ALTERATION OF GLASSES TO MONTMORILLONITE

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The formation of bentonite as the product of the geologic alteration of volcanic glass or ash has been postulated by many writers (4, 12, 14, 16, 18). Their conclusions have been based on the following facts: Thin sections of bentonite show the same structure as particles of glassy material often associated with it; the presence of feldspar and the absence of appreciable amounts of quartz; the presence of nearby alkaline salt deposits, and the chemical composition of the bentonite clay itself. Conditions for the formation of this clay and the range of its stability, however, have been investigated but cursorily, and it, therefore, should be of considerable geologic interest to determine the conditions under which bentonite may be obtained from volcanic glass or ash. This paper presents the results of an investigation of the alteration of glass to bentonite under the influence of high temperatures and pressures.

Most geologists consider the alteration of the glass or ash to have taken place after deposition, due to the leaching action of natural waters. On the other hand, it is probable that in the case of ash, the alteration may have taken place partially in the air, under the influence of volcanic and atmospheric gases. This can readily be imagined when one realizes that volcanic ash may be suspended in the air for considerable periods of time, as demonstrated by the famed eruption of Krakatau, where the ash circled the globe. The leaching process, however, is probably a much more important effect, in view of the fact that it has been proceeding since the deposition of the glass or ash.

Mineralogically, the essential mineral in bentonite is usually montmorillonite, less often beidellite (14). These are hydrous alumino-silicates having a chemical formula of $Al_2O_3 \cdot 4SiO_2 \cdot nH_2O$ and $Al_2O_3 \cdot 3SiO_2 \cdot mH_2O$, respectively, where the alumina in the latter is partially replaced by iron oxide. The former has been shown (1, 5, 6, 7) to consist of a three-layer lattice of silica, alumina and silica planes joined together by oxygen bridges, the unit crystals being held together by electrostatic forces (1). Swelling occurs when water is adsorbed between the unit layer parcels, thus forcing them apart. The swelling of montmorillonite occurs only with particles of colloidal size; Fuller's earth, which has been shown to contain a high percentage of montmorillonite (8), is generally non-colloidal in dispersions of its finest particles and non-swelling, although its adsorptive capacity is very high. Base-exchangeable ions are adsorbed either on the unsaturated oxygen bonds due to the fracture of the unit crystals or to the unsaturated bonds created when an aluminum atom takes the place of a silicon in the silica layer. The aluminum layer may be partially or wholly replaced by iron or magnesium and occasionally by other elements (3, 10). Bentonites in the natural state contain varying amounts of colloidal material, depending on the state of decomposition of the glass, and the purity of the initial deposit of glass or ash.

Previous work on the synthesis of montmorillonite has been restricted entirely to the use of alumina and silica gels. Ewell and Insley (2) prepared beidellite from co-precipitated alumina and silica gels by heating them in an autoclave at 355°C. and 385°C., and found that the presence of soda was necessary for the reaction to take place. Somewhat later, Noll (13) prepared montmorillonite from silica and alumina gels by heating at 300°C. and 87 atmospheres, and found that the reaction took place in alkaline solutions of moderate concentrations. In acid or slightly alkaline solutions, kaolinite was formed. The latitude of concentrations was found to be much greater with $Mg(OH)_2$ than with the other alkalis. The use of gels, however, does not simulate the initial formation of montmorillonite from glass in nature, although some writers (15) have predicted the formation of an intermediate alumina and silica gel structure in the genesis of clay minerals.

PROCEDURE

The reactions were carried out in a platinum crucible placed inside a reactor of the cap and case type, described by Morey and Ingerson (11). The powdered glass was placed in the crucible, the reagent added and the top placed on the crucible tightly, and the crucible placed in the reactor. 75 cc. of water were then added to give the desired pressure; the total volume of the reactor was 230 cc. Heating was accomplished in a thermostatically controlled furnace regulated to within ±10°C. for times varying from 26 to 350 hours. The temperature selected for the reaction was 300°C.

The effect of reagent, time of heating, particle size of the glass and type of glass was investigated. The reagents used were H_2O, H_2SO_4, $NaOH$, KOH, $Ca(OH)_2$ and $Mg(OH)_2$. The glass was ground to pass 200 mesh in most of the runs; some of the glass was ground to less than 10 microns to establish the effect of particle size. A synthetic glass with a composition comparable to that of a Wyoming bentonite was made, and a natural obsidian or volcanic glass from Yellowstone National Park was obtained for use in these experiments.

