where Ω_0 is the angular velocity at the equator. For an equatorial angular velocity Ω_0' somewhat differing from the present-day value, the latitude dependence of Ω can be expressed as

$$\Omega = \Omega_0' \, [1 - 0.19 \, f \, (\Omega_0') \sin^2 \phi] \quad (2)$$

where f is some function of Ω_0' that satisfies the condition that

$$f \, (\Omega_0') = 1 \qquad \text{for } \Omega_0' = \Omega_0 \quad (3)$$

Since the interaction between rotation and convection [which is expected to be the cause of the differential rotation (*12*)] will not change drastically for small changes in Ω_0', we expect that, for values of Ω_0' close to Ω_0, the value of $f(\Omega_0')$ will be close to unity. According to Eq. 2, this means that the speed $d\Omega/d\phi$ of the differential rotation is, in first approximation, proportional to the equatorial angular velocity Ω_0'. Consequently, if the sun rotates somewhat faster than at present, the winding up of magnetic field lines due to the differential rotation will take place somewhat faster, and, on the Babcock-Leighton (*13*) hypothesis of solar activity, we expect a somewhat shorter sunspot cycle (if all other factors that determine the sunspot cycle are assumed to remain the same).

If we use an e-folding time of 2.2×10^9 years for the slowing down of solar rotation, we expect from the presently observed equatorial velocity of 1.91 km/sec (*9*) that the solar equatorial velocity of rotation of 250 million years ago was 2.10 km/sec. We therefore expect the sunspot cycle at that epoch to have been around 10.1 years instead of the present 11.2 years. For an e-folding time of 2.9×10^9 years, the sunspot period at that epoch is expected to have been around 10.3 years. These expected periods differ sufficiently from the present-day one to have a chance of being measurable. Hence, trees of Permian and Triassic age are expected to be suitable for this type of investigation. [Available analyses of petrified trees (*10*) cover only some 10 to 20 million years; periodicities are indistinguishable from the present-day ones, as is expected from the e-folding times mentioned above.]

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References

1. G. H. Herbig, *Astrophys. J.* **141**, 588 (1965).
2. R. P. Kraft, *ibid.* **150**, 551 (1967).
3. P. S. Conti, *ibid.* **152**, 657 (1968).
4. I. J. Danziger, *Astrophys. Lett.* **3**, 115 (1969).
5. G. Wallerstein and P. S. Conti, *Annu. Rev. Astron. Astrophys.* **7**, 99 (1969).
6. E. P. J. van den Heuvel, *Publ. Astron. Soc. Pacific* **81**, 815 (1969).
7. O. Engvold, O. Kjeldseth Moe, P. Maltby, *Astron. Astrophys.*, in press.
8. E. Müller, *ibid.*, in press.
9. C. W. Allen, *Astrophysical Quantities* (Athlone, London, 1963), p. 179.
10. A. E. Douglass, *Climatic Cycles and Tree Growth* (Carnegie Institution of Washington, Washington, D.C., 1936), vol. 3.
11. H. W. Newton and M. L. Nunn, *Mon. Notic. Roy. Astron. Soc.* **111**, 413 (1951).
12. Y. Osaki, *ibid.* **148**, 391 (1970).
13. R. B. Leighton, *Astrophys. J.* **156**, 1 (1969).

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Kaolinite: Synthesis at Room Temperature

Abstract. *To obtain kaolinite at low temperature and pressure from the system $Si(OH)_4$-Al^{3+}-H_2O, the sixfold coordination of aluminum is a necessary prerequisite. Kaolinite was synthesized at* pH *values from 2 to 9 and with a ratio of SiO_2 to Al_2O_3 in solution from 1 to 10 by means of the complexation of Al^{3+} and fulvic acid.*

Clay minerals have a broad distribution in the earth's crust. Their formation in alteration zones, sediments, and soils corresponds to and constitutes evidence for restricted physicochemical conditions in natural media. Therefore, the study of the synthesis of clay minerals will clarify the mechanism and conditions of their natural formation.

For some years we have been interested in the problem of the synthesis of clay minerals at low temperature and pressure. It was first shown by DeKimpe and his co-workers (*1*) that sixfold-coordinated aluminum was essential for kaolinite formation, and subsequent work by Gastuche and his co-workers (*2*) and Wey and Siffert (*3*) confirmed this view. Wey and Siffert made use of an aluminum-oxalate complex as a source of aluminum in solution, where aluminum is in sixfold coordination. Experimental results in the literature show that, if aluminum is not in sixfold coordination as a complex or as a pregibbsitic hydroxide, it is not possible to carry out the synthesis of kaolinite at low temperature.

Although there are only small quantities of oxalates in the organic matter of soils, other organic acids are more common in soils and sediments. Fulvic acid from humus is known to form a complex with aluminum (*4*). We report here the synthesis of kaolinite by means of the formation of a complex of Al^{3+} and fulvic acid.

