*Clays and Clay Minerals*, 1971, Vol. 19, pp. 219–227. Pergamon Press. Printed in Great Britain

# DIAGENETIC DEVELOPMENT OF KAOLINITE

**C. D. CURTIS* and D. A. SPEARS**
Department of Geology, The University, Sheffield S1 3JD, England

(*Received* 11 *August* 1970)

**Abstract**—Experimental solubility data for gibbsite and kaolinite are reviewed and applied to the problem of gibbsite stability within the natural environment. It is concluded that free alumina compounds formed (only) in lateritic soils will tend to silicify spontaneously in all sedimentary environments. This metasomatic reaction should be accompanied by massive volume expansion: unusual textures are to be anticipated.

Petrographic and field descriptions of a number of ancient kaolinitic sediments (some with, some without free alumina) are reviewed. It is concluded that silicification of hydrated aluminum oxides was an important mechanism of kaolinite formation in ancient sediments and that free alumina compounds persist only as a result of the unusual volume expansion associated with kaolinite formation.

## INTRODUCTION

"FREE" hydrated aluminum oxides (especially gibbsite) are common soil constituents in tropical moist climates and are found in surface marine sediments at low latitudes (Biscaye, 1965). Yet they rarely occur in ancient sediments. It is our purpose here to review recently published chemical information in an attempt to establish some logical explanation for the above and to trace the probable diagenetic alteration products of these free oxides.

Garrels was largely responsible for demonstrating the value of thermodynamic reasoning in this type of study. The diagenetic development of sulphides, carbonates, and silicates of iron from hydrated ferric oxides (Garrels and Christ, 1965; Berner, 1964; Curtis and Spears, 1968) has been treated in depth. This problem obviously is analogous to that presently under consideration.

The general form of stability relationships in the system $SiO_2$–$Al_2O_3$–$H_2O$ at 25°C and 1 atm. was outlined in Garrels and Christ (1965), whilst Hess (1966) reviewed naturally occurring assemblages in this system extended to include alkali metals. The present paper starts with an extension of these stability considerations to take account of recently published experimental solubility data.

## STABILITY RELATIONSHIPS IN THE SYSTEM $Al_2O_3$–$SiO_2$–$H_2O$

Understanding of the aqueous solution chemistry of aluminum has been improved by the recent series of reports by Hem and Roberson (Hem and Roberson, 1967; Hem, 1968; Roberson and Hem, 1969) and by Reesman and Keller (1969). Complexes with anions other than $OH^-$ were also considered.

Figure 1, curve (a) is taken from Roberson and Hem (1969) and shows the calculated solubility for a sample of microcrystalline gibbsite ($<0{\cdot}1\ \mu$) in the pure hydroxide system. The three dissolved species taken into account may well be the only important monomeric species, although some uncertainty remains in this matter, i.e.

$$C_{Al} = \frac{[Al^{3+}]}{\gamma Al^{3+}} + \frac{[AlOH^{2+}]}{\gamma AlOH^{2+}} + \frac{[Al(OH)_4^-]}{\gamma Al(OH)_4^-}$$

(where $C_{Al}$ = sum of molal concentrations of all Al species). Experimental precipitation behavior within the range pH 4·5–7·0 is complicated by very slow polymerization of simple octahedral cations, e.g. $AlOH(H_2O)_5^{2+}$, via a range of polynuclear complexes with hydroxyl bridges. Gibbsite is the ultimate polymer. Above pH 7·0, however, $Al(OH)_4^-$ predominates and reactions are fast. Schoen and Roberson (1970) showed that bayerite is the solid to form above pH 5·8.

Some doubt as to the true stability status of the $Al(OH)_3$ polymorphs must remain since certain aspects of precipitation behavior are at variance with natural distribution (gibbsite is far commoner than bayerite).

The solubility of microcrystalline gibbsite corresponds to a $\Delta F°_f$ value of −544·6 kcal/F.W. (Appendix 1). A value of −550·3 kcal/F.W. was obtained (solubility experiments) by Reesman and Keller (1968) for a naturally occurring gibbsitic clay. Single ion solubility equilibria (Appendix 2, equations 1–3) adequately serve to document the

*Session 1970/71 visiting: The Department of Geology, University of California, Los Angeles, Calif. 90024, U.S.A.



https://doi.org/10.1346/CCMN.1971.0190403 Published online by Cambridge University Press

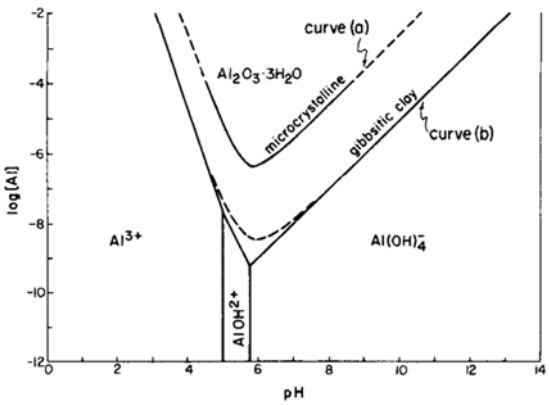



Fig. 1. The nature of gibbsite solubility in water (25°C, 1 atm.).

