EXPERIMENTS ON THE DECOMPOSITION OF SILICATES AND DISCUSSION OF CHEMICAL WEATHERING

by

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ABSTRACT

Experimental investigations of chemical weathering in which powders of potassium feldspar, albite, leucite, muscovite, tremolite, olivine, and volcanic glass are treated with pure water and with dilute solutions of sulfuric, carbonic, and hydrochloric acid have been performed in an apparatus in which the mineral powder is exposed to a circulating water flow. The experiments have been continued recently by treating kaolinite and montmorillonite. The course of decomposition of these minerals depends on water flow rate, grain size, temperature, and pH of the solutions. These experiments in open systems are compared with investigations reported in the literature and with the conditions of natural weathering.

LABORATORY SIMULATION OF CHEMICAL WEATHERING

The phenomena of weathering may be studied in various ways: weathering profiles can be examined, and in this way one can observe rocks that gradually are being changed into weathering products and soils; on the other hand, one can attempt to simulate the process of weathering in the laboratory.

Variables

Simulation of weathering in the laboratory is no easy task because the natural processes that we sum up under the term chemical weathering undoubtedly are very complex. Pure water never is found in nature because always some ions are in solution. Of the solvents in natural water, carbonic acid is a particularly important agent because HCO_3^- derived from its first stage of dissociation is especially active. Sulfuric acid can play an important role under certain conditions. Acid solutions can also result from the liberation of hydrogen ions by ion exchange; e.g. from clay minerals and also from humic organic matter. The action of organic acids also must be taken into account, whether they originate from the oxidation of an organic substance (as in the generation, for example, of oxalic acid from humus) or are produced by organisms. Such factors can produce environments as acid as pH 4, and under exceptional conditions a still lower pH can result.

Alkaline solutions originate when water reacts with silicates containing

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alkalis and alkaline earths. NH_3 or other organic substances having alkaline reactions can be produced by organisms. Many soils whose pH is as high as 9 have been described. Some organic compounds act as chelating agents and can fix elements by formation of complexes. Furthermore, one must recognize that the processes of dissolution of the various minerals in a natural solution affect each other.

In addition, dissolution also is affected by the speed with which the solution moves through the soil or weathering product. Although many such natural systems are open, the rate of flow can become very slow, and in tubs (tinajas) on granite surfaces for example, and similarly elsewhere, the system may become closed. Furthermore, differences in temperature must be considered. Finally, the factor of time is important, and indeed, experiments lasting many months are short in comparison to the long periods of time available in nature.

Experimental Conditions

In attempting to imitate chemical weathering in the laboratory, one must recognize at the start that it is impossible to reproduce all natural conditions in an experiment. In our work we first studied the behavior of single minerals, and we believe that the open system most closely resembles the conditions in soil. The most useful experimental set-up is quite simply a cylinder in which the mineral powder that is to be weathered is present as an aqueous suspension that can be stirred. The apparatus used in our new experiments with clay minerals is built entirely of plastics. An ultrafilter at the bottom of the cylinder lets only the dissolved ions through and not the particles of mineral. The solution is drawn off from time to time and the ions that have entered into solution are determined. With an apparatus of this type, the grain size of the mineral particles, the rate of filtration, and the degree of acidity (pH of the solution) all can be varied. The minerals have been prepared for the weathering experiments by grinding in ball mills, and the size fractions with radius less than $1\ \mu$, and from 3–$10\ \mu$ separated by sedimentation in methyl alcohol.

Our early experiments were also conducted in a ball mill in which the minerals were ground in a 200-ml water solution that was replaced from time to time. We also used a copper dialysis set-up in which the solution was repeatedly distilled and the dissolved substance thus concentrated. We also shook mineral particles in a flask for 7 hr and from time to time filtered off the solution.

EXPERIMENTAL RESULTS AND THEIR RELATION TO WEATHERING

Feldspars

We found that the decomposition of the feldspars is influenced by all the variables mentioned above.

K-feldspar.—As our first experimental material we used the potassium

TABLE 1.—ARTIFICIAL WEATHERING OF POTASSIUM FELDSPAR,
AFTER CORRENS AND V. ENGELHARDT (1938)

pH	3	3	6.6	5.6–6.85–8.3	11
Temperature	20°	20°	20°	20°	20°
Grain size, μ	< 1	3–6 (agitated)	< 1	ball mill	< 1
cm^3/day	70	∼ 74	32	—	32
mg/l. K$_2$O	7.7	11.5	12.3	41.6	14.8
mg/l. Al$_2$O$_3$	5.6	7	1.1	1	6.5
mg/l. SiO$_2$	10	6.5	7	2	15.8
mg/l. solvent	9.1	1.82	1.85	4.5	5.2

feldspar adularia, containing 15.2 percent K$_2$O and 1.7 percent Na$_2$O (Correns and v. Engelhardt, 1938). Table 1 shows the maximum amount of K$_2$O, Al$_2$O$_3$, and SiO$_2$ dissolved from this potassium feldspar in the artificial-weathering solution under various conditions of pH, grain size, and rate of solvent flow. The pH was adjusted to 3, using 0.01 N sulfuric acid. In the case of pH 6.6, double distilled water free from carbonic acid was used. A pH of 11 was produced with ammonia. Dissolution of the glass at this pH was determined previously and deducted.

