Reports

Transformation of Montmorillonite to Kaolinite during Weathering

Abstract. *Extensive deposits of kaolinite in Florida are formed by transformation of montmorillonite during low-temperature supergene weathering. The transformation occurs by intracrystalline leaching of interlayer cations and tetrahedral silica layers. Interposition of stripped layers within montmorillonite creates a regular 1 : 1 mixed-layered montmorillonite-kaolinite, a new clay structure. Kaolin-like layers are nourished by lateral epitaxy, as the iron-rich montmorillonite decomposes. Hexagonal outgrowths of new kaolinite develop at the edges of montmorillonite flakes and nucleate new vertical growth. Kaolinitic sands impregnated with goethite are ultimately formed, and the released silica enriches groundwater and forms secondary chert.*

Transformation of green montmorillonite to gray kaolinite during subaerial weathering has created zones of kaolinite several feet thick over hundreds of square miles of central Florida, demonstrating both the viability of this conversion at low temperature and its role as a major geochemical process. Oyster shells silicified as a byproduct of the transformation [montmorillonite + $H_2O \rightarrow$ kaolinite + SiO_2 + (Fe_2O_3, MgO, K_2O . . .)] are the first marine fossils found in the deeply weathered and much debated Citronelle (?) deposits of Florida.

Any weathering reaction involving commonplace and abundant minerals is geochemically and economically important. The conversion of montmorillonite to kaolinite is especially noteworthy, however, for it represents a major stage in the larger weathering cycle. Structurally it exemplifies the breakdown of complex sheet silicates to simpler 1:1 layer structures. The liberated SiO_2, Fe_2O_3, MgO, and K_2O may enrich groundwater and form secondary chert, geothite, and possibly dolomite, on a regional scale.

The low-temperature conversion has been previously proposed to explain inverse concentration relations between montmorillonite and upward-increasing kaolinite in weathering profiles (*1, 2*). It was also suggested in extrapolation of the higher-temperature hydrothermal replacement of montmorillonite by kaolinite and leaching experiments on micas (*2–4*). Nevertheless, despite its seeming applicability to a number of geochemical problems, the low-temperature conversion of montmorillonite to kaolinite has not been generally accepted by geologists or mineralogists (*5*), primarily because the details of replacement or transformation have not been demonstrated. Moreover, inverse relationship in stratigraphic sequences does not automatically denote conversion of one mineral to another, but may be due to primary facies or sorting changes.

In our field geochemical studies of weathering in Florida it has been possible to avert such ambiguities through stratigraphically controlled comparisons (by x-ray, chemical, and electron-microscope study) of fresh and weathered rock from the same stratum or zone, and therefore of identical original lithology. The unequivocal nature of the field relations is shown in Figs. 1 and 2. The general lithologic sequence of the Bone Valley and Citronelle formations, both of Pliocene age, is one of loose surface sands overlying massive, clayey sands which exhibit only fine gradational textural changes, but yield downward to pronounced graded-bedded and cross-bedded sequences. Disconformities are absent in the upper clayey sands, and thin, primary strata can be traced laterally through several stages of the discordant and obviously secondary zone of weathering.

Clay in the lower unaltered Bone Valley Formation is green to blue-green nontronitic montmorillonite. Clay in the upper zone is generally gray. The zone has been called the Bartow clay by local miners. As shown in Fig. 1 and reported previously (*6*) the gray zone irregularly transgresses the primary bedding from the surface downward, and as its clay is kaolinite it must be the product of subaerial alteration of montmorillonite (*6*). Where the weathered zone occasionally thins or disappears, the Bone Valley Formation is green to a correspondingly higher level and irregular green patches appear in the coextensive gray weathered zone (Fig. 1).

The Citronelle Formation provides another example of the subaerial transformation of montmorillonite to kaolinite. The Citronelle or "unnamed coarse clastices" (*7*) of north-central Florida is a blanket of red-stained kaolinitic quartz sands, not previously known to contain marine fossils, and presumed to be entirely kaolinitic. It has therefore been considered to be of terrestrial or deltaic origin (*7, 8*), and the red mottling has been ascribed to weathering of heavy minerals (*8*).