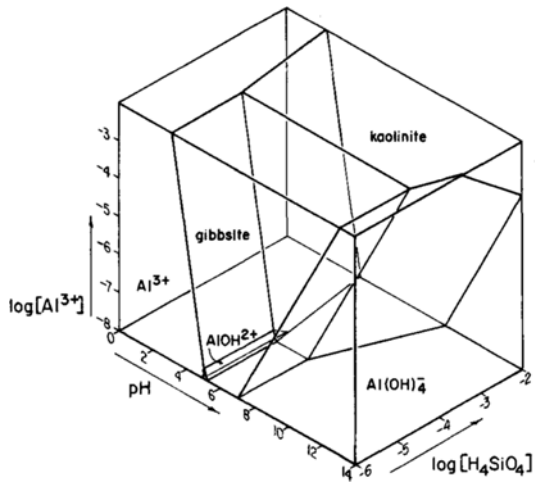



Fig. 2. Kaolinite/gibbsite stability relationships at 25°C, 1 atm. (solid/solution boundary at log [Al] $\leq -7$).

general trend of solubility behavior for this more stable material. The discontinuous curve b (Fig. 1) takes account only of the solubility contribution of each single ion within its pH range of dominance.

It would be misleading to suggest that the relationships depicted in Fig. 1 suffice to explain the behaviour of Al in all natural waters. Stable soluble complexes of Al with $F^-$ and $SO_4^{2-}$ are known, as are Al–Si complexes. The anionic complexes obviously become more important with decreasing pH. Hem (1968) and Roberson and Hem (1969) analyzed the contribution of these complexes to total Al-solubility, presenting graphical plots for determining the relative contributions of $OH^-$, $F^-$, and $SO_4^{2-}$ complexes. In natural waters, $F^-$ is most likely to disturb simple $OH^-$ equilibria. The effect must be considerable in acid waters but generally insignificant at pH values in excess of 7·0.

Figure 1 suggests that naturally occurring gibbsites are stable in the presence of minute total dissolved Al concentrations. At $C_{Al} \geq 10^{-7}$m, for example, the gibbsitic clay is stable throughout the pH range 5·0–8·0. Even microcrystalline gibbsite (minimum stability, is stable for $C_{Al} > 10^{-6}$ m; $5{\cdot}4 < pH < 6{\cdot}7$.

These stability considerations may be extended to take account of a number of solid and solution species in the system $SiO_2$–$Al_2O_3$–$H_2O$. Free energy values for silica containing species are listed in Appendix 1. Appendix 2 lists relationships between the aluminum species so far considered together with silicic acid, quartz, "amorphous" silica, and kaolinite.

Figure 2 demonstrates the general outline of stability relationships ignoring solid silica species. The form is similar to that illustrated by Garrels and Christ (1965, Fig. 10·3). The dominant solvated species are more realistic, as are inferred solubilities.

An instructive section through the block diagram is given in Fig. 3. Account of solid silica species is taken here. Solids are deemed stable when the coexisting equilibrium activity of Al in a solution is less than $10^{-7}$. This value is somewhat lower than that reported in most natural waters. The stability field of gibbsite is, therefore, minimal (unless, as is quite possible, natural water analyses tend to be on the high side due to suspended material). It is immediately apparent, as expected, that kaolinite is stable relative to gibbsite at all but very low dissolved silica activities. Very low

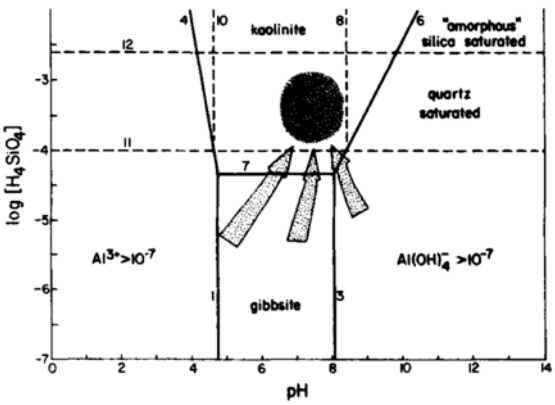



Fig. 3. Kaolinite/gibbsite stability relationships at 25°C, 1 atm. total pressure (system $H_2O$–$SiO_2$–$Al_2O_3$). Heavy shading shows the composition of natural groundwaters. Light shading (arrows) is representative of soil/precipitate water interaction. (The contribution of $H_3SiO_4^-$ to silica solubility at high pH is not documented.)

https://doi.org/10.1346/CCMN.1971.0190403 Published online by Cambridge University Press

values will be found in highly leaching environments such as in the classic lateritic soil situation. The interesting question is: in what other geochemical environments is gibbsite stable?

White, Hem and Waring (1963) compiled reliable information on the chemical composition of subsurface waters. Table 1 summarizes data on water selected from natural environments in which the waters were most likely to be atmospheric precipitation influenced primarily by reaction with the rocks in which they are found. The pH values all exceed 7·0 with surprisingly slight variation. These "meteoric" groundwaters are plotted as the shaded region on the $SiO_2$ vs. pH plot of Fig. 3.

Quite clearly, once atmospheric precipitation has had a little time to react with almost any rock type, gibbsite is no longer stable relative to kaolinite. These groundwaters are dilute solutions and slightly alkaline. Gibbsite should not persist once removed from its characteristically humid, tropical, and well-drained site of formation.