Table 1 shows that not only potassium but also considerable quantities of silicon and aluminum entered into solution; but it must be noted that the quantities of solvent used were not uniform.

Ball milling was the most effective method of releasing potassium; agitation by shaking in a flask also raised the solubility somewhat. Obviously the grinding process continually exposed fresh surfaces, from which the potassium ion most rapidly migrated. The experiments demonstrate, as shown by the changing behavior of Al and Si, that equilibrium was not reached. In the first stages of the filtration experiments one also finds a high rate of solubility that probably is due to destruction of the lattice at the edges of the mineral particles during the grinding of the mineral down to a grain size finer than 1 μ.

After the dissolution action had continued for some time, using a grain size finer than 1 μ at pH 3, and a rate of filtration of 71 ml per day, a kind of equilibrium was reached (Fig. 1) that, for potassium feldspar, bears roughly the relationship 1 K$_2$O : 1 Al$_2$O$_3$: 6 SiO$_2$. The analysis for the whole of the last part of the solution, from 5 to 9.1 liters, yields the ratio 1 K$_2$O : 0.76 Al$_2$O$_3$: 5.44 SiO$_2$. This seems to be a kind of uniform decomposition that is controlled by the formation of a thin decomposition layer of SiO$_2$ and Al$_2$O$_3$ around the potassium feldspar grain; the film so reduces the diffusion of the K ions that their rate of migration roughly equals the decomposition rate of the SiO$_2$–Al$_2$O$_3$ layer.

The composition of this weathering layer can be calculated if one assumes that all the potassium has been removed from it. This assumption, strictly speaking, is not valid. Probably there always will be some potassium in this residue layer, right from the edges to the center of the particles; but the

calculation shows, in any case, that there was no new formation of kaolinite or montmorillonite or similar minerals in these layers, inasmuch as the ratio $SiO_2:Al_2O_3$ does not bear the faintest relationship to that of these clay minerals. Using the same assumption one also can calculate the thickness of this residue layer, and it is found that, for example, in the experiments at pH 3 and the powder with radius finer than 1 μ the thickness of this residue layer amounts to 0.03 μ or 300 Å—a thickness of about 30 elementary cells. This thickness shows no further increase as dissolution continues. For this
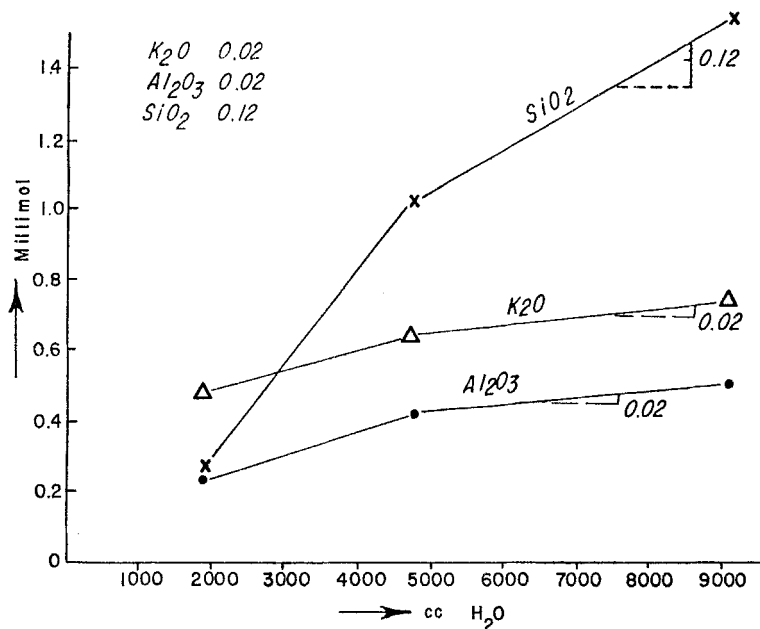

Figure 1.—Decomposition of potassium feldspar (grain size, $R < 1\ \mu$; pH = 3).

reason, the residue layer is thought to decompose at the same rate as the potassium migrates from the feldspar. The diffusion constant determined for the K^+ ion in the residue layer was $D = 1.1 \times 10^{-14}$ cm^2/day. In other experiments with potassium feldspar, this stage of equilibrium was not reached, probably because insufficient quantities of solution were used. These experiments show that, under the conditions given, potassium feldspar breaks up into ions and that these ions are moved.