The products obtained from the reactions were dispersed in water, allowed to sediment, and the colloidal fraction electrodialyzed to remove extraneous salts which might confuse the *x*-ray patterns. Identification was made by means of *x*-ray diffraction patterns and dehydration curves.* The colloidal size of the clay particles made identification of the products by microscopic means impossible. In cases where montmorillonite was formed, dye adsorption tests were made with methylene blue whenever the quantity of material was sufficiently large. Comparison tests were made both on a Wyoming bentonite and on a California bentonite in which all the alumina is replaced by magnesia.

It should be noted here that these reactions differ in several respects from reactions carried out with gels such as reported by Noll, Ewell and Insley and others. With gels, we are dealing with matter present in a more or less degree of hydration, and a much greater mobility as far as rearrangement of its components is concerned. In a glass, although there is a random arrangement of the silica tetrahedra and of the alumina groups, there is nevertheless a certain rigidity toward free movement of the molecules not experienced in gels. Likewise, the diffusion of the reacting ions through the gel mass is much greater than can be obtained through the solid glass; this should make considerable difference in the time of reaction and also perhaps in the end product. Furthermore, these reactions go beyond those of Noll's by introducing into the investigation the effect of time, degree of comminution and type of glass.

RESULTS

Montmorillonite was found to be formed in acid, neutral and basic solutions. The following table shows the conditions under which the clay was formed. As stated above, all reactions were carried out at 300°C.

TABLE 1

Reagent	Ratio $R_2O:Al_2O_3$	Time (Hours)	Product
H_2O		100	Montmorillonite et al.
H_2SO_4	0.2:1	50	Montmorillonite
H_2SO_4	2:1	143	Montmorillonite
$Ca(OH)_2$	0.2:1	40	Montmorillonite
$Ca(OH)_2$	2:1	144	?
NaOH	0.2:1	151	Montmorillonite and kaolin
NaOH	2:1	144	?
NaOH	4:1	148	Montmorillonite
KOH	0.2:1	149	Montmorillonite?
KOH	1:1	148	Montmorillonite et al.
$Mg(OH)_2$	0.2:1	64	Montmorillonite
$Mg(OH)_2$	0.2.1	80	Montmorillonite
$Mg(OH)_2$	0.2:1	149	Montmorillonite
$Mg(OH)_2$	2:1	45	Montmorillonite

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* For further details see H. H. Reynolds, Sc.D. *Thesis*, M.I.T. 1939.

EFFECT OF REAGENTS

In all cases the products were of the non-swelling type of montmorillonite and ranged in color from white to grey and brown. Montmorillonite was formed in all of the alkali solutions, with the greatest latitude of concentration to be found with $Mg(OH)_2$, which is in accord with the findings of Noll. Sulfuric acid showed a greater latitude than the alkalis except for $Mg(OH)_2$; in particular, the products from the acid runs showed a high dye-adsorptive capacity for methylene blue. When obsidian was used, it was found that the natural glass was very stable and in alkali solutions yielded a product similar to orthoclase on heating for 150 hours, but no montmorillonite at these lengths of time. However, when the glass was reacted for 350 hours with sulfuric acid in an acid: alumina ratio of 2:1, it was found that a montmorillonite whose particles were not colloidal was formed, which had a dye-adsorptive capacity comparable to that of a Fuller's earth used in standard oil bleaching operations.

The formation of montmorillonite in both alkali and acid solutions corresponds to the metamorphosis of the glass in nature. In the case of the acid transformation, the reaction may have taken place in part in the air during periods of volcanic activity during which time the percentage of corrosive gases would have been quite high. The transformation could also take place in situ after the deposition of the glass or ash by the leaching action of slightly acid or alkaline solutions. However, the concentrations employed in these experiments do not necessarily give a comparison with the concentrations of the reagents in nature, since the higher concentrations used in this work may act simply to increase the rate of reaction. In nature, a lower concentration of the acidic or basic solution may accomplish the same effect in a longer time. Whether the swelling properties and especially the particle size of montmorillonite and particularly Fuller's earths are due to the formation of the clay under different conditions cannot be stated at present. It may be that the reaction takes a different course under different conditions; the non-colloidal montmorillonite may be merely a stage in the formation of a colloidal clay. If one reaction takes place through the intermediate formation of gels, whereas the other is a process of devitrification and hydration, different end products might be expected. In any event, the results of these experiments seem to indicate that Fuller's earths may be found in acidic leaching solutions.