Although seawater is very poor in dissolved silica due to organic removal, sediment pore waters are silica rich. In a study of the mineralogy of recent deep-sea sediments in the Atlantic Ocean and adjacent areas, Biscaye (1965) recorded the presence of gibbsite. In this environment gibbsite must be metastable, its persistence indicating that the silicification reaction proceeds but slowly at low temperatures. Certainly (Biscaye, p. 810), some of the coarser grained samples (2–20$\mu$) are richer in gibbsite than are the finer grained samples. Kaolinite tends to occur with gibbsite, and a strong correlation was found between these two and proximity to continental areas undergoing intense tropical weathering. The maximum content of gibbsite in the sediments was in fact noted adjacent to small rivers ("local" source) rather than adjacent to the major rivers draining pedogenically diverse basins.

In the geological column where there are analogous sedimentary rocks of tropical derivation, kaolinite is abundant. Only in few instances, however, are aluminum hydroxides also present. It seems that these minerals persist with difficulty over geologic time. This observation is in keeping with the stability fields and groundwater compositions shown in Fig. 3. Prior to further discussion, however, the changes accompanying silica metasomatism will be considered.

## SILICA METASOMATISM

Figure 3 demonstrates that kaolinite is stable relative to gibbsite in almost all natural waters. The pH of subsurface waters ranges narrowly around 7·4 while log siliceous acid activity falls around −3·4. The same pH mean is representative of marine and estuarine sediment pore waters, but siliceous acid activities therein are often higher (limit log $[H_4SiO_4] = -2{\cdot}6$). Dissolved alumina

Table 1. Groundwater analyses
U.S.G.S. Professional Paper 440-F
"Water of low mineral content associated with common rock-types"
These dilute waters were selected from environments in which the waters were most likely to be atmospheric precipitation that was then influenced primarily by reactions with the rocks in which they are found (including associated soil zones).

| Table No. and group description | No. of samples | pH $\bar{x}$ | pH $S$ | ppm $SiO_2$ $\bar{x}$ | ppm $SiO_2$ $S$ |
|---|---|---|---|---|---|
| 1 Granite, rhyolite, and similar rock types | 15 | 7·15 | ±0·48 | 37 | ±19 |
| 2 Gabbro, basalt, and ultramafic rock types | 16 | 7·52 | ±0·79 | 41 | ±13 |
| 3 Andesite, diorite, and syenite | 4 | 7·55 | ±0·24 | 20 | ±9 |
| 4 Sandstone, arkose, and graywacke | 17 | 7·48 | ±0·82 | 23 | ±18 |
| 5 Siltstone, clay, and shale | 18 | 7·27 | ±1·25 | 28 | ±24 |
| 6 Limestone | 14 | 7·50 | ±0·37 | 13 | ±6 |
| 7 Dolomite | 6 | 7·72 | ±0·33 | 14 | ±7 |
| 8 Miscellaneous sedimentary rocks (ironstone, chert, phosphorite, lignite, gypsum) | 5 | 7·20 | ±0·55 | 18 | ±6 |
| 9 Quartzite and marble | 7 | 7·27 | ±0·60 | 11 | ±5 |
| 10 Slate, schist, gneiss, and miscellaneous metamorphic rocks | 15 | 7·09 | ±0·84 | 23 | ±19 |
| 11 Unconsolidated sand and gravel | 20 | 7·65 | ±0·69 | 31 | ±17 |



https://doi.org/10.1346/CCMN.1971.0190403 Published online by Cambridge University Press

values are minute under these conditions (equation 6, appendix 2 gives log $[Al(OH)_4^-] = -8{\cdot}60$ and $-9{\cdot}40$, respectively). At the same pH, the equilibrium value of log $[Al(OH)_4^-]$ coexisting with gibbsite in pure water is $-7{\cdot}66$.

Silicification of gibbsite is a metasomatic reaction and, as such, should be analyzed from the viewpoint of "open-system" thermodynamics (Korzhinsky, 1959; Thompson, 1959). Such an approach permits prediction of the spacial configuration of reacting systems. Essential to the arguments are assumptions concerning relative rates of reaction and diffusive mass transfer. Reactions in solid plus solution systems at high temperatures have been treated in this way (Curtis and Brown, 1969).

Consider (as in Fig. 4) an isolated system containing gibbsite plus water at pH 7·4 and a second, infinite system containing kaolinite plus amorphous silica. Linking the aqueous phases of the two systems establishes concentration gradients down which dissolved species must diffuse. The final configuration will be total conversion of gibbsite to kaolinite as shown. Incomplete reaction configurations may be zoned with sharp solidus compositional discontinuities: such possibilities will be discussed elsewhere.

In general terms, diffusive flux is controlled by diffusion coefficient and by concentration gradient. Diffusion coefficients for most simple dissolved species in aqueous solution are similar. This probably leaves concentration gradient as being dominant in controlling diffusion rate for any species. In Fig. 4 the inward concentration gradient for silica is $\sim 10^5$ times greater than the outward concentration gradient for alumina. Reaction, therefore, should proceed overwhelmingly via inward diffusion of silica. It is difficult to envisage kinetic or other effects that would totally invalidate this picture.