The fulvic acids were obtained from peat (*5*). The aluminum–fulvic acid complex was prepared by adding 1 milliequivalent of Al^{3+} to 10 ml of a fulvic acid solution with a carbon content of 1 g/liter (*6*).

Solutions of monomeric silica, $Si(OH)_4$, with a concentration of 144 parts per million, were prepared from sodium silicate at $p\text{H} = 2.5$. Next, variable quantities of the aluminum–fulvic acid solution were added in order to obtain the following ratios of SiO_2 to Al_2O_3 in solution: 0.1, 0.5, 1, 2, and 10. Portions of each solution were adjusted with NaOH to *p*H values of 4, 5, 6, 7, 8, and 9. The precipitated products were allowed to age for 1 month at room temperature in the presence of the equilibrium solutions. At the end of this time the equilibrium *p*H of the solutions was measured. Later, the synthetic products were centrifuged, washed, and dried at 60°C. Materials thus obtained were studied by x-ray diffraction, infrared spectroscopy, differential thermal analysis, and chemical analysis.

Analysis has revealed the following crystalline phases: gibbsite, bayerite, boehmite, and kaolinite (Fig. 1). Amorphous silicoalumina gels also were found in some samples.

Gibbsite was synthesized under acid conditions with a low ratio of SiO_2 to

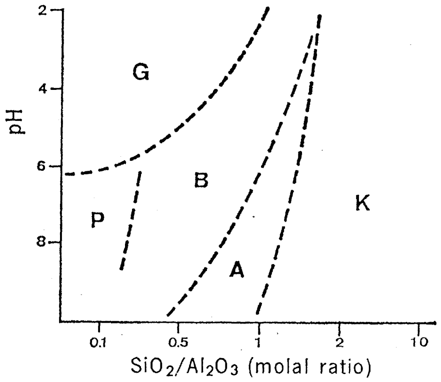

Fig. 1. Synthesized phases as a function of the equilibrium *p*H and the initial SiO_2/Al_2O_3 ratio in solution. *G*, gibbsite; *P*, pseudoboehmite; *B*, bayerite; *A*, allophane (?); *K*, kaolinite.

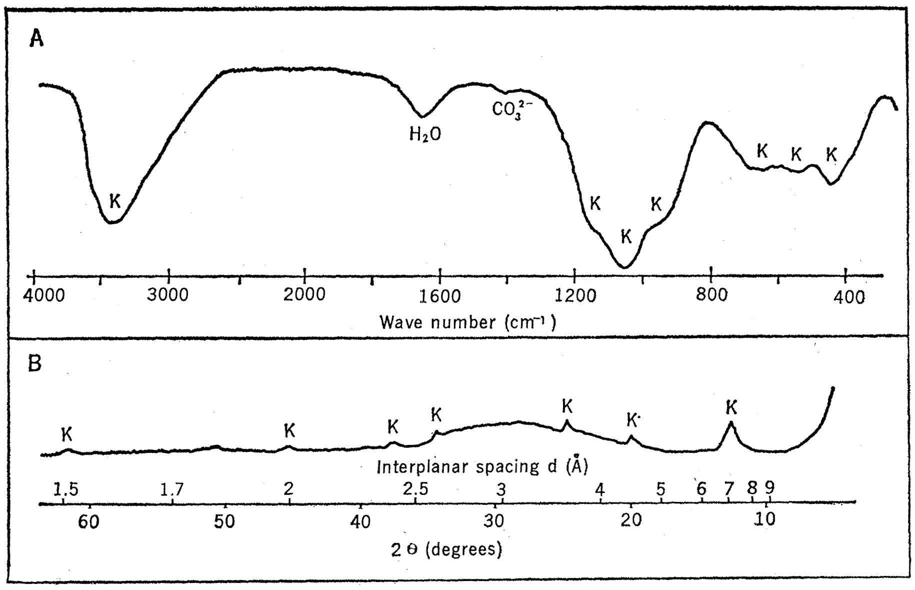

Fig. 2. (A) Infrared spectrum and (B) x-ray diffraction pattern of a synthetic koalinite (pH = 7 and SiO_2/Al_2O_3 ratio in solution = 2).

Al_2O_3. Gibbsite has been synthesized previously only in alkaline solution (*7*) or in dialyzed media (*2*). However, geological and pedological observations are in accordance with our results (*8*).

As an intermediate product of kaolinite formation, bayerite was also synthesized at an acid pH. Bayerite is known to form at pH = 10 according to the Bayer procedure (*2, 9*).

Finally, at ratios of SiO_2 to Al_2O_3 from 1 to 10 we have synthesized a prekaolinite. Although the product is not well crystallized because its aging period was only 1 month, the x-ray diffraction pattern and infrared spectrum show its existence (Fig. 2).

