text{Ca}, \text{Na}_2)_{1.2}\text{Al}_{2.4}\text{Si}_{6.6}\text{O}_{18} \cdot 6\text{H}_2\text{O}$ to $(\text{Ca}, \text{Na}_2)\text{Al}_2\text{Si}_7\text{O}_{18} \cdot 6\text{H}_2\text{O}$, both of which satisfactorily cover the observed composition. The morphology and larger amounts of alkali and group IIA elements preclude this phase from being a clay.

The third overgrowth has a prismatic habit and grows primarily as a template upon plagioclase feldspar. Its composition (Table V) and habit suggest it to be a zeolite. Table VIII compares observed composition with that of thomsonite. Coombs, et al. (1959) gives a range in thomsonite composition from $(\text{Ca}, \text{Na}_2)_{2.1}\text{Al}_{4.2}\text{Si}_{5.8}\text{O}_{20} \cdot 6\text{H}_2\text{O}$ to $(\text{Ca}, \text{Na}_2)_{2.5625}\text{Al}_{5.125}\text{Si}_{4.875}\text{O}_{20} \cdot 6\text{H}_2\text{O}$. The material observed in this study falls within these limits.

Analyses taken on the interior of the 270°C and 310°C prism may be a K deficient thomsonite or another phase entirely. These interior analyses reduce to plagioclase of An_{83} content. One would not predict anorthitic plagioclase to be the stable phase under these conditions, but a number of Ca-zeolites which are essentially anorthite + H_2O would have this bulk composition. One example is thomsonite.

The gradation from clay to zeolite indicates a decrease in a_{SiO_2} with increasing temperature. Whether these phases are only metastable transients or are stable phases is not determined. They do persist for 60 days in equilibrium with the solution. Other experimental work indicates these phases are reasonable in closed systems of appropriate bulk composition at temperatures and pressures found in the present study. Liou (1971) shows Ca-stilbite may have maximum thermal stability to about 180°C at 3 kbar. Reversal reactions were too sluggish to determine the equilibria at lower pressures. Obviously, in a system with variable a_{SiO_2} such as the temperature gradient circulation system, stilbite may be more stable. Higher a_{SiO_2} than that present in Liou's work could increase stilbite field with respect to laumontite. Some Na is available in the present study which may increase the thermal stability of stilbite. Nitsch's (1968) experiments seem to confirm the thermodynamic argument of Coombs, et al. (1959) and find heulandite perhaps 100-150°C more stable than stilbite.

The sequence montmorillonite - stilbite (or heulandite) - thomsonite is reasonable in systems of decreasing a_{SiO_2} . Indeed, thomsonite is probably not stable in the presence of quartz. The present study shows increasing amounts of thomsonite occurring with almost complete removal of quartz. Thomsonite replaces siliceous assemblages such as heulandite + quartz, analcime + quartz, or wairakite + quartz at lower a_{SiO_2} . For this reason thomsonite appears to be stable in systems of low a_{SiO_2} to temperatures in excess of 300°C.

Stating these observations in a different way, if the prisms were reacted at constant a_{SiO_2} , a completely different sequence of alterations would occur with temperature. At high a_{SiO_2} , with increasing temperature montmorillonite would react to form mica. At moderate a_{SiO_2} , stilbite would react to laumontite + quartz with increasing temperature. At very low a_{SiO_2} only thomsonite could appear.

C. Equilibrium and Mineral Assemblages

This study attempts to identify mineral phases as the rock reacts in a temperature gradient. Initially, the rock is entirely out of equilibrium with the circulating fluid. Both rock and fluid change in bulk composition as the reaction proceeds. A steady state occurs after about 14 days and continues until the end of the experiment.

There is no proof that the entire rock is in equilibrium. On the contrary, because this is a dynamic system, one may state there is a transient equilibrium reflected by relatively constant fluid composition causing the precipitation of secondary phases characteristic of the intensive parameters of the experiment. These secondary phases are uniform in composition within a given prism and from prism to prism with respect to major ion content. Water of hydration may change without changing the conclusions about to be presented (See section D and Appendix). These reactions are not reversible, but the secondary phases persist to the duration of the experiment and are reasonable phases for the intensive parameters considered. The secondary minerals and original minerals can be related in a framework of selected intensive variables characteristic of the experiment.