In a road-metal quarry in the city of Mascotte, however, typical Citronelle material is underlain without a stratigraphic break by montmorillonite clay (Fig. 2). The montmorillonite occurs in 3-inch bands of green sandy clay that crop out in a prospect ditch in the floor of the quarry. The overlying 12 to 15 feet of sediment is kaolinitic sand irregularly impregnated by orange and red goethite. One foot beneath the uppermost green clayey band is a second green clayey band containing silicified oyster shells of unreworked aspect. The two green bands

Table 1. Chemical analyses of clays from Bone Valley Formation, Saddle Creek Mines, Florida. Analyses were made of clay fractions ($-2\,\mu$) settled from clays containing quartz, apatite, and accessory minerals. Analyses have been corrected for identified apatite and crandallite after chemical determination of leachable P_2O_5, CaO, and Al_2O_3. Samples: SC 1, montmorillonite, basal part of the formation; SC 2, kaolinized montmorillonite, upper part of formation; SC 12, kaolinite, completely transformed, stratigraphic equivalent of sample SC 2. Analyzed by H. Kramer.

Compound	Composition (%)		
	SC 1	SC 2	SC 12
SiO_2	56.91	51.99	47.38
Al_2O_3	22.65	30.78	35.19
Fe_2O_3	6.29	2.55	1.56
FeO	.11	.21	.20
MgO	3.62	2.19	.86
CaO	1.47	.32	.26
Na_2O	.18	.12	.06
K_2O	.74	.92	.52
Li_2O	.03	.01	.01
H_2O^+	7.34	9.89	11.94
TiO_2	.65	1.03	2.01
Total	99.99	100.01	99.99

are traceable 150 feet eastward to a slightly higher altitude, where the clays are gray and irregularly impregnated by iron oxides, but the thicknesses, stratigraphic interval, and silicified oyster shells persist (Fig. 2).

Optical and x-ray study shows that the green clay is composed of disorganized montmorillonite and poorly crystallized kaolinite. The gray stratigraphic equivalent is almost entirely kaolinite of improved crystallinity, with a barely detectible x-ray diffraction peak in the montmorillonite region. Apparently, at least part of the Citronelle Formation, or possibly all of the superjacent red kaolinitic sand, was originally a green, fossiliferous, marine sequence of iron-rich montmorillonitic sand. The leaching process that transformed the montmorillonite to kaolinite and goethite also removed the fossils; rarely, where permeability was lower, fossils remained to be silicified, and now reveal both the original marine nature of the rock and the alteration process.

X-ray diffraction studies of the clay from the Bone Valley Formation in the Saddle Creek area reveal the alteration sequence (Fig. 3). The blue-green unaltered basal clay (sample SC 1) is a pure montmorillonite which responds to glycolation and heat treatment as a single well-crystallized phase. In sample SC 2, a green clay from a residual green patch in the upper discordant gray zone, a prominent 7.2-Å kaolinite peak is present, and the montmorillonite reflection is disorganized, broadened, and decreased in intensity. The results of heating and glycolation and the (060) reflection of $d = 1.485$ Å preclude the presence of chlorite. Sample SC 12, the fully altered equivalent of SC 2, is virtually pure kaolinite. It is unaffected by glycolation and collapses when heated to 500°C.

Chemical analyses (Table 1) confirm the alteration paragenesis shown by field and x-ray studies. The basal unaltered clay is a ferric-rich montmorillonite of dioctahedral nature, a fact confirmed by x-ray determination of the (060) reflection at 1.495 Å. The fully altered clay (SC 12) has a typical kaolinite composition in its major constituents of SiO_2, Al_2O_3, and H_2O. Its atypically high contents of MgO, Fe_2O_3 and K_2O reflect its origin from iron-rich montmorillonite. Sample SC 2, the partially altered clay, although stratigraphically equivalent to SC 12, has a composition intermediate to that

