HYDROTHERMAL ALTERATION OF MONTMORILLONITE TO FELDSPAR AT TEMPERATURES FROM 245°C. TO 300°C.

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INTRODUCTION

Feldspar has been made synthetically at temperatures as low as 300°C.[2] In these experiments one common procedure was to mix dialyzed SiO_2 and Al_2O_3 in an aqueous alkaline solution and heat the mixture in a steel bomb for a long period of time.

The writer made a number of experiments based on somewhat different reasoning. The mineral montmorillonite has a layer structure[3] whose theoretical formula is $(OH)_2\ Al_2Si_4O_{10}\cdot mH_2O$. It resembles muscovite closely except for the absence of K and a larger ratio of Si to Al. In place of K ions the mineral seems to have H_2O molecules between the well known $(OH)_4\ Al_4Si_8O_{20}$ layers, common to both minerals. Montmorillonite is so finely divided that its x-ray diffraction lines are broad and diffused. It should, therefore, react chemically much more easily than substances of a coarser grain, especially since the above mentioned layers can be forced apart to a certain extent by an excess of H_2O in the system.[4] It should be possible to replace the water by other molecules or ions, or to cause a complete and easy rearrangement of the structure.

EXPERIMENTS AND X-RAY DATA

A montmorillonite (bentonite) from an unknown locality was used. It is a dense pinkish white material and gives the typical x-ray powder diagram of montmorillonite. The diagram of this material was published by the writer in this journal.[5] Half a gram of the sample was put in a gold lined bomb of 50 cc. capacity. Ten cc. of a solution of 1 gm. of $KHCO_3$ in 10 cc. of distilled water were added. The distilled water was boiled just before use. The air above the solution was displaced by CO_2, and the bomb sealed with a sheet of gold. It was placed in a furnace whose temperature was controlled by a Leeds and Northrup potentiometer recorder to ± 3°C. Since the bombs were thick walled and heavy the tem-

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[2] For a detailed description with numerous references see: *Doelter's Handbuch der Mineralchemie*, vol. **2**, pp. 556–567, 1917.

[3] Hofmann, Endell and Wilm, Kristallstruktur und Quellung von Montmorillonite: *Zeit. Krist.*, vol **86**, pp. 340–348, 1933.

[4] Hofmann, Endell and Wilm, *Op. cit.*, p. 345.

[5] Gruner, J. W., The structural relationship of nontronite and montmorillonite: *Am. Mineral.*, vol. **20**, p. 478, 1935.

peratures inside were probably closer to the mean furnace temperature than the extremes recorded by the potentiometer. After completion of an experiment the gold sheet was welded to the gold lining of the bomb, due to the great pressure. The bomb was opened by cutting a circular hole through the sheet. In most experiments in which $KHCO_3$ solution was used, a pressure of CO_2 was noticed when the bomb was opened. The solid material was rinsed into a beaker and then washed thoroughly by repeated decantations, after which it was air-dried for *x*-ray analysis. A microscopic investigation showed the material was so fine grained that only rough values for refractive indices could be obtained. These are within the range of orthoclase.

The lengths of time for the experiments with $KHCO_3$ varied. Seven days was sufficient at 300°C. to produce an orthoclase which yielded a relatively good *x*-ray pattern (see Table 1). Ten days at 272°C. produced practically the same result though the lines in the film are not quite as clear and more diffused. Two weeks at 245°C. yielded material whose lines were broad but approximately in the positions of orthoclase. Due to the diffuse character this pattern cannot be definitely correlated with orthoclase. Six weeks at 245°C. gave a diagram of orthoclase but not so good as the one recorded in Table 1, which is the result of three months heating at 245°C.

Six weeks at 200°C. did not produce any marked change in the montmorillonite pattern. If orthoclase forms at all at this temperature it probably requires time measured in years.

Table 1 contains the interplanar distances d and intensities I of adularia and three of the alteration products. The distances are uncorrected for eccentricity of the camera. The powders were mounted on silk thread and were about 0.8 mm. thick. Fe radiation was used to obtain maximum resolution of lines. The lines of the alteration products, especially those of 272°C. and 245°C., are relatively broad and in some cases overlapping, as compared with adularia. This is as would be expected in such extremely fine-grained material. Many of the small discrepancies in d values are due to the difficulty of finding the exact outer edges of diffuse lines. Line No. 1*a* occurs only in the last two alteration products. It does not belong to orthoclase. It may be due possibly to remaining montmorillonite which has one of its strongest reflections in this region. Other lines of montmorillonite coincide or overlap with orthoclase lines and therefore would be obscured. It is possible, then, that remnants of the original mineral structure still exist. The periodic spacing of the layers must have been, however, badly disturbed or destroyed for the most characteristic and intense basal reflection (001) at d 15Å has disappeared.

TABLE 1. COMPARISON OF X-RAY POWDER PHOTOGRAPHS OF ADULARIA WITH ALTERATION PRODUCTS OF MONTMORILLONITE. Fe RADIATION. RADIUS OF CAMERA 57.3 MM.