Na-feldspar.—Bieger (1952) investigated the sodium feldspar counterpart (albite) of potassium feldspar. The mineral contained 93.1 percent sodium feldspar, 5.7 percent potassium feldspar and 1.8 percent anorthite. Bieger varied the rate of filtration from 50 ml to 100 ml per day, and finally to 200 ml per day. In addition to sulfuric acid he used both hydrochloric and carbonic

acids, and was able to ascertain that stirring the suspension produced a definite effect.

The rate of decomposition of albite is greater at a slow rate of filtration, as one might expect. Stirring also increases the rate of decomposition. Sulfuric acid produces greater dissolution than hydrochloric acid, which, in turn, reacts more strongly than carbonic acid at the same pH. At pH 3 the ratio $SiO_2:Al_2O_3$ in the residue layer is smaller, and the thickness of this layer becomes proportionately larger as the strength of the action increases. But the differences are smaller at pH 4. At pH 6 and 200 ml per day the ratio $SiO_2:Al_2O_3$ approaches 6, whereas at 100 ml it reaches 5.22. The thickness of the residue layer becomes constant at $0.02~\mu$ after the filtration of even a few liters. The lower the rate of filtration, the greater is the quantity of Al_2O_3 remaining in the residue layer. It seems quite possible that in a closed system the ratio $SiO_2:Al_2O_3 = 2$ would be reached. (See also Table 12.)

Apart from the type of acid, Andersson and Lindquist (1956) were able to show that the concentration of neutral salts is important during the process of decomposition of microcline, albite, and petalite. To the solution they added the chlorides of lithium, sodium, potassium and cesium in 0.1M and 1M concentrations, and determined the quantity of SiO_2 that entered into solution. More SiO_2 was dissolved in the lithium chloride solutions than in pure water, whereas the other salts hindered this action.

Leucite

The statement that not only the alkali ions enter into solution in ultra-filtration, but that silicon and aluminum also migrate as ions is proved conclusively by decomposition experiments with leucite carried out by Krüger (1939) using an electrodialysis apparatus. Table 2 shows the results

TABLE 2.—ELECTRODIALYSIS OF LEUCITE

	Millimol		
	K_2O	Al_2O_3	SiO_2
Cathode			
I 18×12 St	1.034	0.018	0.524
II 94×12 St	0.268	0.012	0.286
Anode			
I 18×12 St		0.012	0.195
II 94×12 St		0.006	0.650
Sum	1.302	0.048	1.655
Ratio I	34.5	1	24
II	14.8	1	34.5

Grain size radius $< 1~\mu$, $42°$ C, initial pH $= 5.8$ (after Krüger, 1939).

of the decomposition of leucite powder of grain size radius smaller than 1 μ. The experiment was started in distilled water having a pH value of 5.8 at 42° C. As can be seen, the alkali ion migrates quickly and, as is expected, to the cathode. The strength of the current rose in 2 min from 0.6 mA to 68 mA through the release of alkali ions and sank again, at first rapidly, then more slowly as it approached the zero value. The experiment also demonstrates that the potassium ions enter into solution rapidly at first, but then a protective residue layer is formed, and the K ions migrate only very slowly. Two days after the beginning of the experiment the pH of the solution at the cathode was measured and found to have a value of 10. In time, the pH sank again to 6.2 while the pH of the solution at the anode underwent no change.

It is noteworthy that aluminum and silicon migrated both to the cathode and to the anode. The aluminum that collects at the cathode probably occurs as Al_3^+ or, according to Raupach (1960), as complex ions $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_3(OH)_7^{2+}$. In addition, especially in the first fraction, the negatively charged aluminate ion also is present at the anode. If the silicon were to appear as a part of a free acid, SiO_3^{2+} or SiO_4^{4+}, all of it would have migrated to the anode. At the beginning of the experiments a considerable amount of silica migrated to the cathode, and only at the end did the main quantity migrate to the anode. A probable explanation of this is the formation of positively charged silica complexes as Winslow and Fleeson (1926) observed in highly alkaline concentrations. Armstrong, who carried out similar electrodialysis experiments with microcline and albite in 1940, likewise found SiO_2 present in the cathode fluid. In our experiments, we found that silicate ions migrate predominantly to the anode only when the alkali concentration in the area of the electrodialysis becomes low.

The leucite particles present in the solution are at first so strongly negatively charged that they migrate to the anode during the first 36 hr, in spite of vigorous stirring. If one disperses the particles again and continues the dialysis for an additional 12 hr they will have migrated to the cathode, and after renewed dispersion they return again and again to the cathode. Thus when the pH is high initially, the particles are negatively charged because of the aluminate ions on their surfaces, but after the pH has declined to a neutral value, positively charged aluminum ions or aluminum complex ions predominate on the particle surfaces. These observations do not prove the idea that H^+ or H_3O^+ ions replace potassium or, as it has been termed, are exchanged for potassium. If this were true, the particles then would have to be uncharged, or migrate to the cathode. These observations made in 1939 are in agreement with more recent investigations of clay minerals which, when treated with acids, accept Al^{3+} ions at their surfaces.