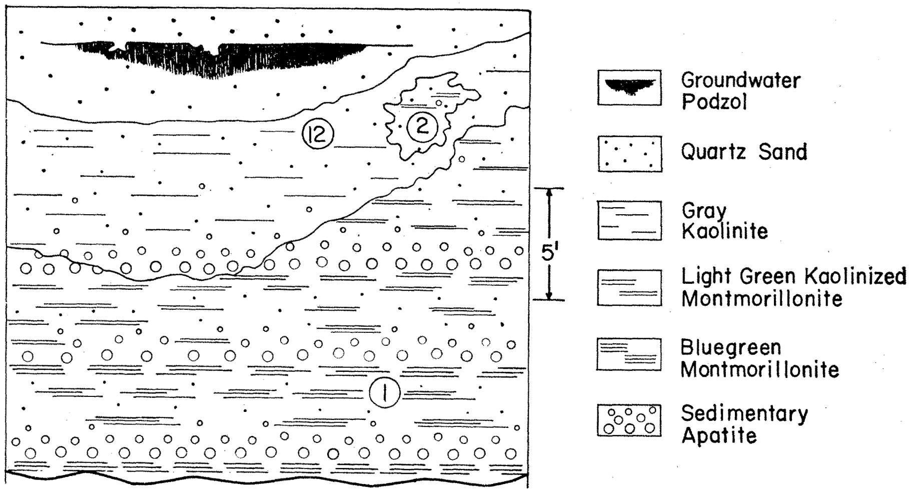

Fig. 1. Field relations of fresh and weathered clay (gray kaolinite) in Bone Valley Formation, Saddle Creek area, Florida (circled numbers are sample positions).

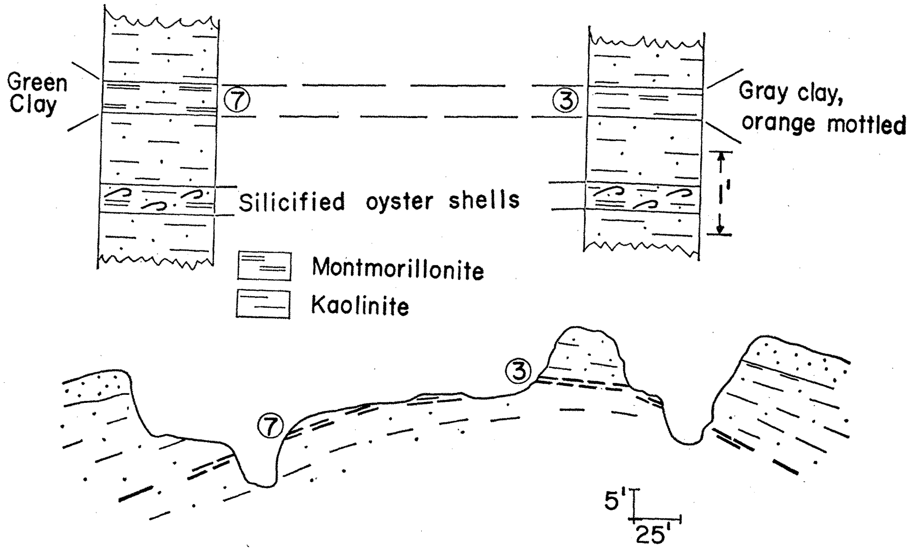

Fig. 2. Stratigraphy and clay relations of exposed Citronelle Formation in borrow pit west of Mascotte, Florida (circled numbers are sample locations).