D. Chemographic Relations

The observed minerals are analysed after the method of Korzhinskii (1959), Zen (1966), and Zen (1974). The principle alterations with increasing temperature are Ca-montmorillonite, stilbite, and thomsonite. Judging from the chemical changes presented previously, the reacting phases are Ca-montmorillonite (beidellite)(Bei,B), stilbite (Stl,S), and thomsonite (Thm,T); the natural phases sericite (Mus,M), plagioclase (Plg,P), and microcline (Ksp,K); and anorthite (Ano,A) which is preferentially removed from the primary feldspar.

These minerals are part of the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{MnO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{H}_2\text{O}$. All Fe is listed as FeO because redox does not appear to be a factor in this experiment. In other words, the rock buffers $\text{FeO}/\text{Fe}_2\text{O}_3$. The minerals are approximated by their microprobe analyses as shown in Table IX. For the purpose of this discussion H_2O is considered mobile, SiO_2 is accounted for by quartz and also may be considered mobile, TiO_2 by sphene, FeO by magnetite and chloritized biotite, MgO and MnO by biotite. Phases other than those listed in Table IX are considered absolutely indifferent. These observations reduce the system to $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3$ with H_2O and SiO_2 as mobile components. A system of seven phases and four components is an $f = -1$ multisystem. An axonometric projection in tetrahedral space for this multisystem is shown in Figure 7. Due to compositional degeneracies, there are six distinct invariant assemblages named by absent phases: [Bei] $\equiv$ [Mus], [Thm], [Stl], [Plg], [Ano], and [Ksp.] The degeneracies are the colinear phases (pseudobinary) Thm, Ano, and Stl and the coplanar (pseudoternary) phases Thm, Ano, Stl, Ksp, and Plg. All reactions involving Bei and Mus are tetrahedral. A total of thirteen univariant assemblages connect the invariant assemblages. Figure 8 displays the univariant equilibria along with the chemographic relations for one of the enantiomorphs. Figure 9 displays a connected net with all possible divariant assemblages.

This development has some limitations which do not affect the overall conclusions. Phases of variable composition within the P, T range under consideration are ignored. Ca-montmorillonite in particular may change in composition with temperature. With the possible exception of water content this does not appear to be the case between 72°C and 119°C.

The multisystem may be oriented exactly in $\mu_{\text{H}_2\text{O}}-\mu_{\text{SiO}_2}$ space. Slopes of the univariant relations are calculated by:

TABLE IX

PHASE COMPOSITION USED IN THE SCHEINEMAKERS' DEVELOPMENT

Beidellite (Bei): $K_{0.4} Ca_{0.4} Na_{0.1} Fe_{0.5}^{+3} Al_{3.4} Si_{7.0} Al_{1.0} O_{20} (OH)_4 \cdot nH_2O$

Stilbite (Stl): $Ca_{0.5} Na_{0.5} K_{0.5} Al_{2.0} Si_{7.0} O_{20} \cdot 7H_2O$

Thomsonite (Thm): $Na_{0.25} K_{0.25} Ca_{2.00} Al_{4.50} Si_{5.50} O_{20} \cdot 6H_2O$

Sericite (Mus): $K_{0.90} Fe_{0.25}^{+3} Al_{1.70} Si_{3.25} Al_{0.75} O_{10} (OH)_2$

Plagioclase (Plg): $0.8 NaAlSi_3O_8 \cdot 0.2 CaAl_2Si_2O_8$

Microcline (Ksp): $0.9 KAlSi_3O_8 \cdot 0.1 NaAlSi_3O_8$

Anorthite (Ano): $CaAl_2Si_2O_8$

Fig. 7. Axonometric projection of the reacting phases in the $Na_{0.5}-K_{0.5}-AlO_{3/2}-CaO$ tetrahedron.

Fig. 8. Balanced reactions and one enantiomorph of each invariant relation.

Fig. 8 (cont.)

[Bei] [Mus]

[Stl]

Fig. 8 (cont.)

Fig. 9. Connected net for the $f = -1$ multisystem.

$$\frac{d\mu_{H_2O}}{d\mu_{SiO_2}} = - \frac{n_{SiO_2}}{\mu_{H_2O}},$$

where n_i = moles of i gained or lost in a given reaction. Slopes for the thirteen distinct univariant reactions are shown in Table X.