If leucite powder is treated in an ultrafiltration apparatus, as Krüger (1939) also did, it is evident that considerably more aluminum, relative to potassium and silicon, is dissolved than in electrodialysis (Table 3). The residue layer was also calculated for these experiments. Table 4 shows that the residue layer alters its composition somewhat during the course of

TABLE 3.—ARTIFICIAL WEATHERING OF LEUCITE (AFTER KRÜGER, 1939)

pH	3	3	3	5.8	6	11
Temperature	22°	22°	42°	42°	22°	22°
Grain size, μ	<1	3–10	3–10	3–10	<1	<1
ml/day	200	200	200			
mg/l. K_2O	15	7.9	10	2.6	5.6	6
mg/l. Al_2O_3	9.2	6.2	7.2	0.1	0.95	3.3
mg/l. SiO_2	8.6	3.5	13	2.2	3.4	9.8

TABLE 4.—RATIO SiO_2/Al_2O_3 IN THE RESIDUE LAYER IN DECOMPOSITION
EXPERIMENTS WITH POWDERED LEUCITE

			pH_3		
Aliquots of filtrate ml	22° C $R < 1\ \mu$	Aliquots of filtrate ml	22° C $R = 3$–$10\ \mu$	Aliquots of filtrate ml	42° C $R = 3$–$10\ \mu$
1200	4.68	2300	9.57	1600	7.58
1400	5.49	2600	10.50	1700	6.99
1500	6.30	2900	11.43	1700	6.01
1400	7.54	2800	11.68	1600	5.57
Total 5500		10,600		6600	

pH 5.8			pH 6.8		pH 11	
Aliquots of filtrate ml	42° C $R = 3$–$10\ \mu$	Aliquots of filtrate ml	22° C $R < 1\ \mu$	Aliquots of filtrate ml	22° C $R < 1\ \mu$
				2100	3.91
6100	2.72	2600	3.68	2200	3.23
10,000	2.66	6400	3.46	5400	2.71
Total 16,100		9000		9700	

dissolution. At pH 3 and 22° C the ratio $SiO_2 : Al_2O_3$ increases, but at 42° C it decreases as filtration proceeds. In the slightly acidic solution at pH 5.8 the ratio $SiO_2 : Al_2O_3$ at 42° C declines to 2.66. A similar decline takes place at pH 6.8 and 11, but at room temperature. The ratio $SiO_2 : Al_2O_3$ lies between

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that of kaolinite and that of montmorillonite. In this respect the decomposition of leucite differs greatly from that of the feldspars. In all these experiments, the thickness of the residue layer increases and a constant thickness is never reached.

The Residue Layer and Pseudomorphs

Because the residue layers obtained by dialysis experiments carried out at low temperatures give no X-ray diffraction or electron diffraction lines, they must be called amorphous. Morey and Chen (1955) reported that crystalline products resulted from decomposition of potassium feldspar and albite in an open, high-temperature system. Table 5 shows a correlation of their results with those obtained by us at low temperatures. At high temperatures the molar proportions in solution are changed in the direction of fewer alkali ions entering into solution, perhaps in part because Morey and Chen worked with a coarse powder (thus with very small specific surfaces) and also because a thicker residue layer forms more quickly at high temperatures. The fragments of the feldspars were covered with a white reaction crust that, on microcline, consisted of muscovite and boehmite. At 200° and 100°C boehmite and kaolinite appeared as precipitates. Similar experiments were carried out in a closed system by Brindley and Radoslovich (1956) using 0.1 N HCl, hence at a pH of 1.

In the experiments by Morey and Chen it might be assumed that we are concerned with the beginning of the formation of pseudomorphs. Such pseudomorphs, e.g. kaolinite after feldspar, have been observed in nature. Therefore, I should like to go briefly into the conditions necessary for the formation of pseudomorphs.

Let us use a simple experiment as a model. If one places cubes of rock salt in solutions of silver nitrate, one can observe that pseudomorphs of silver chloride after rock salt are formed in concentrated silver nitrate solutions, whereas in dilute solutions (less than 0.5 mol/liter) the reaction between sodium chloride and silver nitrate takes place in the solution. At higher concentrations, the reaction occurs partly in the solution and partly on the rock salt crystal. With an increase in concentration, cushionlike aggregates of silver chloride form on the crystal. Above a concentration of about 3 mol/liter, silver chloride pseudomorphs are formed. It is obvious that a necessary prerequisite for the formation of pseudomorphs is first that a precipitate forms on the surface of the crystal; the reaction then proceeds through this precipitate into the crystal. Therefore, the concentration of the reacting ions in the outer solution must be great enough that they are able to penetrate through the initially formed precipitate skin into the crystal.