Line No.	Adularia Pfitsch Tyrol		7 days at 300°		10 days at 272°		3 months at 245°	
	d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
1	4.68	1*b*						
1*a*					4.53	2	4.52	2
2	4.21	3	4.18	2	4.21	1	4.20	2
3	3.94	0.5			3.91	1	3.91	1
4	3.77	2	3.77	2	3.75	1	3.78	2
5	3.61	1			3.59	0.5	3.61	0.5
6	3.480	1	3.43	1	3.43	0.5	3.44	0.5
7	3.313	5	3.313	4	3.292	3	3.290	4
8	3.227	4	3.204	3	3.195	2	3.192	3
9	2.995	2	2.980	1	2.975	2	2.980	3
10	2.901	1	2.880	1	2.880	2	2.892	2
11	2.763	1	2.743	0.5	2.739	0.5	2.752	0.5
12	2.560	3	2.567	3*b*	2.573	3*b*	2.577	3*b*
13	2.378	1	2.383	1	2.394	1	2.394	1
14	2.319	0.5						
15	2.263	0.5			2.269	0.5	2.260	0.5
16	2.165	2	2.161	2	2.164	1	2.164	2
17	2.119	1	2.116	1	2.116	0.5	2.112	1
18	2.050	0.5	2.053	0.5			2.058	0.5
19	1.999	1	2.002	0.5	2.007	0.5	2.004	1
20	1.968	1	1.964	1	1.967	1	1.965	1
21	1.915	1	1.926	1	1.922	0.5	1.919	1
22	1.881	0.5						
23	1.848	1	1.840	0.5	1.840	1	1.837	0.5
24	1.792	4	1.786	3	1.782	2	1.785	2
25	1.768	1						
26	1.740	0.5						
27	1.718	0.5			1.716	0.5		
28	1.690	0.5						
29	1.671	0.5	1.666	0.5	1.675	0.5	1.670	0.5
30	1.643	0.5	1.645	0.5	1.648	0.5		
31	1.622	1	1.620	0.5	1.616	0.5		
32	1.589	0.5	1.583	0.5				
33	1.565	1	1.555	0.5	1.563	1	1.560	0.5
34	1.528	1	}		}		}	
35	1.510	1	1.511}	1*d*	1.516}	2*d*	1.518}	3*d*
36	1.490	3	1.493	2	1.496	2	1.493	2
37	1.474	0.5	1.471	0.5	1.475	0.5		
38	1.447	1	1.452	0.5	1.449	0.5		
39	1.435	1	1.427	0.5	1.431	1	1.429	1
40	1.422	0.5						
41	1.402	1	1.401	0.5	1.404	0.5	1.402	1

TABLE 1. (*Continued*)

Line No.	Adularia Pfitsch Tyrol		7 days at 300°		10 days at 272°		3 months at 245°	
	d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
42	1.381	1	1.378	0.5	1.377	0.5	1.375	0.5
43	1.345	0.5						
44	1.334	1			1.335	0.5		
45	1.312	0.5					1.310	0.5
46	1.294	0.5	1.303	1*d*	1.304	1*d*	1.294	0.5
47	1.284	1	1.285	1	1.283	0.5		
48	1.273	1	1.270	0.5	1.272	0.5	1.278	1
49	1.264	1					1.260	0.5
50	1.253	1	1.248	0.5	1.247	0.5		

b = broad line
d = double line

The reaction occurring in the bomb may be expressed by the following equation:

$$3[(OH)_2Al_2Si_4O_{10}\cdot 2H_2O]+4KHCO_3\rightarrow$$
$$4KAlSi_3O_8+2Al(OH)_3+8H_2O+4CO_2$$

It will be noticed that aluminum hydroxide is one of the products. This might have remained in the colloidal state in which case it would have been decanted with the wash water. The first water from the beaker had a somewhat milky appearance. At any rate, *x*-rays did not reveal the presence of a crystallized hydroxide.

One may wonder why K_2CO_3 solutions were not used in any of the experiments. This reagent dissolves completely large quantities of the mineral, unless it is added in just the proper combining proportion which obviously is not feasible in the case of montmorillonite. Otherwise, it may have the same effect as $KHCO_3$.

The following equation

$$3[(OH)_2Al_2Si_4O_{10}\cdot 2H_2O]+2KHCO_3\rightarrow$$
$$2[K(OH)_2Al_2(Si_3Al)O_{10}]+6SiO_2+2CO_2+8H_2O$$

expresses a reaction producing muscovite from montmorillonite. This reaction on the basis of simple structural considerations should be expected to occur more easily than the one yielding orthoclase. No explanation for its absence can be advanced by the writer at present.

In one experiment a ten per cent solution of KCl was tried at 300°C. After 19 days no change was noticeable in the *x*-ray pattern of the montmorillonite.

Conclusions

Montmorillonite was heated in aqueous solutions of $KHCO_3$ in gold-lined pressure bombs. Seven days at 300°C. produced good orthoclase. The *x*-ray powder photograph is easily identified as that of adularia. At 272°C. the feldspar pattern became distinct after 10 days. At 245°C. six weeks to three months were necessary to produce the orthoclase structure. Six weeks at 200°C., on the other hand, had no apparent effect on montmorillonite. Potassium chloride solution (10%) does not seem to attack montmorillonite at 300°C. in 19 days. Muscovite, which by reason of its structural similarity could have been expected to form from montmorillonite, failed to appear in any of the experiments. The probable reaction in the bombs is as follows:

$$3[(OH)_2Al_2Si_4O_{10}\cdot 2H_2O]+4KHCO_3\rightarrow$$
$$4KAlSi_3O_8+2Al(OH)_3+8H_2O+4CO_2$$

While it is highly probable that orthoclase may form at temperatures below 245°C. it is impossible to make an estimate as to the lowest temperature of formation. The finding of authigenic feldspars in sedimentary rocks seems to indicate temperatures at least as low as 100°C.