The two possible nets with stable invariant points are presented in Figures 10a, 10b, 11a, and 11b. The Figures were generated assuming:

- 1) homotypical stable connection between [Plg] and [Thm],
- 2) homotypical metastable connection between [Plg] and [Thm],
- 3) heterotypical connection between [Plg] and [Thm] with [Thm] stable, and

TABLE X
SLOPES OF THE UNIVARIANT CURVES IN $\mu_{\text{H}_2\text{O}} - \mu_{\text{SiO}_2}$ SPACE

<u>Reaction</u>	<u>Slope</u>
[Plg](Bei)	.6
[Plg](Stl)	144/276
[Plg](Thm)	150/322
[Plg](Ano)	552/1172
[Ano](Bei)	-30/58
[Ano](Stl)	5040/1452
[Ano](Ksp)	-3702/4918
[Ano](Thm)	282/1694
[Bei](Stl)	0
[Bei](Thm)	-54/126
[Stl](Ksp)	-144/1344
[Stl](Thm)	∞
[Thm](Ksp)	-480/784

4) heterotypical connection between [Plg] and [Thm] with [Plg] stable. Any two invariant assemblages could be chosen and treated in this manner. Only two possible nets may be generated for this system: 3) and 4). No homotypical connections are possible using the [Plg] and [Thm] invariant assemblages. The generated Figures 10 (case 3) and 11 (case 4) are related geometrically. Figure 10 becomes Figure 11 upon rotation by 180° and converting stable to metastable.

Of these two enantiomorphic nets only one is best representative of the experimental conditions. The important divariant assemblages are:

- 1) At low temperature (72°C to 119°C): Bei, Mus, Plg, Ksp (AST)
- 2) at intermediate temperature (161°C): Ksp, Mus, Plg, Stl (ABT)
- 3) at high temperature (209°C to 310°C): Ksp, Plg, Mus, Thm (ABS)
- 4) at very high temperature (greater than 310°C): Ksp, Ano, Plg, Mus (BST)

As temperature increases, the phases become less hydrous. In this experiment they also become less siliceous. A reaction path will run from upper right to lower left. Both Figures 10 and 11 show this trend. However, the enantiomorph shown in Figure 11 shows a number of reactions producing

Fig. 10a. Entire net with heterotypical connection of [Plg] and [Thm] with [Plg] stable.

Fig. 10b. Enlargement of a portion of 10a. Divariant fields are taken from the connected net - Figure 9.

Fig. 11a. Entire net with heterotypical connection of [Plg] and [Thm] with [Plg] stable.

Fig. 11b. Enlargement of a portion of 11a. Divariant fields are taken from the connected net - Figure 9.

thomsonite at high $\mu_{\text{H}_2\text{O}}$ and μ_{SiO_2} which is not observed experimentally. Reaction paths in Figure 10 will only grow thomsonite at lower μ_{SiO_2} . Figure 10 shows a possible sequence of univariant reactions producing Bei, then Stl, and finally Thm with decreasing $\mu_{\text{H}_2\text{O}}$ and μ_{SiO_2} :

Any path above and paralleling the arrow in Figure 10 is a possible path.

A schematic P-T diagram is shown in Figure 12. Figure 12 has the same morphology as Figure 10 with only the stable invariant assemblages shown. The relevant univariant and determining divariant assemblages are included. The invariant assemblages are shown in compositional space in Figure 13.

Attempts to obtain the slopes in P-T space were unavailing because entropy values are not known for a number of the solid solutions considered here. Generating entropy data according to Fyfe, *et al.* (1959) was not successful. The unknown hydration of Ca-Montomorillonite was a further problem. Molar volumes were estimated from unit cell data and from the work of Robie, *et al.* (1979). These are presented in Table XI.

The isobaric reaction path will lie across the center of the diagram. At relatively low pressure the univariant relations:

terminate the zeolite stability field in favor of anhydrous phases at lower pressure.

The determining divariant assemblages, AST, ABT, ABS, and BST, will be observed with the net oriented as shown. Minimum pressures will be determined by the location of [Bei]. Maximum pressures will be determined by the slope of [Bei](Stl) at high P. The other univariant curves are bracketed by the prism temperatures as shown in Figure 12. Lack of experimentally determined univariant reaction in this system and poor thermodynamic data make more detailed orientation impossible. Gradient experiments at lower and at higher pressures would aid in orienting the net further.

