

The products of the interaction of feldspars with aqueous solutions at 25°C

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Abstract—Chemical analyses of 300 solutions produced by the artificial weathering of eight different feldspars in fourteen experiments of up to 1200 hr duration were used to study the evolution of water during weathering. The range of pH was between 4 and 5.5. Within 4 hr of dissolution, the activity of Al was controlled by the pH and the solubility of microcrystalline gibbsite. After 100 hr of dissolution, the pH and microcrystalline halloysite controlled the activities of Al and silicic acid in all of the solutions.

Microcrystalline halloysite was the only phase identified in the weathering of plagioclases in distilled water and 1 atm CO₂ partial pressure. Montmorillonites, halloysite and other clay minerals were produced from oligoclase in aqueous solutions containing high initial concentrations of Ca, Mg, K and SiO₂.

The experimentally determined log solubility product of microcrystalline gibbsite was -32.78 ± 0.04 and log *K* for the hydrolysis of microcrystalline halloysite was 11.58 ± 0.05 . The results suggest that very poorly crystalline metastable phases may control the initial compositions of some waters in contact with rocks containing feldspar minerals.

INTRODUCTION

This investigation was undertaken to determine the processes controlling the aqueous chemistry during the artificial weathering of feldspars. Various mechanisms have been suggested in the past including partial equilibria between the aqueous phase and the products of gibbsite and clays (HELGESON, 1968, 1971; HELGESON *et al.*, 1969), equilibria between the solution and gibbsite or halloysite (HEM *et al.* 1973) and equilibria between amorphous aluminosilicate phases (PACES, 1972, 1973). A less likely mechanism suggested is the adsorption of aqueous silica and aluminum species onto mineral and clay surfaces (MCKEAGUE and CLINE, 1963; BECKWITH and REEVE, 1963, 1964; MILLER, 1973).

Since the composition and nature of the products of artificial weathering experiments have been ambiguous in many previous studies (MANUS, 1968; PETROVIC, 1976) a strong effort was made to precisely characterize the product phases with the aid of X-ray diffraction, electron diffraction, differential thermal analysis, electron microscopy, chemical analysis and solution chemistry.

The results of this investigation may not only describe the change in composition of water in the artificial weathering of feldspars but may also help clarify the initial stages of the irreversible evolution of some natural waters in contact with highly reactive felsic rocks.

EXPERIMENTAL PROCEDURES AND MATERIALS USED

All the experiments were carried out at 25°C and 1 atm CO₂ partial pressure. A detailed description of the apparatus, the experimental set-up, the feldspars used,

and their chemical composition and surface areas were previously given by BUSENBERG and CLEMENCY (1976). In the first eight experiments, eight different feldspars were dissolved in distilled-deionized water. In the next five experiments, oligoclase was dissolved in solutions having one of five different compositions: 0.10 M CaCl₂ plus 10.3 mg/l Mg, 0.10 M MgCl₂, 0.10 M KCl, 70.0 mg/l SiO₂, or 35.0 mg/l SiO₂. The last two solutions were prepared by dissolving appropriate amounts of sodium silicate in distilled-deionized water and removing the Na with Amberlite IR-120 cation resin as described by HEM *et al.* (1973).

CHEMICAL ANALYSES OF THE SOLUTIONS

The pH measurements and the chemical analyses for Ca, Mg, Na, K, Fe and SiO₂ were done by procedures previously described by BUSENBERG and CLEMENCY (1976). Aluminum was determined by the catechol violet method of DOUGAN and WILSON (1974).

CHARACTERIZATION OF THE SOLID PHASES

Chemical analysis of the solids was performed by the methods of SHAPIRO (1975). The product phases were further characterized by X-ray diffraction by the procedures given by CARROLL (1970), GRIM (1968) and JACKSON (1975). The procedures outlined by JACKSON (1975) were followed for the differential thermal analysis. The electron diffraction patterns were indexed using the procedures outlined by ZVYAGIN (1967).

COMPUTATIONS

The activities of all aqueous species and the ion activity products for the various minerals were calculated by a modified version of the computer program WATEQ (TRUESDELL and JONES, 1974; BUSENBERG and CLEMENCY, 1976). The thermodynamic data compiled by TRUESDELL and JONES (1974) was used throughout unless otherwise specified.