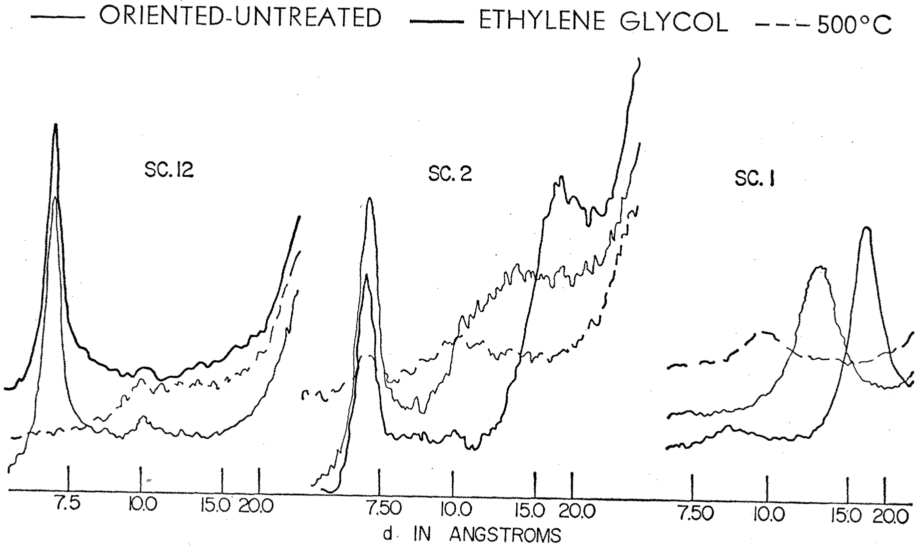

Fig. 3. X-ray powder diffraction patterns of clays at Saddle Creek. Compare with Fig. 1. Basal unaltered clay, SC 1; Intermediate alteration, SC 2; Advanced alteration, SC 12.

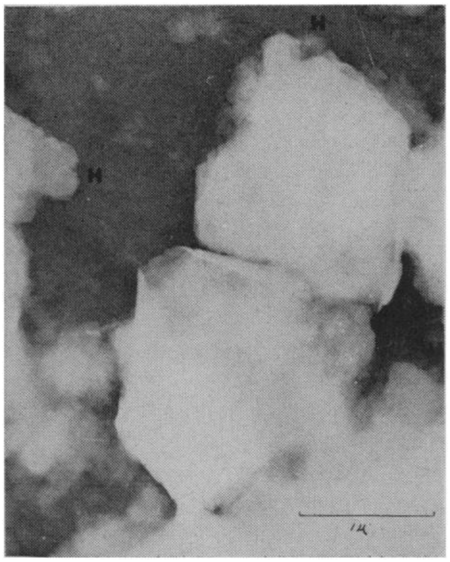

Fig. 4. Partly kaolinized montmorillonite from Achan and Mascotte (*7*, Fig. 2), showing development of hexagonal morphology (*H*) on grains with curls and wisps characteristic of montmorillonite.

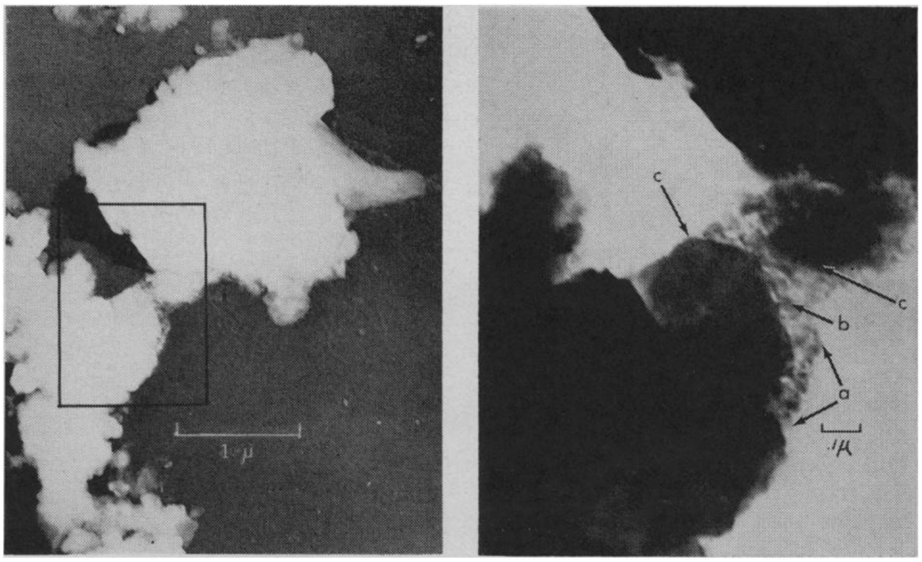

Fig. 5. Advanced kaolinization of montmorillonite (Mascotte, sample 3, Fig. 2). Left, hexagonal outgrowths on new kaolinite project from large flake with residual curving edge of montmorillonite. Right, enlargement (shadow is white): crystallites (*b*) and hexagonal plates (*c*) of kaolinite in morphological orientation to thin sheet (*a*, 40 Å thick) upon which they were nucleated.

of SC 1 and SC 12. It contains approximately 45 percent montmorillonite and 55 percent kaolinite, but it is disproportionately rich in Al_2O_3, which accords with conversion from a 2 : 1 to a 1 : 1 sheet silicate.