Metasomatic kaolinization, therefore, is additive (to one part in $10^5$ in the simplest approximation). It follows that in the reaction (pH independent)

$$Al_2O_3 3H_2O_{c.} + 2H_4SiO_{4aq.} = H_4Si_2Al_2O_{9c.} + 5H_2O_{l.}$$

some 158·23g gibbsite are transformed to 258·17g kaolinite. Assuming mean density values listed in Deer, Howie, and Zussman (1965), the volume expansion is 65·93 cm$^3$ to 97·42 cm$^3$ (some 48 per cent of the original). Such a volume increase will cause either marked porosity decrease or bed expansion wherever gibbsite is an important constituent. Stresses within the bed could be nonuniform and might be accommodated by either flow or fracture of the clay depending on the interaction of stress and physical properties of the material.

## CHARACTERISTICS OF SOME ANCIENT KAOLINITIC SEDIMENTS

### *Introduction*

Based on the kaolinite/gibbsite stability fields, we have concluded that only at very low dissolved silica activities is gibbsite stable relative to kaolinite. In modern environments such low activities are to be found in highly leached soil environments. Once a sediment is deposited in water, or a soil is submerged, the movement of pore water is severely restricted, and the dissolved silica concentration increases to a level at which gibbsite is no longer the stable phase. The abundance of gibbsite in modern tropical sediments, together with its virtual absence from the majority of sedimentary rocks, is in itself very good evidence that gibbsite is eliminated during diagenesis. Kaolinite is most likely to result from this alteration, and it is the probable consequences of this reaction which will be dealt with in the following discussion. It must be stressed, however, that in many diagenetic environments, pore waters are concentrated ionic solutions. Kaolinite may not be the only clay to develop from gibbsite.

### *"High-alumina" sedimentary rocks containing free alumina*

One such rock is the Ayrshire Bauxitic Clay (Scotland). The aluminum hydroxides present have been identified as boehmite and diaspore (Lapparent, 1936). This clay was concluded to have formed by lateritic weathering of a sequence of Namurian lavas resting on a slowly subsiding land surface. The deposits are intimately associated with the basic lava flows and in many cases appear to represent *in situ* soils. In some instances the clay is thought to have been transported over short distances and sedimented in lagoons (Wilson, 1922). Although referred to as bauxitic clay, 57 analyses (Wilson, 1922, Fig. 7) show that most samples contain little free alumina; the analyses approximate closely to ideal kaolinite.

Wilson interpreted petrographic evidence as implying formation of kaolinite after the clay was deposited and suggested that "this (process) was in reality a resilicification of much of the free alumina originally present in the rock" (p. 16). A volume change associated with this transformation was noted in porosity reduction. Lapparent (1936, p. 3) also noted that kaolinite was later than the boehmite and went so far as to state that "it would be erroneous to suppose that the hydroxides of aluminum arise from the alteration of kaolinite as has sometimes been suggested."

The textures developed within the Ayrshire Bauxitic Clay are very variable. Homogeneous

https://doi.org/10.1346/CCMN.1971.0190403 Published online by Cambridge University Press

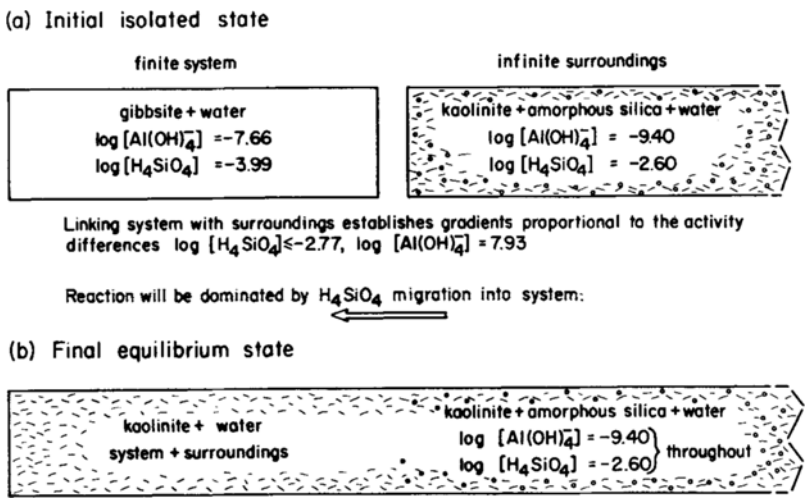



Fig. 4. Metasomatic reaction between gibbsite and amorphous silica saturated water.

material is found, some (as noted above) showing evidence of porosity reduction. At the other ex treme heterogeneous oolitic and fragmental textures occur. The fragmental form has been linked with ash texture (Eyles *et al.*, 1949). It is not at all difficult, however, to envisage all these textures arising as a consequence of silicification of homogeneous starting materials.

Progressive additive metasomatism of a gibbsite/water system would commence with porosity reduction. Within a *confined* system, further reaction would promote either flow or fracture. Continuing reaction after fracture would generate an oolitic texture in precisely the same way that weathering of igneous rocks causes spheroidal texture on a larger scale. Weathering itself is a typically metasomatic reaction involving $O_2$ and $H_2O$ addition. Centres of "oolites" obviously would be the most probable loci for gibbsite preservation as a consequence of low porosity surroundings.

In our opinion, the chemical model outlined in the present paper increases confidence in the textural interpretations due to Wilson and Lapparent. Diagenetic silicification of free alumina minerals (sometimes in confined environments) appears to have been an important mechanism of kaolinite formation in the Ayrshire deposits.