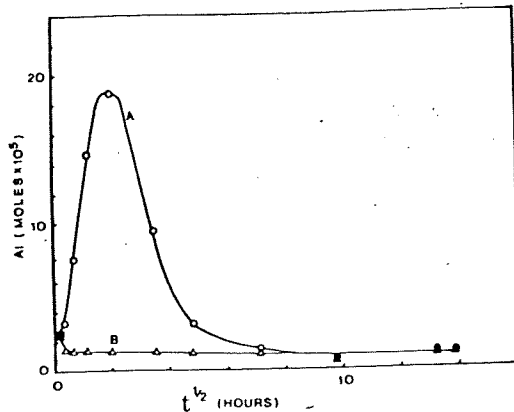


Fig. 1. The analyzed concentration of Al as a function of time. Solutions (A) and (B) were filtered through 0.45 and 0.10 μm respectively. See text for details.

EXPERIMENTAL RESULTS

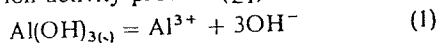
The analyses of eight series of solutions were previously reported by BUSENBERG and CLEMENCY (1976). The aluminum concentrations of these solutions have since been more accurately redetermined using the catechol violet method and the complete analysis of the five additional series of solutions are tabulated and entered into the files of NAPS.* The pH range of all the solutions was between 4 and 5.5.

INTERPRETATION

Evidence for the formation of microcrystalline gibbsite

Composition of the product phase. In the solutions produced by the artificial weathering of feldspars, no significant differences in the concentrations of Al were normally observed in the same samples filtered through 0.45, 0.1 and 0.025 μm filters except for two instances. In the case shown on Fig. 1, significantly higher concentrations were observed for the samples filtered through the 0.45 μm filters. The higher Al concentrations were caused by solids passing through the 0.45 μm filters and then dissolving during the chemical preparation of the sample for Al analysis. Very small quantities of these solids passing through the 0.45 μm filters were recovered on 0.1 μm filters. The solids were found to be X-ray amorphous. Chemical analysis after fusion with sodium hydroxide (SHAPIRO, 1975) revealed that the solid was an aluminum hydroxide phase. Figure 1 also shows that this amorphous phase disappears after a few hours' dissolution when the silicic acid concentration increases in the solution.

The chemistry of the solutions. Additional evidence for the existence of a microcrystalline gibbsite phase was obtained from the solution chemistry. The logarithm of the ion activity product (Q_1) for the reaction



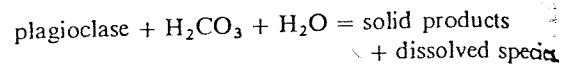
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for the fourteen solutions after 4 hr of dissolution with all types of feldspars was -32.86 ± 0.11 . The $\log Q_1$ for all the solutions sampled between 4 and 100 hr was -32.78 ± 0.04 . The $\log Q_1$ obtained is a constant and in good agreement with -32.77 and -32.65 , the reported $\log K$ of cryptocrystalline gibbsite given by HELGESON (1969) and HEM and ROBERTSON (1967) respectively.

The data strongly suggest that the solutions reached equilibrium very rapidly with cryptocrystalline gibbsite in every case. The isolation of the product phase is strong evidence that it precipitates out from the solutions during the initial stages of feldspar dissolution. This metastable phase and pH control the activities of aluminum species in solution during the first few days of reaction in the artificial weathering of all types of feldspars.

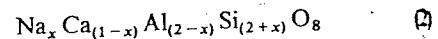
Evidence for the formation of a halloysite phase

Mass balance. The artificial weathering of feldspars can be represented by the equation:



The changes in the composition of the solution with time can be used to determine the chemical composition of the product phase when the composition of the plagioclase is known.

A generalized formula for plagioclase can be written as follows:



where x is the mole fraction of Na in the plagioclase formula. If m_{Na} moles of Na are released by the dissolution of plagioclase in the time interval between t_1 and t_2 ; then the number of moles of plagioclase dissolved (N) in the same time interval will equal

$$N = m_{\text{Na}}/x \quad (3)$$

if no Na is conserved in the product phase. If no Ca is conserved in the product phase, then the moles of Ca released into the aqueous solution in the same time interval will equal

$$m_{\text{Ca}} = N(1-x) \quad (4)$$

The moles of silica released into the aqueous solution will depend on the composition of the solid phase precipitating from the aqueous solution. If Al is conserved in the mineral gibbsite, then all the silica will be released into the aqueous solution. The silicic acid concentration is given by the equation

$$m_{\text{H}_4\text{SiO}_4} = N(2+x) \quad (5)$$

When the Al is conserved in the mineral halloysite or kaolin, then the silicic acid concentration of the solution can be represented by the equation

$$m_{\text{H}_4\text{SiO}_4} = [(2+x) - (2-x)]N = 2 \cdot x \cdot N \quad (6)$$

Equations (3), (4) and (5) predict the amount of the various species released into the aqueous solution