EFFECT OF THE TYPE OF GLASS

The obsidian was found to be much more stable than the synthetic glass having a composition comparable to that of the Wyoming bentonite. This is quite in accord with the findings of Königsberger and Müller (9), who reported obsidian to be extremely stable under hydrothermal conditions. This stability is probably due to the high silica content, since it is necessary first to remove the excess of silica from the glass before the alteration can be complete. The $Al_2O_3:SiO_2$ ratio in the glass is 1:9, while in the montmorillonite this ratio is 1:4 or 1:5. The silica is presumably transported either as a solution or in the form of a silicic acid sol. The two types of glasses used in these experiments represent the extremes of alumino-silica glasses found in nature.

EFFECT OF TIME

To determine the effect of time on the reaction, runs were made under similar conditions of reagent, temperature and pressure, but for varying lengths of time. It was found in every case, that whereas montmorillonite could be formed in 150 hours, heating for 290 hours under the same conditions gave a product which could no longer be identified as montmorillonite. With $Mg(OH)_2$ solutions and synthetic glass, montmorillonite was formed at 64, 80, and 149 hours, but not with 289 hours heating. These results indicate that montmorillonite is not the end-product of the reaction, but is an intermediate step. That montmorillonite is comparatively stable, however, is shown by the fact that it can be produced over a considerable time range; if it were unstable, the period of time during which it could be detected would be more critical. These facts lead to the conclusions that either the bentonite beds are still in process of transformation, that the leaching action has ceased to be of any consequence, that the conditions necessary to effect the change are no longer present, or that the present rate of reaction is too slow to be detected at present. Inasmuch as these reactions took place at 300°C., it is probable that the reduction in temperature in bentonite beds has so reduced the reaction rate that the bentonite is stable at present earth temperatures, although the reactions may be still proceeding at extremely low rates. In fact, it is generally conceded by geologists that the alteration of the glass usually took place at temperatures not much higher than the boiling point of water.

EFFECT OF COMMINUTION

The effect of particle size of the glass was investigated by making several runs with glass of 200 mesh particle size and similar runs with glass ground to about 10 microns. It was found that the size of the reacting glass has a considerable effect on the reaction. Whereas montmorillonite was formed with the 200 mesh glass on heating for 150 hours, the finely ground glass gave an *x*-ray pattern which could not be identified. All the runs with the finely ground glass, regardless of the reagent used, showed the same *x*-ray pattern.

These facts indicate that the alteration, at these temperatures at least, is a surface phenomenon, and not merely an inter-molecular rearrangement. Presumably the surface of the glass is attacked, causing the alteration of the glass at that point. The reaction then proceeds through a hydration and adsorption of ions onto the crystal lattice of the clay particle, the rate of reaction of the interior of the glass particle depending to a certain extent upon the diffusion of the reagent through the reacted glass. It seems likely that the reaction is partially a devitrification phenomenon, in which the alumina and silica groups rearrange under the influence of temperature to give a crystalline structure. The alteration of glass to montmorillonite is probably a combination of the chemical reactions attendant with leaching, and a devitrification of the glass. The relative magnitude of these effects depends to a certain extent upon the stability of the glass.

General Discussion

The montmorillonite produced in acid solution was brown in color and had a high adsorptive capacity; this is no doubt a form of Fuller's earth, and indicates that this type of clay may have been formed from acid waters acting on volcanic glass. None of the montmorillonite produced showed swelling. There may be several reasons for this. In the alteration of the glass from the random network of silica tetrahedra which Warren and Biscoe (17) have shown to exist in a glass, to the three-layer lattice of montmorillonite, it is possible that these three-layer stacks were imperfectly formed and were still joined together by oxygen bonds. Relatively few such bonds would be required to prevent swelling, yet it is probable that such an alteration of the structure would not appear in an *x*-ray diffraction pattern. Furthermore, the high temperature and high pressure treatment might have so distorted the lattice that swelling was impossible. By employing different conditions in this type of reaction, it should be possible to obtain a swelling montmorillonite from glass.