Fig. 12. Schematic P-T diagram for the multisystem. The divariant assemblages are illustrated using compositional tetrahedra. Univariant relations are also shown in the same manner.

Fig. 13. Invariant assemblages for the three stable points.

TABLE XI
MOLAR VOLUMES

Phase	Volume (cm ³)	Reference
albite	100.1	Robie, et. <u>al.</u> , 1979
microcline	108.7	Robie, et. <u>al.</u> , 1979
anorthite	100.8	Robie, et. <u>al.</u> , 1979
Plagioclase (0.8Ab·0.2An)	100.2	After Robie, et. <u>al.</u> , 1979
quartz	22.7	Robie, et. <u>al.</u> , 1979
muscovite	140.7	Robie, et. <u>al.</u> , 1979
stilbite	329	After Coombs, et. <u>al.</u> , 1959
thomsonite	350	After Coombs, et. <u>al.</u> , 1959
water	---	Steam tables, 1970

Perhaps the most relevant net for this experiment is presented in Figure 14. Only the determining divariant fields are labeled. At constant P and $\mu_{\text{H}_2\text{O}}$, the slopes of the univariant equilibria are determined by:

$$\frac{dT}{d\mu_{\text{SiO}_2}} = \frac{-\Delta n_{\text{SiO}_2}}{\Delta S}$$

Of course, exact orientation is not possible due to lack of entropy data. The diagram can be relatively well defined because of known T and decreasing μ_{SiO_2} in the observed mineral assemblages. Figures 10 and 12 show the same sequence of divariant equilibria can be observed at fixed P and T (Figure. 12) and fixed $\mu_{\text{H}_2\text{O}}$ and μ_{SiO_2} (Fig. 10).

E. Geochemical Thermometry

Chemically calculated temperature by both the silica geothermometer and the Na-K-Ca geothermometer (Fournier and Truesdale, 1973, 1974) are presented in Table XII. The second yields temperatures slightly low compared to the known temperature high of 310°C. This is due to mixing of waters trying to equilibrate at lower temperature with the maximum temperature rock-water interaction. The calculated temperature, still, is a good approximation of the maximum reservoir temperature. The silica geothermometer never equilibrates with respect to quartz at 310°C (approx. 950 ppm) (Fournier and Rowe, 1966). This may be due to three causes: 1) mixing with waters of lower temperature, 2) other reactions (i.e. zeolite and montmorillonite reactions) holding the silica activity below that of the quartz-water system, and 3) precipitation of silica in the hydrothermal line before sampling. One and two are relatively more important. Three is avoided by keeping the system heated between the reaction vessel and the sampler. No scaling was observed in this region.

Once a steady state is reached (after about 14 d) the Na-Ca-K geothermometer gives much more representative temperatures based on the maximum observed temperature than does the silica geothermometer. Also the Na-Ca-K geothermometer persists metastably near the maximum temperature in the hydrothermal system than does the silica.

Fig. 14. Schematic $T-\mu_{\text{SiO}_2}$ diagram. Only the determining divariant assemblages are shown.

TABLE XII
GEO THERMOMETER TEMPERATURES
(Calculation are based on Table VI, h=hot, c=cold)

Duration	T_{SiO_2} ($^{\circ}\text{C}$)		$T_{\text{Na-Ca-K}}$ ($^{\circ}\text{C}$)	
	h	c	h	c
7	241	206	306	297
14	249	209	324	311
30	246	235	299	301
60	260	232	286	295

V. CONCLUSION

Reacting rock with water in a controlled temperature gradient with flow from cold to hot produces a number of interesting observations. The assemblage which was originally quartz saturated, a biotite granodiorite, becomes increasingly silica undersaturated. The final assemblage contains thomsonite which is characteristic of environments without free silica. With increasing temperature, mass transport causes a decrease in the combined silica and combined water. A pH increase is also suggested but not observed directly.

The detailed chemographic relations presented here are generally applicable to any chemical system. Their usefulness is beyond question in determining representative phase assemblages and indicating features of the experimental system not observed directly. These include reactions not observed directly at different temperatures, pressures, and chemical potentials. In this case, it is possible to use phases more closely approximating the observed phases. While the development becomes more complex it is more applicable to the experimental system.