Similar in many respects to the Ayrshire material are the high alumina clays of the Mercer Formation (Pennsylvanian) of western Pennsylvania (Foose, 1944; Williams, 1960, 1968). The latter author suggests that the clays developed on topographic highs whilst peat and other sediments accumulated in the adjacent topographic lows; "extensive leaching over a period of time probably altered illite to kaolinite and kaolinite to boehmite and diaspore". Lateritic soil development is seen as being responsible for free oxide formation, but the possibility of resilicification was not discussed.

In the Mercer Formation clays, diaspore occurs as nodules (1–5 mm) in a kaolinite matrix. The two components vary in most proportions from nearly pure diaspore through to flint clay (Foose, 1944, p. 567). This nodular texture is not unlike the so-called oolitic texture of the Ayrshire clay; a similar mechanism of formation may be postulated.

It is significant also that the iron content of the Mercer clays varies directly as the alumina content. Whilst ferric oxides are common constituents of sediments at deposition, pore solutions after burial usually become strongly reducing, and ferric compounds are either transformed or leached. Restricted pore-water circulation (low porosity) obviously would favour the preservation of ferric iron from reduction and free alumina from silicification. Complex color textures due to iron pigmentation are to be anticipated.

Two environmental factors emerge from the above studies as being essential to the development and preservation of "free-alumina" clays. Lateritic soils (by analogy with present-day distribution) call for moist tropical climates and well-drained sites of formation. In order that free oxides should constitute a significant fraction of sediment at deposition, zero (i.e. submergence of *in situ* soil profiles) or slight transport should occur. Otherwise, of course, dilution by more usual (silica-rich) sediments would take place. Sedimentation must be considered on a strictly local scale.

https://doi.org/10.1346/CCMN.1971.0190403 Published online by Cambridge University Press

*High-alumina sedimentary rocks without free alumina*

A number of relatively pure kaolinitic rocks are known with unusual and distinctive textures. Since partial silicification of free-alumina minerals seems to be well documented and the silicification process a spontaneous one, it is only to be expected that this process should have gone to completion somewhere in the column.

Sequences already discussed (Ayrshire and Mercer) suggest strongly that climatic conditions were favourable for laterite development within the Carboniferous (Westphalian A and B, respectively). Free alumina minerals were at least possible sediment precursors during these times. As already outlined, their effect on sediment composition would be most marked within depositional basins of small extent.

The compositional variation between diaspore-rich and flint clays in the Mercer Formation is lateral (Foose, 1944, p. 571). Lateral facies relationships are discussed in detail in Keller's (1968) account of flint clays.

In the Missouri clays, also of Pennsylvanian age, the facies sequence is believed to be from marine illitic shales, through kaolinite–illite clays to kaolinitic flint clays and finally to diaspore and boehmite-bearing clays. A similar sequence has also been described from the Russian "toasted clays" (Chuckhrov, 1970). Based on the North American occurrences, Keller proposed (1968, p. 125) that "flint clay is characteristically a facies member in a non-marine mudstone sequence that includes high-alumina minerals, or potentially so, grading through flint clay into plastic clay and thence extending into marine shale".

The present authors envisage these deposits to have originated in the following manner: (1) Kaolinite and gibbsite formed sub-aerially on a positive area adjacent to the basin of deposition. (2) This material was supplied to the immediate area of the basin either over a long period or relatively quickly as in the case of a marine transgression. (3) With distance from the local source there was progressive mixing with less mature sediment. (4) Diagenetic elimination of some of the free-alumina minerals in the bauxitic clays followed (total elimination in the flint clays). Kaolinite content was enhanced. The survival of the free-alumina minerals near or at the source of the sediment was favoured firstly by the higher initial gibbsite content and secondly by the prior removal of free silica. In diagenetic environments where cation contents are high, gibbsite need not alter to kaolinite, but it should be noted that the association of the flint clays with the non-marine environment is an association with diagenetic pore waters of relatively low cation content. In the marine environment, pore waters are much concentrated, and alteration of gibbsite to 10 Å minerals is probable.

The explanation favoured by Keller (1968) for facies relationships involving flint clays was that parent illitic and/or kaolinitic clay colloids were transported into swamps and these underwent dialysis, alteration, and eventual crystallization *in situ*. In some cases desilification proceeded further to give high-alumina minerals, particularly diaspore and boehmite.

Formation of kaolinite by leaching of illite material in swamp environments formerly was favoured by European workers concerned with the genesis of thin bands of kaolinitic mudstone (tonsteins) that occur in coal-bearing strata. These bands persist laterally over great distances and are of considerable stratigraphic value. Recently, however, a volcanic origin has been substantiated (Price and Duff, 1969; Williamson, 1970; Spears, 1970).

A different approach to the mechanism of kaolinite formation was adopted by Bouroz (1964). The composition of thin dirt-partings in coal seams was determined on the basis that this is where the alteration of illite to kaolinite should be most effective, firstly because of the association with coal and secondly because of the very fine-grained nature of the sediment. Excluding the partings of volcanic origin, he found one parting had a mixed clay content, two contained more than 80 per cent illite, and eleven contained more than 90 per cent illite. These results certainly do not support the hypothesis of kaolinization of illite in the swamp environment.