Fig. 2. L... of silica i... bytownite... solids the... present th... from the... weatherin... circles an... which aci... bytownite

when so... in the p... release... tion whe... with a S... the initi... in silicio... theoretic... duced b... ton (5)... formatic... atomic... The c... udcrabl... ated fro... of produ... artificial

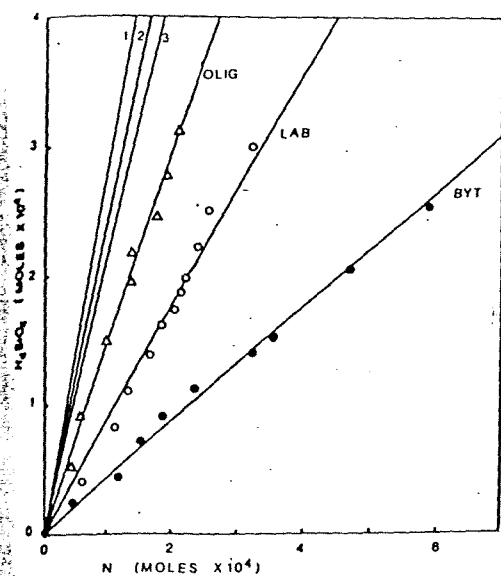


Fig. 2. Lines 1, 2 and 3 represent the theoretical release of silica into the solutions from oligoclase, labradorite and bytownite respectively when silica is not conserved in the products that are forming. Lines OLIG, LAB and BYT represent the theoretical release of silica into the solutions from these three feldspars when the solid forming during weathering has a 1 Si/Al atomic ratio. The triangles, open circles and solid circles represent the observed release of silicic acid into the solution by oligoclase, labradorite and bytownite respectively. N represents the number of moles of feldspar dissolved.

When sodium, calcium and silica are not conserved in the product. Equations (3), (4) and (6) predict the release of the various species into the aqueous solution when some of the silica is conserved in a product with a Si/Al ratio of one. Figure 2 shows that after the initial 48 hr of dissolution, the observed increases in silicic acid concentration closely approximate the theoretical values (lines OLIG, LAB and BYT) predicted by equation 6 and not those predicted by equation (5). This information is strong evidence for the formation of a product phase with a one Si to Al atomic ratio.

The composition of the product phase. After considerable effort, the solid reactant phases were separated from the product phases, and a few milligrams of products recovered. The products produced by the artificial weathering of feldspars in distilled water

Table 1. The silicon to aluminium atomic ratio in the feldspars and the products formed during the dissolution of plagioclases in distilled water and 1 atm CO_2 partial pressure

Mineral	Si/Al Ratio Plagioclase	Si/Al Ratio Products
Albite	3.0	1.08
Oligoclase	2.2	0.98
Andesine	1.8	1.00
Labradorite	1.7	0.89
Bytownite	1.3	1.03
Anorthite	1.1	1.02
Average		1.0

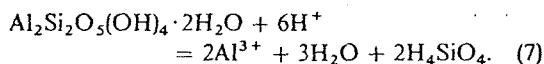
consist of a very poorly crystalline to amorphous material. The poor X-ray diffraction patterns prevented their precise identification by standard procedures (CARROLL, 1970; JACKSON, 1975).

A significant effort was made to characterize the products by other procedures. Chemical analysis of a few mg of product by the single solution method of SHAPIRO (1975) showed that it consisted of essentially only silica and alumina with all other oxides present in trace quantities. The atomic Si to Al ratios calculated from the chemical analyses are given on Table 1. All the ratios are very close to one, and the average of all the analyses are 1.0 and significantly different from the reactant phases. The Si to Al ratio of one is characteristic of kaolin, halloysite and some amorphous aluminosilicates. The differential thermal analysis of two of the samples gave significant endothermic peaks centered at 160°C. These are characteristic of halloysites and amorphous materials (BRINDLEY, 1961; GRIM, 1968).