Geothermometry must be used with care. Blind application of geothermometry to a natural system should be avoided. Generally, this experiment indicates the Na-Ca-K geothermometer better represents maximum observed temperatures and better preserved these temperatures metastably until the fluids can be sampled. Until now this had not been shown experimentally.

Movement of silica into the cool reaches of the experimental system has implications to a fractured reservoir. In HDR sealing (cementing) of the fracture near the well bore will occur during periods of low or nonflow. The relatively low temperatures at the well bore fracture interface will produce silica precipitation. Amounts and character of the other overgrowths do not appear to be a problem for continued circulation.

VI. APPENDIX - HYDRATION OF MONTMORILLONITE

The previous development assumes no hydration of montmorillonite while at least 7 moles of excess water may be added to each mole of montmorillonite. This appendix will show addition of H_2O to montmorillonite will not change the interpretations based on nonhydrated material.

Chemical potential diagrams were prepared for each montmorillonite composition based on $K_{0.4}Na_{0.1}Ca_{0.4}Fe_{0.5}Al_{3.4}Si_7Al_1O_{20}(OH)_2 \cdot nH_2O$ where n ranges from 0 to 7. Slopes were recalculated for each new water content (Table A-1). The

TABLE A-1
SLOPES FOR CHEMICAL POTENTIAL DIAGRAM WITH VARIABLE MONTMORILLONITE WATER CONTENT

	<u>OH₂O</u>	<u>H₂O</u>	<u>2H₂O</u>	<u>3H₂O</u>	<u>4H₂O</u>	<u>5H₂O</u>	<u>6H₂O</u>	<u>7H₂O</u>
[Plg](bei)	.6	.6	.6	.6	.6	.6	.6	.6
[Plg](stl)	144/276	144/236	144/196	144/156	144/116	144/76	144/36	-144/4
[Plg](thm)	150/322	150/242	150/162	150/82	150/2	-150/78	-150/158	-150/238
[Ano](bei)	-30/58	-30/58	-30/58	-30/58	-30/58	-30/58	-30/58	-30/58
[Ano](stl)	5040/1452	5040/52	-5040/1348	-5040/2748	-5040/4148	-5040/5548	-5040/6948	-5040/8348
[Ano](ksp)	-3702/4918	-3702/5198	-3702/5478	-3702/5758	-3702/6038	-3702/6318	-3702/6598	-3702/6878
[Ano](thm)	282/1694	282/1414	282/1134	282/854	282/574	282/294	282/14	-282/266
[Bei](Stl)	0	0	0	0	0	0	0	0
[Bei](thm)	-54/126	-54/126	-54/126	-54/126	-54/126	-54/126	-54/126	-54/126
[Stl](ksp)	-144/1344	-144/1384	-144/1424	-144/1464	-144/1504	-144/1544	-144/1584	-144/1624
[Stl](thm)	∞	-1296/360	-1296/720	-1296/1080	-1296/1440	-1296/1800	-1296/2160	-1296/2520
[Thm](ksp)	-480/784	-480/824	-480/864	-480/904	-480/944	-480/984	-480/1024	-480/1064
[Plg](ano)	552/1172	552/892	552/612	552/332	552/52	-552/228	552/508	552/788

previous text presents a discussion for $n = 0$. When $n = 1$ the μ - μ diagram changes configuration as shown in Figure A-2 and 2a. The univariant relations are the same as in Figure 10. The [Plg] invariant assemblage is now to the NE of the other points. The only two connections are homotypical stable and metastable connections of [Plg] and [Thm] whereas they are heterotypical in Figures 10 and 11. The homotypical stable connection in A-2a corresponds to Figure 10. This same morphology holds for $n = 2$ thru 7 (see Figs. A3-A8). Because of the changes in slopes, the invariant assemblages are closer together spatially. As one can see from the connected net, Figure 9, the divariant assemblages do not change.

Figs. A1-8. Effect of additional water of hydration of monmopillonite ($\cdot nH_2O$ where $n = 0$ to 7).

Fig. A1. $n = 0$

Fig. A2. $n = 1$

Fig. A2a. $n = 1$, enlarged

Fig. A3. $n = 2$

Fig. A4. $n = 3$

Fig. A5. $n = 4$

Fig. A6. $n = 5$

Fig. A7. $n = 6$

Fig. A8. $n = 7$

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