One final topic relevant to this discussion is textural and structural features of the flint clays themselves. The hardness and sub-conchoidal fracture of flint clays are unusual for argillaceous rocks. Electron micrographs show that these distinctive properties are due to interlocking kaolinite grains, producing a texture which has been likened to that of an igneous rock (Keller, 1968, p. 115). It is difficult to escape the conclusion that some of the kaolinite crystallized *in situ*, as would be the case if this kaolinite developed from gibbsite. On the other hand, it is more difficult to explain this texture if the kaolinite formed by the *in situ* degradation of an illitic clay, for this involves loss of elements and, initially at least, an increase in pore volume.

The principal features of flint clays, apart from their kaolinite composition, have been enumerated by Smith and O'Brien (1965). These are: (1) Deposits are of local extent and often of sinuous form. (2) They generally have a brecciated or

https://doi.org/10.1346/CCMN.1971.0190403 Published online by Cambridge University Press

conglomeratic structure and conchoidal or sub-conchoidal fracture. (3) They are conspicuously varicolored. We believe that most if not all of these features are consistent with spontaneous resilicification of free aluminum (and iron) oxide minerals derived from lateritic soil profiles. The typically observed form of deposits is to be expected if material is derived from a local source. The structures can be attributed to expansion following the addition of silica rather than to contraction. The brecciated structure is so characteristic of kaolinite deposits in Scotland and the north of England that they have been referred to as fragmental clay rocks (Richardson and Francis, 1971). The North American flint clays appear to be similar in many respects. The conchoidal or sub-conchoidal fracture has been dealt with above. The varicoloured appearance likewise may be attributed to limitation of porosity, the usual diagenetic reduction and redistribution processes being hampered in an irregular way.

## CONCLUSIONS

Recent solubility experiments suggest that gibbsite is unstable relative to kaolinite except in extremely silica-poor solutions. Sites of lateritic weathering would appear to be the only natural environments (at the present time) where free alumina solids may form and persist as equilibrium phases. When eroded and deposited as sediment, gibbsite invariably should silicify spontaneously to kaolinite in "freshwater", and to more complex phyllosilicates in the strong ionic solutions of marine environments. Further analysis of experimental relationships suggests that the silica metasomatism should be accompanied by massive volume expansion.

The petrographic and field evidence from some ancient bauxite deposits lends support to these predictions. Resilicification should not be confined to deposits which still contain free-alumina minerals, for there must also be deposits in which resilicification is complete. In this paper it has been suggested that many flint clays fall into this category. This assertion is supported by the geometry of the deposits, the facies relationships with other beds, the structures within the deposits, the textures as revealed in electron micrographs and indirectly by physical properties, and finally, of course, by the monomineralic kaolinite composition.

*Acknowledgments*—One of us (C. D. C.) would like to state his appreciation of research facilities and technical assistance made available by the Department of Geology at UCLA. Vicki Doyle and Jeanie Martinez (UCLA) assisted materially with the production of the final manuscript.

## REFERENCES

Berner, R. A. (1964) Stability fields of iron minerals in anaerobic marine sediments: *J. Geol.* **72**, 826–834.

Biscaye, P. E. (1965) Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans: *Bull. Geol. Soc. Am.* **76**, 803–832.

Bouroz, A. (1964) Les composants petrographiques principaux des schistes houillers et leur signification sedimentologique: *C. R. 5e Congrès. Intern. Carbonifère. Paris, 1963* pp. 289–301.

Chukhrov, F. V. (1970) Analogues of flint clays in Soviet literature: *Clays and Clay Minerals* **18**, 1–5.

Curtis, C. D. and Brown, P. E. (1969) The metasomatic development of zoned ultrabasic bodies in Unst, Shetland: *Contr. Mineral and Petrol.* **24**, 275–292.

Curtis, C. D. and Spears, D. A. (1968) The formation of sedimentary iron minerals: *Econ. Geol.* **63**, 257–270.

Deer, W. A., Howie, R. A. and Zussman, J. (1962) Rock Forming Minerals. *Sheet Silicates* Vol. III, Longmans, London.

Eyles, V. A., Simpson, J. B. and MacGregor, A. G. (1949) Geology of Central Ayrshire: *Mem. Geol. Surv. Gt. Britain.*

Foose, R. (1944) High-alumina clays of Pennsylvania: *Econ. Geol.* **39**, 557–577.

Garrels, R. M. and Christ, C. L. (1965) *Solutions, Minerals and Equilibria*, 450 p. Harper & Row, New York.

Hem, J. D. (1968) Graphical methods for studies of aqueous aluminum hydroxide, fluoride and sulphate complexes: *U. S. Geol. Surv. Water-supply Paper 1827-B*, 33p.

Hem, J. D. and Roberson, C. E. (1967) Form and stability of aluminum hydroxide complexes in dilute solution: *U.S. Geol. Surv. Water-supply Paper 1827-A*, 55p.

Hess, P. C. (1966) Phase equilibrium of some minerals in the $K_2O$–$Na_2O$–$Al_2O_3$–$SiO_2$–$H_2O$ system at 25°C and 1 atmosphere: *Am. J. Sci.* **264**, 289–309.

Keller, W. D. (1968) Flint clay and a flint-clay facies: *Clays and Clay Minerals* **16**, 113–128.

Korzhinsky, D. S. (1959) *Physico-chemical basis of the analysis of the paragenesis of minerals.* Translated from the Russian by Consultants Bureau Inc., New York.

Lapparent, J. de (1936) Boehmite and diaspore in the bauxitic clays of Ayrshire: *Sum. Prog. Geol. Surv. Gt. Britain for 1934*, pt. ii, p. 1.