Study of the clays by electron microscopy verifies the conversion of montmorillonite to kaolinite. The unaltered montmorillonite lacks crystal outline, is fluffy, and breaks down at the edges into nondistinctive flakes and wisps. With initial kaolinization the edges of montmorillonite flakes are discontinuously modified by regular outlines and hexagonal outgrowths. Thus, individual flakes may exhibit two distinctive morphologies as shown in Fig. 4. As alteration progresses lateral outgrowths are more pronounced, and individual kaolinite crystals and small, almost completely kaolinized aggregates appear. Many of the aggregates, however, display some residual evidence of origin from montmorillonite, usually by having curved or curled edges, which lack hexagonal symmetry (see Fig. 5).

The development of regular outlines and hexagonal outgrowths at edges of montmorillonite flakes is evidence of lateral epitaxy, and implies the prior stripping of a silica layer to create a 1 : 1 kaolin-prototype for some distance in from the edge.

An independent argument for intracrystalline stripping of the tetrahedral layers is furnished by x-ray evidence of mixed-layering between montmorillonite and kaolinite. X-ray patterns of partly transformed clay from the three localities studied contain a small "extra" reflection in the low-angle region. As shown in Fig. 6, this low-angle *d*-spacing equals the sum of the kaolinite and montmorillonite (001) spacings initially and after heating to 115°C, thus precluding abnormally hydrated montmorillonite as its cause. It also does so after glycolation and expansion of montmorillonite, and after further heating to 300°C and collapse of montmorillonite to 10 Å. An additional small reflection appears at 13 Å in some samples when montmorillonite collapses after heating to 300°C. This 13-Å reflection collapses to 11 to 12 Å on further heating to 500°C and is tentatively attributed to interlayer accumulation of $Al(OH)_3$ to possibly create vermiculite-like material. On heating to 500°C the reflections due to kaolinite and the superlattice disappear. Higher order reflections for the mixed-layer montmorillonite-kaolinite have not been verified beyond doubt, presumably because of the low intensity of the primary reflection.

The superlattice of kaolinite-montmorillonite and the lateral outgrowths from it reveal that alteration of montmorillonite to kaolinite is a structural transformation. Intermediary phases, such as allophane gels or halloysite crystals, are not necessary precursors to kaolinite and have not been detected. We can also discount the operation of metasomatic replacement by total solution and metathesis as the major process, although, precipitation may be the cause of many of the small new growths of kaolinite.

Evidence of much more extensive outgrowth in the more fully kaolinized material (Fig. 5), coupled with the lack of prominence of mixed-layering throughout the transformation sequence studied, reveals that the structural transformation is not completed merely by extended stripping of intracrystalline silica. Moreover, the final product

Table 2. Analyses of water (parts per million) from wells in Pinellas County. Data from R. C. Heath and P. C. Smith, *Florida Geol. Survey Rept. No. 12* (1954), pp. 1–139.

