Reports

Kaolinite Synthesis at 25°C

Abstract. *The addition of quercetin, an organic flavone ($C_{15}H_{10}O_7$), to aqueous solutions containing silica and aluminum and adjusted to final* pH's *from 6.5 to 8.5 produced a 1 : 1 aluminosilicate precipitate which, after 6 to 16 months of aging in solution at 25°C, contained as much as 5 percent well-formed kaolinite plates. Similar solutions containing no organic material produced relatively amorphous precipitates with the same composition and stability (standard free energy of formation = − 897 ± 1 kilocalories per mole) but with substantially smaller amounts of crystalline material even after 2 years of aging.*

Until rather recently the only really successful syntheses of kaolinite had been carried out at high temperature and pressure in closed reaction vessels. During the 1960's, several groups and individuals in Europe had attained a greater degree of success in lower temperature ranges. De Kimpe (*1*) and Siffert (*2*) used as a starting material an aluminosilicate gel formed by reacting organically complexed forms of silicon and aluminum to produce kaolinite. Harder (*3*) obtained quartz, kaolinite, and some other minerals from dilute inorganic solutions aged at 3° to 60°C, and Linares and Huertas (*4*) obtained kaolinite at room temperature in an aging solution in which aluminum was complexed by fulvic acid.

There also have been syntheses by research workers in the United States. Kittrick (*5*) reported a synthesis of kaolinite in which the mineral was crystallized on montmorillonite surfaces during aging at 25°C of a solution supersaturated with respect to kaolinite. Polzer *et al.* (*6*) obtained small amounts of halloysite during aging at 25°C of dilute solutions of aluminum and silica near neutral *p*H.

In a continuation of the work described by Polzer *et al.* (*6*) Hem *et al.* (*7*) showed that material with the composition and approximate solubility of halloysite could be consistently synthesized from aqueous solutions at 25°C during aging periods ranging from 6 months to 2 years. Although essentially amorphous to x-rays, the precipitate contained a few small crystals, recognizable in electron micrographs at × 50,000 to × 100,000 magnification, as kaolinite or halloysite.

During our research on the aqueous chemistry of aluminum we have observed that small amounts of an organic complexing agent in solutions otherwise identical to those described by Hem *et al.* (*7*) cause a substantially greater fraction of the precipitate to become crystalline kaolinite during aging at 25°C. We illustrate here the improved material produced and speculate briefly concerning possible mechanisms.

Kaolinite and related 1 : 1 clay minerals commonly are described as having a gibbsite layer alternating with a silica layer, but this may give a somewhat misleading and oversimplified view of the structure. Hem and Roberson (*8*) demonstrated that gibbsite is readily precipitated from $10^{-3.5}M$ aluminum perchlorate solutions when the *p*H is raised to a value between 4.5 and 6.5. At *p*H's greater than this the precipitate is bayerite and nordstrandite. Structures of the three polymorphs are described by Schoen and Roberson (*9*). Each is a layered mineral with each layer consisting of two close-packed sheets of hydroxyl ions held together by aluminum ions that occupy two-thirds of the available octahedral coordination sites.

The silica layer of kaolinite, as in other layer-type silicates, is composed of oxygen ions in tetrahedral coordination with silicon, with three of the oxygens in each tetrahedron shared with adjacent tetrahedra. The formula for such a stucture may be written as $Si_2O_5^{2-}$, and in kaolinite the unshared oxygen of each tetrahedron displaces a hydroxide from the adjacent hydroxide sheet of the gibbsite layer and becomes bound to an aluminum ion. In the adjustment required to maintain a charge balance, two-thirds of the hydroxide in this half of the gibbsite layer must be changed to oxygen and the units are tied together by an extensive network of Al–O–Si bonds.