The results emphasize the possible importance of the acids from the organic matter of the soil in the removal of aluminum. The mobilization process in soil formation called "cheluviation" (*10*) is well known. The organic acids aid in promoting silicate hydrolysis by the formation of soluble complexes, mainly with aluminum. As an example, we know that this process occurs in the genesis of podzols; the eluvial horizon is impoverished in Al_2O_3, and at the end of the evolution a pure silica residue remains. The aluminum organic complex can migrate to the B horizon and then under acid conditions kaolinite and gibbsite are formed.

Let us now consider the aluminum hexacoordination problem. The reported experimental results show clearly that the presence of aluminum in a fulvic acid complex is essential to the formation of the aluminous octahedral layer in sixfold coordination. This previous hexacoordination makes possible an easy synthesis of kaolinite and gibbsite. The crystalline structure of gibbsite is composed of oxygen in hexagonal close packing with aluminum located in the holes (only two out of three available positions). This gibbsitic structural layer is necessary to the formation of kaolinite because it unites with a tetrahedral layer of silica.

On this basis a mechanism for the process of kaolinite formation can be suggested. When the pH of the ternary system consisting of $Si(OH)_4$, the aluminum–fulvic acid complex, and H_2O in acid medium is changed, colloidal aluminum hydroxide begins to precipitate slowly. This hydroxide may be formed by a competitive reaction among the organic ligands and the hydroxyl ions leading to a pregibbsitic structure; later, by a surface reaction, monomeric silica can be adsorbed. In this way, a tetrahedral layer of silica is "soldered" over an octahedral layer of aluminum, with the result that a 1 : 1 clay mineral, kaolinite, is formed. This proposed mechanism is in accordance with the ideas of DeKimpe and his co-workers (*1*), of Caillere and Henin (*11*), and of Gastuche and his co-workers (*2*) about the role of the octahedral layer in the formation of clay minerals.

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References and Notes

1. C. DeKimpe, M. C. Gastuche, G. W. Brindley, *Amer. Mineral.* **46**, 1370 (1961); G. W. Brindley and C. DeKimpe, *Nature* **190**, 254 (1961).
2. M. C. Gastuche, J. J. Fripiat, C. DeKimpe, *Colloq. Int. Cent. Nat. Rech. Sci. No. 105* (1962), pp. 57–82, 207–210; J. J. Fripiat and M. C. Gastuche, *Int. Clay Conf. Stockholm* **1**, 53 (1963); C. DeKimpe, M. C. Gastuche, G. W. Brindley, *Amer. Mineral.* **49**, 1 (1964).
3. R. Wey and B. Siffert, *Colloq. Int. Cent. Nat. Rech. Sci. No. 105* (1962), pp. 11–24; B. Siffert, thesis, University of Strasbourg, Strasbourg, France (1962).
4. P. Duchaufour, *Precis de Pedologie* (Masson, Paris, 1965).
5. J. Linares and F. Huertas, *Bol. Geol. Miner.*, in press.
6. The complexing capacity of fulvic acids was determined by the method of F. Scheffer, B. Ulrich, P. Hiestermann [*Z. Pflanzenernaehr. Dueng. Bodenk.* **78**, 168 (1957)].
7. J. H. De Boer, J. M. H. Fortuin, J. J. Steggerda, *Proc. Acad. Sci. Amsterdam* **B57**, 434 (1954).
8. G. Millot, *Geologie des Argiles* (Masson, Paris, 1964).
9. H. P. Rooksby, in *The X-Ray Identification and Crystal Structures of Clay Minerals*, G. Brown, Ed. (Mineralogical Society, London, 1961), chap. 10.
10. G. Pedro, M. Jamagne, J. C. Begon, *Soil Sci.* **107**, 462 (1969); L. P. Swindale and M. L. Jackson, *Congr. Int. Sci. Solvay 6th Paris* (1956), p. E233.
11. S. Caillere and S. Henin, *Colloq. Int. Cent. Nat. Rech. Sci. No. 105* (1962), pp. 31–44.
12. We thank Prof. J. L. Martin-Vivaldi, Department of Crystallography and Mineralogy, University of Madrid, Madrid, Spain, for suggestions and assistance.

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Maize from an Adena Mound in Athens County, Ohio

Abstract. *The discovery of a carbonized ear of maize in an Adena burial mound at Athens, Athens County, Ohio, is the first indisputable evidence of Adena maize horticulture. The mound contained typical middle Adena features, including a bark prepared burial, and has yielded charcoal radiocarbon dated at 280 B.C. ± 140 years.*

Salvage excavation of two Early Woodland burial mounds on a hilltop at the south edge of the city of Athens, Athens County, Ohio, has produced the first indisputable evidence of maize in an Adena component. The smaller mound, Daines Mound 1, was completely excavated during the summers of 1964 and 1965. Daines Mound 1 yielded an assemblage of typical Adena material, none of which was suitable for radiocarbon dating.

Excavation of the larger mound, Daines 2, was begun in 1965. A carbonized ear of maize was discovered here (Fig. 1). The specimen lay on