SiO_2	Ca	Mg	Na	HCO_3	SO_4	Cl	F	*p*H
42	138	37	76	245	46	308	0.2	7.1
25	62	9	23	196	3	52	0.3	7.7
18	66	5	15	142	63	23	0	7.7
29	58	11	18	187	4	48	0.3	7.5
36	63	28	32	223	3	107	0.6	7.5
28	162	23	255	207	57	560	0.2	7.3
29	186	36	193	215	42	540	0.1	7.5
15	72	8	18	231	3	43	0.1	7.4
19	72	8	27	216	3	57	0.1	7.2
10	49	13	135	63	39	262	0.0	7.5

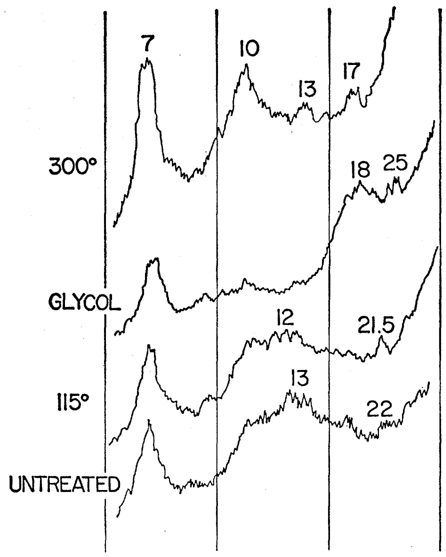

Fig. 6. X-ray patterns of sample Mascotte 7 (Fig. 2). Patterns show diffraction effects ascribed to regular 1 : 1 mixed layer montmorillonite-kaolinite (*d*-spacings in angstrom units).

of such a process could not be kaolinite, for montmorillonite differs from kaolinite crystallographically, in dimensions and layer orientation, and chemically, in having appreciable octahedral iron. Instead we see a pattern of epitaxial enlargement vividly illustrated in Fig. 5. Extended sheet-like outgrowths of kaolinite (*a*, Fig. 5), some 30 to 50 Å thick, have nucleated additional vertical stackings of isolated rune-shaped crystallites, and ultimately, greatly thickened and extended hexagonal plates (*c*, Fig. 5). The hexagonal plates and the rune-shaped crystallites share a common morphological orientation with the basal sheet, which has acted as a template for their deposition.

In consideration of the sequence of morphological changes, and of the mixed-layering, we propose the following pattern for transformation.

1) Acid leaching of interlayer cations and synchronous or immediately subsequent hydration and stripping (leaching) of silica layers (*a*, Fig. 7).

2) Replacement of vacant tetrahedral oxygen sites by hydroxyls to create a highly polar kaolin-like arrangement in the residual 1:1 sheet (*a*, Fig. 7).

3) The highly charged outside layer of hydroxyl protons contracts the interlayer space to approximately that of kaolinite, of identical charge polarity, creating a 21-Å superlattice (*b*, Fig. 7).

4) Extension of the kaolin-like sheet laterally, by epitaxial growth of true kaolinite, and development of hexagonal modifications and outgrowths at the edges of montmorillonite flakes.

5) The primitive kaolinite crystals are nourished and enlarge (*c*, Fig. 7), as the montmorillonite continues to break down. New layers of kaolinite are added (*d*, Fig. 7; and Fig. 5).

6) Small flakes of montmorillonite may be completely converted by stripping. Large flakes may develop many simultaneous growth salients as shown in the hexagonal projections of Fig. 5.

The chemistry of this transformation is undoubtedly more complex than this provisional outline suggests; but the following conclusions and regional effects are tentatively suggested from petrographic and field observations.

The altering medium is mildly acidic (*p*H 6.5 to 5.0 ?) ground water, most probably rain water enriched with humic acids, as suggested by the incomplete removal of apatite nodules and the failure to develop the more acidic secondary aluminum phosphates, such as crandallite or wavellite, in many areas of clay alteration. These latter minerals are present in adjoining flood plain areas of highly acid lateritic alteration (*6*).

Silica remains in solution and is transported from the zone of weathering, unless fixed by replacement of calcareous material, such as unleached calcite fossils. Secondary chert and opal are observed close to transformed material (Fig. 2) in sufficient quantity to confirm the transformation, but the total quantity of such chert is insignificant compared to the extent and thickness of the altered zones. In the Bone Valley Formation this zone is several feet thick over hundreds of square miles. Thus the volume of altered montmorillonite requires considerable precipitation of chert or considerable transport of silica in solution. Analyses of Florida ground water give many high values for dissolved silica (Table 2). Regional conversion of montmorillonite to kaolinite is a probable source of this silica (*9*). The silica-rich ground water is probably silicifying underlying limestones with chert and opal, and possibly enriching the Gulf of Mexico as well. Analyses of springs in Florida show that emergent waters are not unusually siliceous (*10*). Ledges of chert are common, however, in zones of Hawthorn, Tampa, and Suwannee limestones subjacent to weathered clayey sediments, throughout central and northern Florida.