In aqueous solution at *p*H's below about 8 and for total concentrations less than $10^{-3}M$, essentially all the silicon would be in monomeric form, as $Si(OH)_4$, with a tetrahedral arrangement of four hydroxide ions around each silicon, and zero net charge (*10*). Forming a polymeric structure with $Si(OH)_4$ as starting material to go to a framework of $Si_2O_5^{2-}$ poses obvious problems. If dissolved silica were present in a solution predisposed to precipitate gibbsite, however, the solid might be able to pick up a properly oriented silica layer during crystallization to form the kaolinite structure in at least part of the precipitate. This premise was tested by Hem *et al.* (*7*), and modestly favorable results were obtained. The solid had a mole ratio of silica to aluminum near 1 over a considerable range of solute concentrations. Moreover, after aging for 6 months or more, the solutions gave relatively constant and consistent ion activity products for participating species in the ratios dictated by the kaolinite formula. Finally Hem *et al.* (*7*, p. 15) were able to reverse the reaction by lowering the *p*H of an aged solution to dissolve part of the precipitate and still return to the same ion activity product after additional aging.

From the expression

$$\Delta G_f^\circ = -RT \ln K$$

(where ΔG_f° is the standard free energy of formation, R is the gas constant, T is the temperature in degrees Kelvin, and K is the ion activity product) the mean value of the activity product for the precipitate adjusted to zero ionic strength by means of the Debye-Hückel expression gave a standard free energy of formation (standard state, 1 atm and 298°K) of −897

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kcal/mole with an experimental uncertainty of ± 1 kcal. This value is only about 1 kcal less negative than the value given by Robie and Waldbaum (*11*, p. 25) for halloysite. It seemed appropriate to call the material formed in these experiments synthetic halloysite. The chemical composition of the material is similar to that of kaolinite whose formula is identical with that of completely dehydrated halloysite.

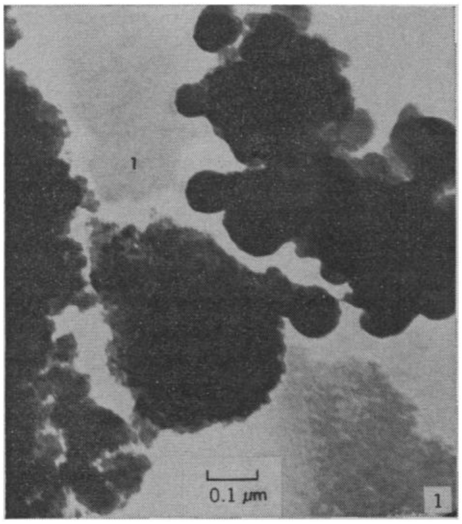
Because the solid assumed to be present has been so elusive in previous attempts at synthesis, some additional evidence of crystallinity and structure is especially desirable. The simplest and most widely used technique for identifying crystallinity, a routine x-ray diffractometer scan, did not furnish any positive evidence of structure in the aluminosilicate precipitates. The plastic filter membrane with a layer of precipitate that had collected on it was fastened to a glass microscope slide for this examination. A small percentage (10 percent or less) of crystalline material in an amorphous matrix would generally be undetected by such a scan, and the small particle size of all the solid material limited still further the sensitivity of this technique.

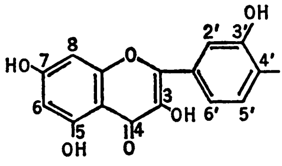
The electron microscope provides a means for selectively viewing the very small particles, and a comparison of the shapes of those that are obviously crystalline with the appearance of known material has provided most of the physical evidence of crystallinity obtained in this study. Both very small units having the characteristic irregular hexagonal shape of kaolinite plates and the rolled-up sheets of halloysite have been photographed. The low yield of crystalline material made it necessary to mount and view many dispersions of the solid. Figure 1 is typical of the rather poorly organized material usually seen.

Electron diffraction patterns were readily obtainable for solids examined under the electron microscope, an indication that crystallinity was present. We were unable to make detailed quantitative interpretations of these patterns, however.

The possibility of making kaolinitic clay more efficiently by adjustment of the experimental conditions of Hem *et al.* (*7*) was given further study. As noted earlier, the conversion of two-thirds of the hydroxide into oxygen in the inner half of the gibbsite layer is required in order to attach the silicon-oxygen sheet. If the gibbsite structure is already extensive, the necessary amount of rearrangement and ejection of water molecules surplus to the new Al–O–Si linkages may well be very difficult. If a precursor species in solution already had an O–Al bond, this might make the clay synthesis easier to accomplish.