Price, N. B. and Duff, P. McL. D. (1969) Mineralogy and chemistry of tonsteins from Carboniferous sequences in Great Britain: *Sedimentology* **13**, 45–69.

Reesman, A. L. and Keller, W. D. (1968) Aqueous solubility studies of high-alumina and clay minerals: *Am. Mineralogist* **53**, 929–942.

Reesman, A. L., Pickett, E. E. and Keller, W. D. (1969) Aluminum ions in aqueous solutions: *Am. J. Sci.* **267**, 99–113.

Richardson, G. and Francis, E. H. (1971) Fragmental clayrocks (F. C. R.) in coal bearing sequences in Scotland and north-east England: *Proc. Yorks. Geol. Soc.* **38**, 229–260.

Roberson, C. E. and Hem, J. D. (1969) Solubility of aluminum in the presence of hydroxide, fluoride and sulphate: *U.S. Geol. Surv. Water-supply* Paper 1827-C, p. 37.

https://doi.org/10.1346/CCMN.1971.0190403 Published online by Cambridge University Press

Schoen, R. and Roberson, C. E. (1970) Structure of aluminum hydroxides and geochemical implications: *Am. Mineralogist* **55**, 43–77.

Smith, W. H. and O'Brien, N. R. (1965) Middle and late Pennsylvanian flint clays: *J. Sediment. Petrol.* **35**, 610–618.

Spears, D. A. (1970) A kaolinite mudstone (tonstein) in the British coal measures: *J. Sediment. Petrol.* **40**, 386–394.

Thompson, J. B. (1959) Local equilibrium in metasomatic processes. In *Researches in Geochemistry* (Edited by Abelson, P. H.), Wiley, New York.

White, D. E., Hem, J. D. and Waring, G. A. (1963) Chemical composition of subsurface waters. Chapter F, Data of Geochemistry: *U.S. Geol. Surv. Prof.* Paper 440-F, p. 67.

Williams, E. G. (1960) Relationship between the stratigraphy and petrography of Pottsville sandstones and the occurrence of high-alumina Mercer clay: *Econ. Geol.* **55**, 1291–1302.

Williams, E. G., Berbenback, R. E., Falla, W. S. and Udagawa, S. (1968) Origin of some Pennsylvanian underclays in western Pennsylvania: *J. Sediment. Petrol.* **39**, 1179–1193.

Williamson, I. A. (1970) Tonsteins – their nature, origins and uses: *Mining Mag.* **122**, 119–125, 203–211.

Wilson, G. V. (1922) The Ayrshire bauxitic clay: *Mem. Geol. Surv. Gt. Britain.*

## APPENDIX 1
## FREE ENERGY DATA USED

| Species | $\Delta F_f^\circ$ | Ref. and comments |
|---|---|---|
| $SiO_{2\ quartz}$ | −204·71 | Weise, S. S., Margrave, J. F., Feder, H. M. and Hubbard, W. N. (1962) The heats of formation of silica and silica tetrafluoride: *J. Phys. Chem.* **66**, 381. |
| $H_4SiO_{4aq.\ silicic\ acid}$ | −312·65 | Reesman, A. L. and Keller, W. D. (1967) Chemical composition of illite: *J. Sediment. Petrol.* **37**, 592–596. Calculated from Weise value. |
| $Al_2O_3{\cdot}3H_2O_{gibbsite}$ | −544·6 | Hem, J. D. and Roberson, C. E. (1967) Form and stability of aluminium hydroxide complexes in dilute solution: *U.S.G.S. Water-supply Paper 1827-A.* |
| $Al^{3+}_{aq.}$ | −115·0 | Garrels and Christ (1965). |
| $Al(OH)^{2+}_{aq.}$ | −164·9 | Raupach, M. (1963) Solubility of simple aluminium compounds expected in soils – I. Hydroxides and oxyhydroxides: *Aust. J. Soil Res.* **1**, 28–35. |
| $Al(OH)^{-}_{4aq.}$ | −311·3 | Reesman and Keller (1968) (Hem and Roberson = −311·7). |
| $H_2O_{l.}$ | −56·69 | Garrels and Christ (1965). |
| $SiO_{2\ glass}$ | −202·82 | Garrels and Christ (1965) (recalculated relative to Weise). |
| $H_4Al_2Si_2O_{9\ kaolinite}$ | −904·0 | Reesman and Keller (1968) Average of numerous sample experiments. |

## APPENDIX 2
## EQUILIBRIA

$$Al_2O_3 3H_2O_{c.} + 6H^+_{aq.} = 2Al^{3+}_{aq.} + 6H_2O_{l.}$$
$$\log [Al^{3+}] = 7{\cdot}27 - 3pH \quad (1)$$

$$Al_2O_3 3H_2O_{c.} + 4H^+_{aq.} = 2Al(OH)^{2+}_{aq.} + 4H_2O_{l.}$$
$$\log [Al(OH)^{2+}] = 2{\cdot}295 - 2pH \quad (2)$$

$$Al_2O_3 3H_2O_{c.} + 2H_2O_{l.} = 2Al(OH)^{-}_{4aq.} + 2H^+_{aq.}$$
$$\log [Al(OH)_4^-] = -15{\cdot}058 + pH \quad (3)$$