Transmission and scanning electron microscopy showed that the products consisted of agglomerations of irregularly shaped particles. Typical examples are shown on Figs. 3A and 3B. Electron diffraction of these particles gave patterns characteristic of polycrystalline material (Figs. 3C and 3E). Very rarely, spotted patterns characteristic of larger crystalline particles (Fig. 3D) were obtained. The electron diffraction patterns were indexed using aluminum metal as an internal standard by the procedures described by BELK and DAVIES (1968) and ZVYAGIN (1967). The d-spacings obtained were in every case identical to those of metahalloysite given by BRINDLEY (1961). Metahalloysite is not a primary product phase but can only be produced by the irreversible dehydration of halloysite during sample preparation for electron diffraction and by the heat generated by the electron beam (KOHYAMA *et al.*, 1978; BRINDLEY, 1961).

The artificial weathering of these plagioclases in distilled water produced particles resembling amorphous material in morphology but which were nevertheless microcrystalline halloysite as shown by electron diffraction. It can also be concluded from the character of the X-ray and electron diffraction patterns that the material produced is highly disordered and near the boundary separating the amorphous from the 'crystalline state' (ZVYAGIN, 1967).

Solution chemistry. The dissolution of halloysite and kaolinite can be represented by the equation:



The logarithm of the activity product of reaction 7 ($\log Q_7$) was calculated for the solutions at 100 hr, at 200 hr, and at the end of the experimental runs as well as for all the data from 150 hr to the end of the experimental runs. The results are given on Table 2. The $\log Q_7$ for all the data suggest that after 100 hr, the ion activity products of all the solutions achieved a constant value that did not change even

Table 2. The number of data points, the mean of the log Q_7 and the standard error of the mean are given for all the solutions at about 100, 200, more than 400 hr as well as for all the data points after 150 hr of dissolution. The logarithms of the solubility products of halloysite and kaolin at 25°C are also given

Time (Hours)	Number	Mean Log Q_7 Log K Halloysite Log K Kaolinite	Standard Error of the Mean
100	14	11.57	0.18
200	14	11.58	0.17
>400	14	11.60	0.21
All Data >150 Hrs.	96	11.58	0.05
Hem et al. (1973) (Halloysite)	36	11.28	0.08
Kittrick (1966) (Kaolinite)		7.19	

though the chemical composition of the solutions changed considerably by further dissolution of the feldspars. The data in Table 2 strongly suggests that the solutions reached equilibrium with microcrystalline halloysite. The log Q_7 for reaction (7) calculated from the data is 11.58 ± 0.05 and is in good agreement with the log K value of 11.28 ± 0.08 for aged halloysite obtained by HEM *et al.* (1973). The presence of microcrystalline halloysite in the product phases supports the hypothesis that the halloysite and pH controlled the activities of the aluminum and silicic acid in these aqueous solutions after 100 hr of artificial weathering of all types of feldspars. All these solutions were highly supersaturated with respect to kaolin as shown on Table 2.

Evidence for the formation of montmorillonite and other phases

Mass balance. The mathematical treatment used is described by equations (2)–(6). The solutions examined were those formed by the artificial weathering of oligoclase with aqueous solutions having high initial concentrations of one of the following components: CaCl_2 , MgCl_2 , KCl or silicic acid. The three thicker lines on Fig. 4 represent the increase of silicic acid concentrations as a function of the number of moles of oligoclase dissolved and the composition of

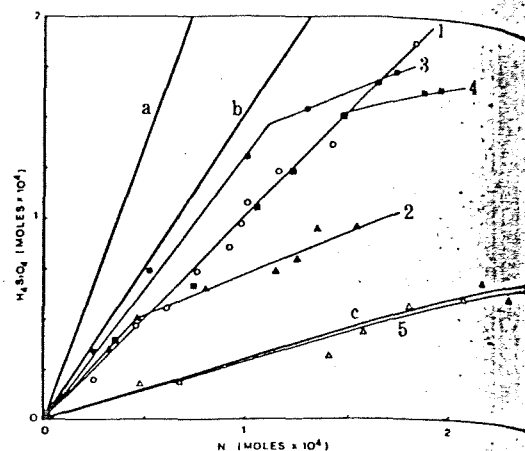


Fig. 4. Lines a, b and c represent the theoretical release of silicic acid into the solutions when the solids formed during the dissolution have an atomic Si/Al ratio of 0, 1 and 2 respectively. Lines 1, 2, 3, 4 and 5 represent the observed release of silicic acid as a function of moles of oligoclase dissolved (N) in solutions containing 0.1 M KCl, 0.1 M CaCl_2 , 0.1 M MgCl_2 , 35 mg/l SiO_2 and 70 mg/l SiO_2 respectively. See text for details.

the precipitating product phase. The experimental data indicates that after 50 hr of dissolution the products had initial Si to Al ratios of between 1.2 and 2 as determined by mass balance. The experimental ratios abruptly changed to about 2 in all but one case. The initial Si to Al ratios could be explained by the formation of an amorphous aluminosilicate product with a highly variable chemical composition. An alternate and preferable explanation supported by chemical analysis and X-ray data (Table 3) is the formation of two or more products with different Si to Al ratios. The observed ratios result from the weighed average of all the ratios of the products.