In a study of the effects of organic complexes on the behavior of aluminum, we observed that, when the organic flavone compound quercetin was present in small concentrations in a solution supersaturated with respect to gibbsite, the precipitation process was considerably altered. Quercetin was used in these experiments because it has a structure (Fig. 2) resembling the colored organic material occurring in some natural water and is available in pure form. It is chemically stable and forms complexes with many metals. Precipitated aluminum hydroxide sufficiently well organized to produce a gibbsite x-ray diffraction pattern was formed in only one quercetin-containing solution. Polynuclear ionic aluminum hydroxide species that formed in the quercetin solutions were small and did not grow into gibbsite microcrystals, as observed by Smith and Hem (*12*), in the absence of organic material. The growth of aluminum hydroxide polymer was inhibited even





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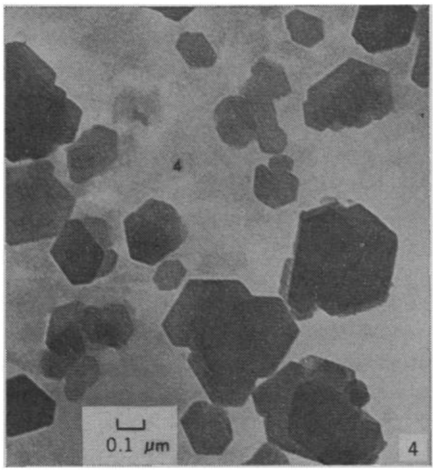

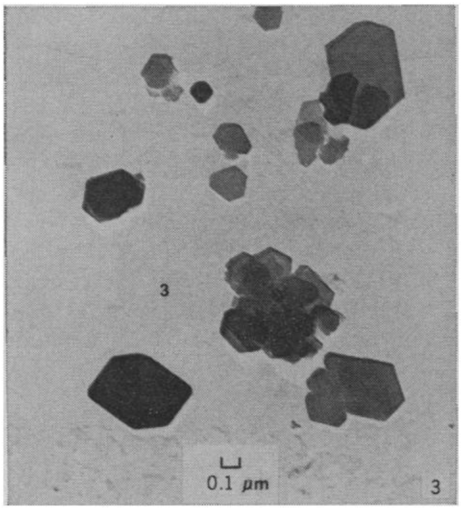

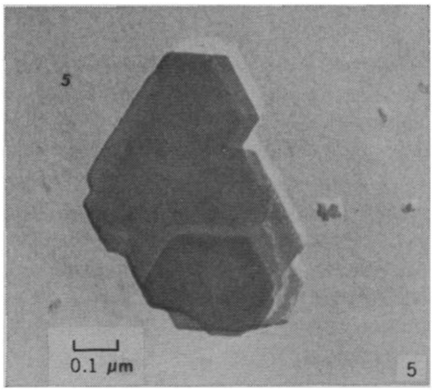

Fig. 1. Electron micrograph of solids recovered after 106 days of aging from solution 17C. Supernatant *p*H, 8.17; aluminum concentration, 1.4 mg/liter; silica concentration, 2.2 mg/liter; magnification, × 56,000. Fig. 2. Structure of quercetin ($C_{15}H_{10}O_7$). Fig. 3. Electron micrograph of solids recovered after 155 days of aging from solution Q20G. Supernatant *p*H, 7.54; aluminum concentration, 0.19 mg/liter; silica concentration, 25.4 mg/liter; magnification, × 22,000. Fig. 4. Electron micrograph of solids recovered after 155 days of aging from solution Q20G. Supernatant *p*H, 7.54; aluminum concentration, 0.19 mg/liter; silica concentration, 25.4 mg/liter; magnification, × 35,000. Fig. 5. Electron micrograph of solid recovered after 481 days of aging from solution Q24G. Supernatant *p*H, 7.66; aluminum concentration, 0.17 mg/liter; silica concentration, 22.4 mg/liter; magnification, × 60,000.

when the organic compound was present in concentrations too small to complex more than a few percent of the aluminum ions.

We tested the effect of the presence of small amounts of quercetin on the synthesis of clay minerals by repeating some of the experiments of Hem *et al.* (*7*) in which synthetic halloysite was produced, with the addition of $10^{-5.30}M$ quercetin at the time the reagents were mixed to begin to form precipitates. Reactions were again slow and, in *p*H, aluminum concentrations, and silica concentrations, the aging solutions containing quercetin were similar to the ones lacking quercetin. However, after about 6 months of aging, solids recovered from solutions in the *p*H range 6.5 to 8.5 contained as much as 5 percent relatively well-crystallized kaolinite (Figs. 3 and 4) mixed with the much larger amount of amorphous precipitate. The yield and crystallinity of the material illustrated were far superior to the results obtained in the experiments of Hem *et al.* (*7*) in which only inorganic materials had been used. As before, however, it was not possible to obtain x-ray diffraction peaks because the crystals were small and could not be separated from the amorphous matrix.