In our filtration experiments the concentration is always so low that the reaction takes place in the solution, even at the lowest rates of flow. This generally seems to be the case in soils; in any case one finds the feldspars in permeable soils partly dissolved. At an increased speed of reaction, as in the experiments of Morey and Chen, we probably have an intermediate stage in which the reaction takes place partly in the surface layer, but the precipitates

TABLE 5.—COMPARISON OF EXPERIMENTS ON DECOMPOSITION OF FELDSPARS
AT HIGH AND ROOM TEMPERATURES

	Morey and Chen (1955)	Correns and v. Engelhardt (1938)		Morey and Chen (1955)			Bieger (1952)
Ratio of millimols in solution	Microcline* $350°$C, 350 kg/cm^2	Adularia R $< 1\ \mu$ † $20°$C, pH 6.6	Ratio of millimols in solution	$350°$C 350 kg/cm^2	$200°$C 140 kg/cm^2	$100°$C‡	Albite R $< 1\ \mu$ † $18°$C, pH 6 Average
K$_2$O	1.1	11.7	Na$_2$O	0.64	1.72	2.35	9.6
Al$_2$O$_3$	1	1	Al$_2$O$_3$	1	1	1	1
SiO$_2$	6.76	10.7	SiO$_2$	3.96	8.86	13.57	9
In solution ppm = mg/l.	268	20	In solution ppm = mg/l.	318	53	6.4	8.1
Residue (residue layer)	Muscovite Böhmite	Amorphous $\dfrac{SiO_2}{Al_2O_3} = 5.56$	Residue (residue layer)	Analcite Muscovite	Böhmite Kaolinite	Muscovite Böhmite Kaolinite	Amorphous $\dfrac{SiO_2}{Al_2O_3} = 5.8$
Percolation	194 l. per 103 days	1.83 l. per 58 days	Percolation	78 l. per 38 days	279 l. per 2 days	384 l. per 2 days	2.4 l. per 12 days

* Particles passed 6.35 mm and caught on 0.833 mm screens.

† R = radius.

‡ City water pressure.

do show that reaction also occurs outside the crystal. Pseudomorphs of kaolinite after feldspar form in a completely or almost completely, closed system and probably at elevated temperatures.

Amphiboles

Apart from the framework silicates already mentioned, the amphibole tremolite was investigated by Tunn in 1940 (Table 6). The residue layer,

TABLE 6.—COMPOSITION AND THICKNESS OF THE RESIDUE LAYER DURING THE DECOMPOSITION OF TREMOLITE $[(Ca_2Mg_{10}(OH)_2Si_8O_{22})]$; PARTICLE RADIUS < 1 μ (AFTER TUNN, 1940)

	Thickness μ	$\dfrac{SiO_2}{MgO}$	$\dfrac{MgO}{CaO}$
pH 3	0.01	2.1	
pH 5.8	0.01	1.1	
pH 9	0.035		4.3

using powder of radius finer than 1 μ at pH 3 and 5.8, has a thickness of approximately 0.01 μ and 0.03 μ at pH 9. The residue layer was of constant thickness for the duration of all three experiments. At pH 3 the calculated ratio of SiO_2:MgO is 2.1, and at pH 5.8 it is 1.1. In alkaline solutions the residue layer consists essentially of $Mg(OH)_2$ with some $Ca(OH)_2$.

Olivine

In the orthosilicate olivine investigated by Hans Joachim Hoppe (1947) the behavior of the magnesium ions is also of importance. The olivine used in the experiments contained 0.22 mol FeO and 1.18 mol MgO. Table 7 shows

TABLE 7.—COMPOSITION AND THICKNESS OF THE RESIDUE LAYER DURING THE DECOMPOSITION OF OLIVINE, AFTER H. JOACHIM HOPPE (1947)

pH	Grain size μ	Amount of solution (liter)	Residue layer		Thickness μ
			$\dfrac{MgO}{FeO}$	$\dfrac{SiO_2}{FeO}$	
3	3–10	9.4	1.79		0.196
3	< 1	4	3.77		*
4.6	< 1	5.2		0.04	0.100
5.8	< 1	6.8	2.74		*
9	< 1	4.1	5.5		*

* Thickness not constant.

that in an acid solution of pH 3, the residue layer is calculated to be free from SiO_2 but rich in iron. I stress the term "calculated", as it probably is safe to assume that some SiO_2 still is present in the residue layer. At pH 4.6 a layer consisting essentially of iron hydroxide but very little SiO_2 is obtained. At pH 5.8 Mg is again present, and at pH 9 even more. The residue layers were relatively thick, and were of constant thickness in only two of the experiments.