The occurrence of opal and the probably related silica-rich ground waters further imply that the clay transformation is not controlled by the solubility of quartz. It may be related to the higher solubilities of cristobalite or amorphous silica, if related to aqueous silica solubilities at all in a complex natural system characteristically enriched in "humic acids."

The regional development of secondary iron oxides may be another

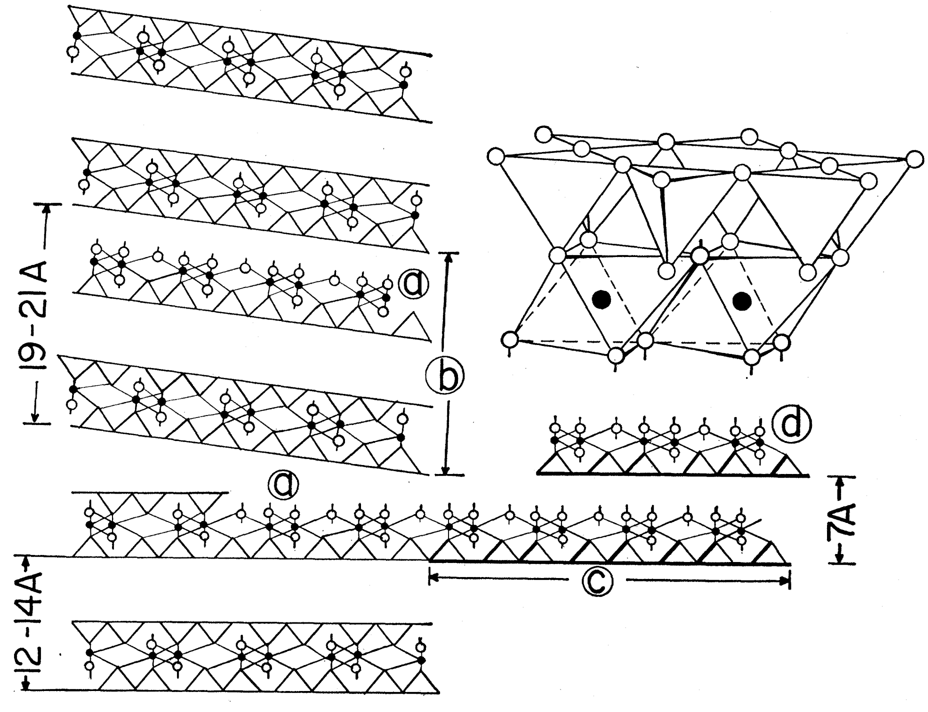

Fig. 7. Proposed transformation of three-layer montmorillonite to two-layer kaolinite. Material with thickened basal line (*c, d*) represents new growth initiated epitaxially after stripping of silica layer *a*; see text.

important byproduct of the clay conversion. Goethite and limonite form concretions, hardpan, and pervasive mottling and coloration in most exposures of Citronelle and in many other surface clays. In the Citronelle Formation at Mascotte and throughout the Bone Valley Formation this iron comes from weathered clays. Initially the green clay becomes mottled by red specks which are seen under the electron microscope to be goethite needles of sub-micron size within montmorillonite aggregates. As kaolinization advances the goethite pervades the rock. Subsequent bleaching and reconcentration along fractures and plant root zones obscure the origin of goethite. Its relation to clay weathering, however, is evident during initial alteration (Fig. 2). Chemical analyses (Table 1) show that the ferric-rich clay of the region is a sufficient source of all the secondary iron. Perhaps much of the unfossiliferous red and orange, kaolinitic Citronelle and mineralogically similar latosols throughout Florida and adjacent states may have originated by weathering of marine montmorillonitic sediments.