These experiments have shown that montmorillonite can be produced from glass under the conditions shown above. It is recognized, however, that an analogy between conditions of these experiments and the conditions existent in geologic times must not be pushed too far. Montmorillonite or bentonite beds were formed at temperatures considerably below 300°C. While the effect of an elevated temperature is an enhanced rate of reaction, it may also result in a different type of reaction. So that the fact that montmorillonite may be produced at 300°C. does not necessarily mean that the same conditions would yield montmorillonite at 150°C. However, these reactions may have a value much beyond their significance to geologists.

Inasmuch as clays differ widely, even in the same locality, it would be of considerable importance to be able to produce a clay of known characteristics. Particularly in countries where such clays are scarce or nonexistent and must be imported at some cost, as in Rumania for example, it is conceivable that a method of manufacturing clay from its constituents, silica and alumina, may be of considerable value. Since silica and alumina are common and cheap materials, considerable expense could be incurred in such a process and still show a profit over transportation charges. In addition, it should be possible to produce clays of any desired properties by using appropriate means, so that one could tell, a priori, what type of clay he would obtain from certain materials under certain conditions. Where a small amount of clay of given characteristics was desired in a certain industry, this method should prove quite feasible.

It is proposed to continue this work under different conditions. Since we can simulate nature in all her effects except time, it is desired to compensate for this by the accelerating effect of other factors. As pointed out above, elevated temperatures offer certain definite objections. It is now proposed to carry out this alteration of glass at lower temperatures, but to circulate the leaching solutions at rates enormously faster than occur in nature. In this manner, the glass will be continually attacked by new solution, which corresponds to natural conditions, and laboratory results should be entirely comparable to those obtained in nature.

Summary

It has been shown that montmorillonite can be produced by high temperature and high pressure alteration of both a synthetic glass having a composition of that of montmorillonite, and a natural obsidian under acid, neutral and basic conditions. The conditions have much more latitude in the case of $Mg(OH)_2$ than with the other alkalis. The obsidian was found to be very stable and yielded a Fuller's earth only after fifteen days' heating. The montmorillonite produced was nonswelling, and that produced in acid medium showed the characteristics

of Fuller's earth. Though admittedly, conditions did not simulate geologic conditions, nevertheless, the conditions of formation at these temperatures have been indicated. Attention has been called to the possibility of using this method to produce clays of given characteristics synthetically in countries where natural clays are scarce, or in those industries where a highly specialized clay is desired in relatively small quantities.

REFERENCES

1. BRAGG, W. H., *Proc. Royal Soc.*, **XXX,** No. 140, 39.
2. EWELL, R. H., AND INSLEY, H., *Jour. Res. Nat. Bur. Stand.*, **15,** 173 (1935).
3. FOSHAG, W. F., AND WOODFORD, A. O., *Am. Mineral.*, **21,** 238 (1936).
4. HEWETT, D. F., *Jour. Wash. Acad. Sci.*, **7,** 196 (1917).
5. HOFMANN, U., ENDELL, K., AND WILM., D., *Zeits. Krist.*, **86,** 340 (1933).
6. HOFMANN, U., ENDELL, K., AND BILKE, W., *Zeits. Elektrochemie,* **41,** 471 (1935).
7. HOFMANN, U., AND BILKE, W., *Koll. Zeits.*, **77,** 238 (1936).
8. KERR, P. F., *Am. Mineral.*, **17,** 192 (1932).
9. KÖNIGSBERGER, J., AND MÜLLER, W., *Centr. Min.*, **1906,** 353, 399 (1906).
10. MARSHALL, C. E., *Jour. Phys. Chem.*, **41,** 935 (1937).
11. MOREY, G. W., AND INGERSON, E., *Am. Mineral.*, **22,** 1121 (1937).
12. NELSON, W. S., *Bull. Geol. Soc. Am.*, **33,** 605 (1922).
13. NOLL, W., *Chemie der Erde,* **10,** 129 (1935–36).
14. ROSS, C. S., AND SHANNON, E. V., *Jour. Am. Ceram. Soc.*, **9,** 77 (1926).
15. SCHWARZ, R., AND WALCKER, R., *Zeits. anorg. allgem. Chemie,* **145,** 304 (1925).
16. *U. S. Bureau of Mines, Technical Paper* **438** "Bentonite" by Davis and Vacher.
17. WARREN, B. E., AND BISCOE, J., *Jour. Am. Ceram. Soc.*, **21,** 49 (1938).
18. WHERRY, E. T., *Jour. Wash. Acad. Sci.*, **7,** 576 (1917).