Natural Weathering of Basaltic Rocks in Light of Experimental Results

Basalts.—Working with olivine basalts from the area surrounding Göttingen, Bolter (1961) showed that olivine is attacked first and is changed into a green nontronite. In more strongly weathered sections the nontronite is brownish owing to included goethite, and in a later stage it may be replaced by saponite. The reactions for olivine seem to match the decomposition of the feldspars. In the first stages of decomposition of the feldspars a mineral of the montmorillonite group forms. With more severe decomposition the montmorillonite is replaced by a poorly crystallized mineral of the kaolin group which, in the final stages, can amount to from 70 to 90 percent of the whole. The pyroxenes are simply decomposed and dissolved without formation of an intermediary product. Thus we have in all three newly formed clay minerals of the montmorillonite group (montmorillonite, nontronite, and saponite) and in addition a poorly crystallized kaolinite. I should like to believe that the montmorillonite minerals do not form with the composition of their theoretical formulas but instead as mixtures of $Al_2(OH)_2Si_4O_{10}$, $Mg_3(OH)_2Si_4O_{10}$ and $Fe_2(OH)_2Si_4O_{10}$. One must also consider that Al and Fe may well replace some silicon in the tetrahedral layer. The names then should only denote the predominant compounds. Calculations from the analysis of the grain size fraction with radius <1 μ from a strongly decomposed basalt sample yielded 54 percent saponite, 20 percent nontronite, 2 percent montmorillonite and 13 percent kaolinite. A residue of 9 percent plagioclase and 2 percent goethite could also be calculated.

Let us consider the previously discussed experimental results to explain Bolter's (1961) observations on the decomposition of olivine basalts. Apparently the initial pore solutions, which are high in alkalis and alkaline earth from the decomposition of olivine and feldspar, led to the formation of nontronite adjacent to the olivine, and of montmorillonite adjacent to feldspar. The alkalies and alkaline earths were gradually removed and the pH of the solution thereby lowered. Then, as in the experimental decomposition of olivine, iron was precipitated as the hydroxide goethite. The solution became more acidic by absorption of carbon dioxide, probably from the atmosphere. The goethite was dissolved and saponite formed, and the montmorillonite then was replaced by kaolinite. Sigvaldason (1959) has observed that montmorillonite is formed in basalt by the action of alkaline solutions from hot volcanic fumaroles and springs. The montmorillonite is changed by acidic solutions to kaolinite. The greater the acidity of the solutions, the better crystallized is the kaolinite (Table 8, Fig. 2).

TABLE 8.—DECOMPOSITION OF BASALT BY ALKALINE SOLUTIONS FROM
FUMAROLES (FIG. 2), AFTER SIGVALDASON (1959)

Sample no.	SB 1	SB 2	SB 3	SB 4	SB 5	SB 6	SB 7
Percent montmorillonite	28	70	80	50	30	40	0
Basal spacing	14.7	14.9	15.2	11.8	11.8	12.2	—
Percent kaolinite	0	<1	<1	30	50	40	13
Temperature, °C				73	88	97	97
pH				3.5	3.5	2.0	1.5
Percent calcite	6	~4	2.6	0	0	0	0

Basaltic glass.—Under other conditions, for example those found in tropical areas, the process of chemical weathering possibly would be quite different and, likewise, the content of glass would have an effect. In 1941 Hans-Jürgen Hoppe investigated the decomposition of basaltic glass (sideromelane). In this complicated system, as in artificial glasses, a residue layer is formed.
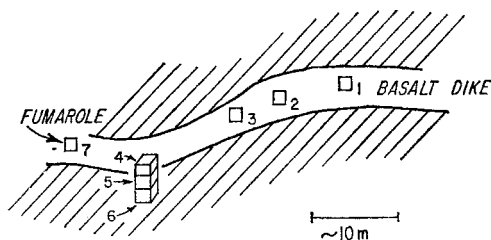

FIGURE 2.—Map showing positions of samples collected for alteration study. Samples 4, 5, and 6 are from a vertical profile. After Sigvaldason (1959).

The residue grows in thickness as the action continues and is more permeable than that of the feldspars. If one computes the alkali-free residue layers of this volcanic glass, it is evident that the SiO_2 and CaO content decreases and that the MgO and Fe_2O_3 content increases. So much for the weathering of basalts.

Micas

In the weathering of metamorphic rocks and of sediments the destruction of the layer silicates, especially mica, plays a very important role. Böhmeke (1946) experimented with a muscovite nearly corresponding to the formula K $Al_2(OH)_2$ $(AlSi_3O_{10})$, but carrying 0.4 percent Na_2O. Table 9 shows that considerable amounts of potassium are derived from muscovite and enter into solution. Here, as opposed to potassium feldspar, there is not even a close approach to equilibrium. Potassium goes into solution preferentially.