The widespread conversion of montmorillonite to kaolinite has important geomorphic consequences. This process of supergene groundwater leaching initiates the breakdown and removal of clay (*11*). The loss of much silica and some montmorillonite considerably increases the porosity and permeability of the clayey quartz sands, an effect abetted by the cementing action of new crystal formation and by loss of swelling property. Additional void space develops by groundwater translocation of clay, a process manifest in the secondary films of kaolinite (clay cutans) which line fractures and floor cavities (*6, 12*) throughout the weathered section. The mutually enhancing effects of clay degradation and clay translocation in the mature soil zone eventually remove the intergranular clay to create a residual quartz-sand mantle (*11*) which has been interpreted as a marine Pleistocene terrace in many areas. Where montmorillonite is still present high in the section the loose sand mantle is thin (*13*).

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13. We are indebted to E. J. Young for help in the field, to Colin Davis for assistance in electron microscopy, and to J. Anthony Denson for his skillful reproduction of electron micrographs. Publication authorized by the director, U.S. Geological Survey.

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Rhinoviruses: A Description

This paper was drawn up at the request of the Virus Subcommittee of the International Committee on the Nomenclature of Bacteria and Viruses in order to clarify its decision that certain viruses recently isolated from colds and similar diseases in man should be gathered into a subgroup of the picornaviruses to be called rhinoviruses.

The name rhinovirus will include certain viruses which are similar to but distinct from enteroviruses and which form a subgroup of the picornaviruses, already defined by the International Committee. The rhinoviruses have previously been called by their discoverers and others, coryzaviruses (*1*), enterovirus-like viruses (*2*), ERC viruses (*3*), muriviruses (*4*), rhinoviruses (*5*), and Salisbury strains (*6*). The first one to be isolated (*7*) was classified as ECHO 28 (*8*).

Estimates of the particle diameter have been obtained by ultrafiltration and vary from 15 to 30 $m\mu$ (*3, 9, 10*). The shape and subunit structure are under investigation.

Analysis of purified virus has not been reported, but the apparent hydrated density is about 1.3 (*9*) which suggests that the infectious particle is nucleoprotein; multiplication of many strains is not inhibited by 5-fluorodeoxyuridine which inhibits the synthesis of DNA; infectious RNA has been extracted from one strain (*3*).

Virus survives storage for weeks at 4°C and indefinitely at −70°C. Strains remain infectious after being frozen and dried.

All strains are ether-stable, but completely or almost completely inactivated by holding at *p*H 5 or 3 for a period of 1 to 3 hours (*3, 9, 11, 12*). They are generally more stable at 50°C than are enteroviruses and are partially or, in some hands, completely stabilized by $1M$ $MgCl_2$.

Either of the following tests will demonstrate that a rhinovirus is acid-labile. (i) Virus in tissue culture fluid is mixed with an equal volume of $0.1M$ sodium citrate–citric acid buffer *p*H 4, and another portion is mixed with the same volume of $0.1M$ sodium phosphate buffer *p*H 7. The mixtures are held at 37°C for 1 hour, diluted with an equal volume of $0.5M$ phosphate buffer *p*H 7.2, and then diluted 1:5 or more in medium and titrated for infectivity. (ii) In an alternate procedure virus in tissue culture fluid is mixed with nine volumes of Eagle's medium without sodium bicarbonate (final *p*H 3.0) and another portion is mixed with nine volumes of Eagle's medium prepared with $0.01M$ tris buffer (final *p*H 7.2 to 7.4). The mixtures are held at 20° to 25°C for 3 hours and then titrated for infectivity.

The lowest dilution of virus held at an acid *p*H should not infect any culture, whereas a dilution of the control virus suspension at least ten-fold higher than this should infect all cultures inoculated. Thus, when calculated by the method of Reed and Muench (*13*) a hundred fold or greater reduction in titer is observed.

The published results of tests with human and animal sera indicate that there are many serotypes, apparently over 30 (*3, 10, 11, 14*). In order to confirm these results and to establish agreed prototypes the International Reference Laboratories are preparing antisera in goats with viruses purified by limit dilution or by picking plaques (*15*). These antisera will be tested