It was shown previously that after 100 hr, the solutions appear to be in equilibrium with halloysite which is present in the products. Halloysite is the mineral with the 1 Si to Al ratio and all other products including montmorillonite, which is the most abundant (Table 3), have higher ratios. The halloysite

Table 3. The products formed during the dissolution of feldspars and the methods used to identify them are listed below. ED = electron diffraction; TM = transmission electron microscopy; A = chemical analysis; C = X-ray diffraction using an 18 cm camera; and D = X-ray diffraction using a diffractometer

Experiment	Gibbsite	Halloysite	Kaolinite	Mica	Mont.	Chlorite
Albite	A	ED				
Oligoclase		ED, C, D				
Andesine		ED, C, D	TM			
Bytownite		ED				
Labradorite		ED				
Anorthite		ED, C, D				
Orthoclase		C				
Microcline	A	C, D		C, D		
Oligoclase in						
35 mg/l SiO_2		C, D			C, D	
70 mg/l SiO_2					C, D	
0.1 M KCl		C		C, D	C, D	
0.1 M CaCl_2		C			C, D	
0.1 M MgCl_2		C, D			C, D	C, D

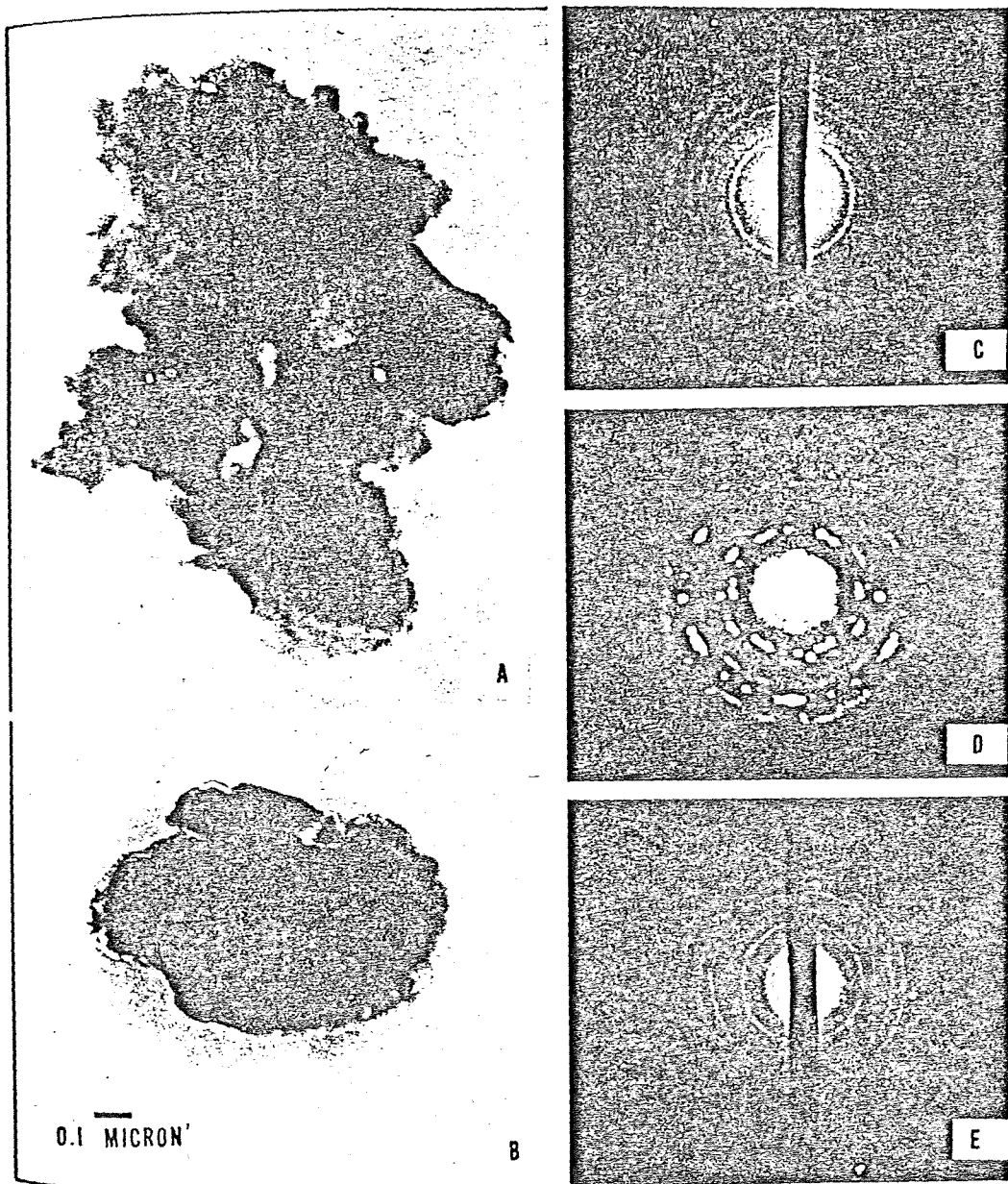


Fig. 3. Electron transmission micrographs of particles produced by the dissolution of oligoclase (A) and anorthite (B) in distilled water. C, D, and E are the electron diffraction patterns of particle (A), (B) and a particle produced during the dissolution of bytownite respectively.

The composition of the finer-grained products produced by the dissolution of oligoclase in solutions containing high concentrations of SiO_2 , Ca, Mg or K. Data have been recalculated to 100% H_2O , H_2O^+ and some minor constituents were not determined because of the extremely small size of the samples available for analysis. The Si to Al atomic ratio is also given for these products

oxide	Experiment				
	35 mg/l SiO_2	70 mg/l SiO_2	0.1 M KCl	0.1 M CaCl_2	0.1 M MgCl_2
SiO_2	68.48	67.03	71.45	70.98	70.00
Al_2O_3	27.74	29.49	21.42	24.98	24.34
Fe_2O_3	0.87	0.21	1.98	0.45	0.62
MgO	0.81	0.76	1.10	0.35	3.98
CaO	0.98	0.84	0.46	3.73	0.13
K_2O	1.08	1.06	3.59	0.39	0.90
Na_2O	0.93	0.02	0.01	0.02	0.03
Si/Al	2.1	1.9	2.8	2.5	2.4

initially coprecipitated with montmorillonites and other products giving ratios between 1 and 2. This evidence suggests that halloysite stopped precipitating when the solutions evolving along the halloysite-montmorillonite phase boundary moved into the montmorillonite stability field resulting in a sharp increase of the Si to Al ratio of the products to a value of 2.