TABLE 9.—DECOMPOSITION OF MUSCOVITE, AFTER BÖHMEKE (1946)

pH	3	3	5.8	5.8	~8.5	11
Temperature	22°	42°	22°	42°	22°	22°
Grain size, μ	<1	3–10	<1	3–10	<1	<1
ml/day	200	200	200	200	200	200
mg/l. K_2O	21	21	6.5	8.6	8.5	31.8
mg/l. Al_2O_3	6.2	6.0	0.64	0.3	1.5	5.8
mg/l. SiO_2	15.1	27.7	5.1	3.3	3.6	12.1

Dissolved SiO_2 is present in less than the stoichiometric potassium/silica ratio in muscovite by a factor of 5 to 10. A similar disparity in alumina is even more marked—by a factor of 12 to 30. It is evident that under the conditions of these experiments the octahedral layer is only very feebly attacked. Table 10

TABLE 10.—COMPOSITION OF THE RESIDUE LAYER OF MUSCOVITE, AFTER BÖHMEKE (1946)

pH	Temperature, °C	Grain size, μ	SiO_2/Al_2O_3
3	22°	<1	1.94 → 1.79
3	42°	3–10	1.86 → 1.45
5.8	22°	<1	1.73 → 1.65
5.8	42°	3–10	1.79 → 1.44
8.5	22°	<1	1.93 → 1.89
11	22°	<1	1.92 → 1.91

shows the calculated composition of the K_2O-free residue layers. The proportion $SiO_2:Al_2O_3$ remains a little less than 2, and it seems that the value becomes even smaller in the course of decomposition. In all experiments the thickness of the residue layer increases with length of treatment: for example, at pH 3 and 42° C the increase is twentyfold.

I should like to think that these experiments strongly confirm the assumption that micas (like those that we call dioctahedral illite) containing smaller amounts of potassium are formed during weathering of muscovite. The investigations of Rimšaite (1957), who worked with weathered coarse micas, likewise support this view.

Clay Minerals

Recently, together with Dr. Annerose Heydemann, we have begun to examine kaolinite and montmorillonite in an ultrafiltration apparatus built completely from plastics. The minerals are elutriated with methyl alcohol,

and a grain size of radius smaller than 1 μ is used. The surface of the kaolinite was determined as 60 m^2/g and that of the montmorillonite as 700 m^2/g. The results of the first experiments at pH 7 are shown in Fig. 3. The quantity of SiO$_2$ entering into solution is so much greater than the quantity of Al$_2$O$_3$ that a logarithmic scale was used as the ordinate. As in the experiments with feldspar, the quantities entering into solution at the beginning increased extremely rapidly. Since the clay minerals were not ground, we are dealing with a real solution effect caused by the large surface area. At the end of the experiments (after 63 days) the quantity of Al$_2$O$_3$ in the solution (passed at
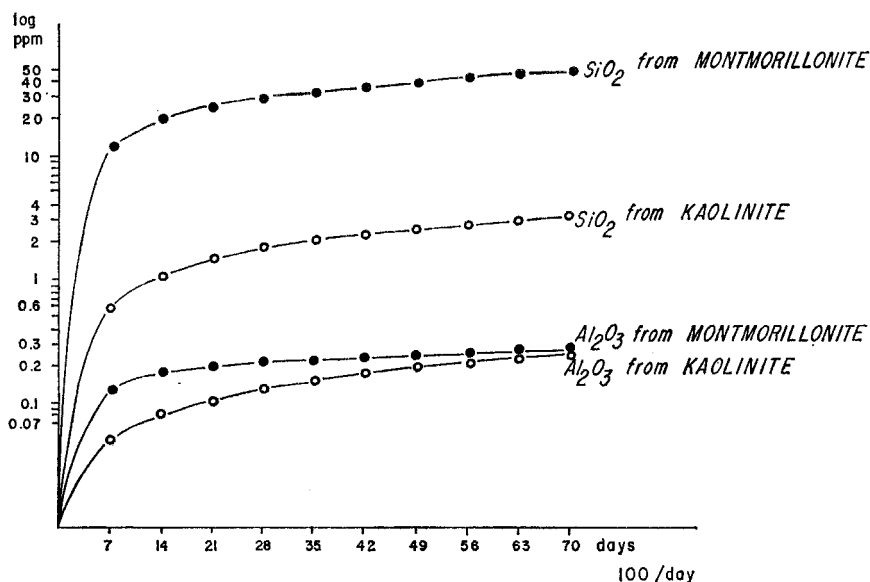

Figure 3.—Decomposition of montmorillonite and kaolinite, grain size with radius < 1 μ in water at pH 7. After Heydemann (1961).

the rate of 100 ml per week) that is derived from kaolinite is 0.01 ppm, and 0.02 ppm from montmorillonite. The quantity of SiO$_2$ entering into solution from kaolinite is 0.2 ppm, and 1.5 ppm from montmorillonite. Aluminum hydroxide therefore must remain in the clays. This behavior of the two clay minerals could be of significance in the origin of bauxite.