We checked the reproducibility of these results by preparing a new series of solutions duplicating those which yielded the kaolinite crystals. Well-crystallized material of kaolinitic appearance was present in substantial quantity in all these solutions after 16 months (Fig. 5).

Evidently conditions favorable for clay-mineral synthesis at 25°C can be produced in systems favoring precipitation of aluminum hydroxide and aluminosilicate by relatively subtle changes in the system. The presence of an organic constituent in amounts too small to complex a measurable fraction of the aluminum evidently is one means of accomplishing this. The principal effect of the organic constituent here was probably to slow the polymerization of polynuclear aluminum hydroxide species, in the *p*H range 6.5 to 8.5 where the polymerization normally is very rapid. This permitted more reactants to follow the slow reaction path leading to kaolinite that is better crystallized. When aluminum hydroxide polymers have reached a size sufficient to display the typical gibbsite or bayerite structure, the aluminum-silica interlayer bonding is evidently rather difficult to establish. Polymerization of aluminum hydroxide is slowed by a lowering of the *p*H, but the attachment of silica to form the clay mineral is also inhibited by low *p*H. In addition to its effects on the the kinetic factors, the aluminum-quercetin complex that forms may facilitate the development of Al–O–Si bonding, because it contains Al–O bonds. Even if the amount of complexed aluminum is small, the ligands would be available for recycling after formation of the Al–O–Si linkages. Further adjustment of the conditions in these experiments may increase the yield of crystalline material and possibly increase the rate of the reaction.

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Spectroscopic Measurements of Stratospheric Nitric Oxide and Water Vapor

Abstract. *Spectroscopic measurements have been made of the nitric oxide and water vapor concentrations in the stratosphere at an altitude of 28 kilometers. The measurements, carried out in situ with the use of a spin flip Raman laser, represent the first accurate determination of nitric oxide as a function of time (as the sun rose) from about 6:30 to 14:00 C.D.T.*

Measurements of NO concentrations in the stratosphere are important because of the crucial role that NO plays in the chemical cycle which determines the O_3 concentration of the inversion layer (18 to 28 km)—the stratosphere. Recently, a number of theorists have tried to delineate the changes in the O_3 cycle due to the additional NO introduced into the stratosphere (*1*) by the proposed flights of a fleet of supersonic transports. Attempts have also been made to interpret the O_3 cycle in light of the fact that the hypothesized injection of large quantities of NO during the years of atmospheric nuclear testing (*2*) resulted in no significant changes in the ambient O_3 concentrations in the stratosphere. The reactions important (*1*) in determining the generation of the local NO concentration include the reaction of NO_2 with atomic oxygen produced during the photodissociation of O_2 (Eq. 1) and the photodissociation of NO_2 by the solar ultraviolet radiation at wavelength < 4000 Å (Eq. 2).

$$NO_2 + O \rightarrow NO + O_2 \quad (1)$$

$$NO_2 + h\nu \rightarrow NO + O \quad (2)$$

Both of these reactions are well understood (*1*), and in both the solar ultraviolet radiation produces NO from NO_2. It is also believed that, in the absence of sunlight, for example, at night, the NO thus created rapidly reacts with O_3 and is converted into NO_2. In all of the models, however, the common feature is the lack of precise knowledge of the background concentration of NO during the daytime. Thus the effect of additionally introduced NO calculated in any model is, at best, open to question. To be able to make a reasonable estimate of the effects of the flight of supersonic transports, it is important to know the present concentration of NO in the presence and in the absence of the ultraviolet radiation from the sun. In the experiments reported here we have been able to measure the NO concentration at an altitude of 28 km before, during, and after the sunrise. Since the technique used here is a spectroscopic one, it is generally applicable to other constituents also. Thus, we have been able to measure the stratospheric H_2O concentration which also is of interest in some of the chemical reactions important in the stratospheric balance.