Composition of the product phases. The products formed by the dissolution of oligoclase in solutions containing high initial concentrations of CaCl_2 , MgCl_2 , KCl or silicic acid were identified by X-ray diffraction using standard clay mineralogical procedures (CARROLL, 1970; JACKSON, 1975). The results are shown on Table 3. Since the halloysite component of the products formed significantly larger particles, it was separated from the finer particles by settling procedures. The chemical analysis of the products with the smaller particle size and the Si to Al ratios of these products are given on Table 4. These ratios observed are characteristic of natural smectites (GRIM, 1968). Since the products are not single phases, the exact formulas of the phases cannot be calculated but are apparently very complex as indicated by the chemical analyses. It is also very likely that the formulas of the products varied as the composition of the solutions changed with time.

CONCLUSIONS

During the artificial chemical weathering of feldspars, the composition of the resulting aqueous solution is controlled by the solubilities of highly disordered and very poorly crystalline products of the weathering reactions. All solutions appeared to have rapidly reached equilibrium with a metastable microcrystalline gibbsite. The X-ray amorphous phase precipitated in the aqueous solutions was identified by chemical analyses. After 100 hr of dissolution in dis-

solved water, a poorly crystalline halloysite phase controlled the activities of aluminum and silicic acid in all cases. This solid was isolated and identified by electron diffraction and chemical analysis.

The products of the dissolution of oligoclase in solutions containing high initial concentrations of Ca, Mg, K and SiO_2 were montmorillonite, halloysite and some other clay minerals. The chemical analyses suggest that these products have complex chemical formulas and their compositions may vary from experiment to experiment. Mass balance calculations indicate that these solutions evolved along the halloysite-montmorillonite phase boundary for a considerable length of time, then moved into the montmorillonite stability field. Trace quantities of kaolinite were found in one experiment; however, all the solutions were highly supersaturated with this phase.

The results suggest that under certain conditions, metastable poorly crystalline phases control the initial compositions of waters in contact with reactive felsic rocks.

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