$$H_4Al_2Si_2O_{9c.} + 6H^+_{aq.} = 2Al^{3+}_{aq.} + 2H_4SiO_{4aq.} + H_2O_{l.}$$
$$\log [Al^{3+}] = 2{\cdot}929 - \log [H_4SiO_4] - 3pH \quad (4)$$

https://doi.org/10.1346/CCMN.1971.0190403 Published online by Cambridge University Press

$$H_4Al_2Si_2O_{9c.} + 4H^+_{aq.} + H_2O_{l.} = 2Al(OH)^{2+}_{aq.} + 2H_4SiO_{4aq.}$$
$$\log [Al(OH)^{2+}] = -2{\cdot}049 - \log [H_4SiO_4] - 2pH \quad (5)$$

$$H_4Al_2Si_2O_{9c.} + 7H_2O_{l.} = 2Al(OH)^-_{4aq.} + 2H^+_{aq.} + 2H_4SiO_{4aq.}$$
$$\log [Al(OH)_4^-] = -19{\cdot}401 - \log [H_4SiO_4] + pH \quad (6)$$

$$H_4Al_2Si_2O_{9c.} + 5H_2O_{l.} = Al_2O_3 3H_2O_{c.} + 2H_4SiO_{4aq.}$$
$$\log [H_4SiO_4] = -4{\cdot}344 \quad (7)$$

$$H_4Al_2Si_2O_{9c.} + 3H_2O_{l.} = 2SiO_{2c.} + 2Al(OH)^-_{4aq.} + 2H^+_{aq.}$$
$$\log [Al(OH)_4^-] = -15{\cdot}413 + pH \quad (8)$$

$$H_4Al_2Si_2O_{9c.} + 4H^+_{aq.} = 2SiO_{2c.} + 2Al(OH)^{2+}_{aq.} + 3H_2O_{l.}$$
$$\log [Al(OH)^{2+}] = 1{\cdot}939 - 2pH \quad (9)$$

$$H_4Al_2Si_2O_{9c.} + 6H^+_{aq.} = 2SiO_{2c.} + 2Al^{3+}_{aq.} + 5H_2O_{l.}$$
$$\log [Al^{3+}] = 6{\cdot}917 - 3pH \quad (10)$$

$$SiO_{2c.} + 2H_2O_{l.} = H_4SiO_{4aq.}$$
$$\log [H_4SiO_4] = -3{\cdot}988 \quad (11)$$

$$SiO_{2\ glass} + 2H_2O_{l.} = H_4SiO_{4aq.}$$
$$\log [H_4SiO_4] = -2{\cdot}60 \quad (12)$$

**Résumé** – Les données concernant la solubilité expérimentale de la gibbsite et de la kaolinite sont passées en revue et appliquées au problème de la stabilité de la gibbsite dans l'environnement naturel. On en conclut que les composés à alumine libre formés (seulement) dans les sols latéritiques tendront à se silicifier spontanément dans tous les environnements sédimentaires. Cette réaction métasomatique devrait être accompagnée d'une expansion massive du volume: des textures inhabituelles sont donc à attendre.

Les descriptions pétrographiques et de terrain d'un certain nombre de sédiments kaolinitiques anciens (certains avec, certains sans alumine libre) sont passées en revue. On en conclut que la silicification des oxydes d'aluminium hydratés a été un mécanisme important pour la formation de kaolinite dans les sédiments anciens, et que les composés à alumine libre persistent seulement en tant que résultat de l'expansion en volume inhabituelle, associée à la formation de kaolinite.

**Kurzreferat** – Es werden experimentelle Löslichkeitsdaten für Gibbsit und Kaolinit überprüft und auf das Problem der Stabilität von Gibbsit in natürlicher Umgebung angewendet. Es wird der Schluss gezogen, dass (ausschliesslich) in lateritischen Böden gebildete freie Tonerdeverbindungen dazu neigen werden in allen Sedimentärumgebungen spontan zu verkieseln. Eine solche metasomatische Reaktion würde von massiver Volumenausdehnung begleitet werden. Ungewöhnliche Gefüge sind zu erwarten.

Es werden petrographische und Feldbeschreibungen einer Anzahl alter kaolinitischer Sedimente (manche mit, manche ohne freie Tonerde) überprüft. Es wird der Schluss gezogen, dass Verkieselung hydratisierter Aluminiumoxyde ein wichtiger Vorgang bei der Kaolinitbildung in alten Sedimenten war und dass freie Tonerdeverbindungen nur als eine Foloe der ungewöhnlichen, mit der Kaolinitbildung verbundenen Volumenausdehnung weiter vorhanden sind.

**Резюме** — Рассмотрены и применены для решения проблемы устойчивости гиббсита в природной обстановке экспериментальные данные по растворимости гиббсита и каолинита. Сделан вывод, что соединения свободного глинозема, образованные (только) в латеритовых почвах, будут иметь тенденцию к спонтанной силисификации в любой среде в осадках. Эта реакция замещения должна сопровождаться значительным увеличением объема; при этом можно ожидать появления необычных текстур.

Проанализированы петрографические данные и условия залегания ряда древних каолинитовых осадков со свободным глиноземом и без него. Авторы пришли к заключению, что силисификация гидратированных окислов алюминия является важным механизмом образования каолинита в древних осадках и что соединения свободного глинозема сохраняются только благодаря необычному увеличению объема при образовании каолинита.

https://doi.org/10.1346/CCMN.1971.0190403 Published online by Cambridge University Press