Investigations by Echle (1961) of Keuper clays taken from drill samples and from outcrops showed no demonstrable differences in the composition of the clay minerals (illite and chlorite). Nordmeyer (1959) also could find no trace of decomposition of the clay minerals (illite and chlorite) in the weathering soils of the red Triassic sandstone and of the upper Permian. Under the climatic conditions in Germany decomposition probably is slight, perhaps because the soil solutions already contain Al and Si ions.

CONCLUSIONS

Our investigations have not solved the problem of the chemical weathering of silicates. We did not expect them to, but I believe, nevertheless, that they have brought us a little further in our knowledge of the mechanism. The often-reported hypothesis that an exchange of alkali ions for hydrogen or hydronium ions occurs in the weathering of feldspar and mica certainly is not correct. One should limit use of the word "exchange" to those situations in which a component is interchanged without otherwise altering the framework. When the framework as such is decomposed it is misleading to speak of an exchange. That hydrogen or hydronium ions appear in the decomposition products also is doubtful. Now it seems probable that the residual Al^{3+} ions carry the charge. Because the decomposition of the silicate framework, even in a simple experiment, is so complex, I left out thermodynamic calculations like those attempted, for example, by Garrels and Howard (1959) on the one hand, and Hemley (1959) on the other. I fear that still further experimental work must be done before this desirable scientific goal is reached.

Even if we have not achieved a final understanding of the mechanism, the experiments nevertheless have given us hints in other directions, about the stability of minerals for example. It has been known for a long time that the vulnerability of the more common minerals to weathering varies. The investigations at various pH values and filtration rates show that the stability of a mineral is also dependent upon external conditions. In Table 11 the dissolved

TABLE 11.—AMOUNT IN SOLUTION IN PERCENT OF THE ORIGINAL MATERIAL
IN 4 LITERS OF FILTRATE (GRAIN SIZE: $< 1 \mu$)

pH of the solution	Olivine	Potassium feldspar	Albite	Leucite	Tremolite	Muscovite
3	15.8	10.3	7–13.6	9.1	6.3	5.7
5.8	6.1	< 5.4*	1.6– 3.5			2.2
6.8				1.9		
9	7.9				10.8	2.5
11		10.4		8.6		7.2

* Extrapolated from 2 l.

quantity in 4 liters of filtrate is expressed as a percentage of the amount of starting substance and at various pH values. Olivine is, as is known, the most easily destroyed mineral. Potassium feldspar, albite, and leucite follow close together, and then tremolite, which is attacked more strongly in alkaline solution, and finally muscovite. Table 12 shows the effect of experimental conditions, especially the rate of filtration, on albite. Finally the effect of the grain size on the rate of weathering must be taken into

consideration. As Table 13 shows, only olivine shows no dependence on grain size.

The dependence on the weathering conditions, without doubt, also is valid for the so-called heavy minerals. Here observations of the products of weathering, like those carried out by Bakker (1959, 1960) and his school, indicate that different heavy minerals are stable under different climatic conditions.

In my exposition I have touched on an extremely vast field and I do not imagine that I have treated it in any way exhaustively. However, I do hope that, at least, I have added some light to the concept of the chemical weathering of silicates and stimulation for further work in this field.

TABLE 12.—FILTRATION EXPERIMENTS ON POWDERED ALBITE, GRAIN SIZE RADIUS < 1 μ, SHOWING RELATION BETWEEN DISSOLVED AMOUNT (IN PERCENT) OF THE ORIGINAL MATERIAL AND pH, KIND OF ACID, SPEED OF PERCOLATION, AND STIRRING

pH	HCl	H_2SO_4	Speed of percolation ml/day	Stirring
3	10.3	13	50	stirred
3	7	7	100	not stirred
3	10	13.6	100	stirred
3	6.6	7.1	200	stirred
	H_2CO_3	H_2SO_4		
4		4.4	200	stirred
4	3.3		200	stirred
6	3.5		100	stirred
6	1.56		200	stirred

TABLE 13.—RELATION BETWEEN AMOUNT (IN PERCENT) OF THE ORIGINAL MATERIAL DISSOLVED AND GRAIN SIZE AT pH 3

Radius	1.85 liter	4 liters			
	Potassium feldspar	Leucite	Olivine	Tremolite	Sideromelane
< 1 μ	5.6	9.1	15.8	9.1	
3–10 μ	3.1*	2.7	15.7	4	4.2

* Shaken.

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