# MINERALOGY, CRYSTALLINITY, O<sup>18</sup>/O<sup>16</sup>, AND D/H OF GEORGIA KAOLINS

ALI ASGHAR HASSANIPAK<sup>1</sup>

School of Geophysical Sciences, Georgia Institute of Technology Atlanta, Georgia 30332

#### ERIC ESLINGER<sup>2</sup>

Department of Geology, West Georgia College Carrollton, Georgia 30117

Abstract – Mineralogy, kaolin crystallinity, Fe content,  $\delta O^{18}$ , and  $\delta D$  were determined for late Cretaceous "soft" and early Tertiary "hard" Georgia kaolins. The crystallinity of the <0.5-, 0.5–1.0-, and 1.0–2.0- $\mu$ m size fractions of soft kaolins was higher than that of equivalent size fractions of hard kaolins.  $\delta O^{18}$  and  $\delta D$  of the soft and hard kaolins ranged between 18.5 to 23.1‰, and -64 to -41‰, respectively, and could not be used to discriminate soft from hard kaolins. The trends of crystallinity vs.  $\delta O^{18}$  were different for kaolins collected at different localities, and, for a given sample,  $\delta O^{18}$  generally decreased with increasing crystallinity and with increasing crystallite size. These data indicate that the Tertiary kaolins could not have been simply derived from the Cretaceous kaolins by winnowing unless post-sedimentation recrystallization of one or both occurred.  $\delta D$  vs.  $\delta O^{18}$  systematics indicate that the late Cretaceous to early Tertiary Georgia kaolins crystallized over a temperature range of about 15°C in the presence of waters that varied little in isotopic composition.

Key Words-Crystallinity, Hardness, Isotope, Kaolin, Origin, Oxygen isotopes.

### INTRODUCTION

The Georgia kaolins are commonly divided into mostly late Cretaceous "hard" varieties and mostly early Tertiary "soft" varieties. The soft kaolins have high crystalline perfection and low Fe contents, whereas the hard kaolins have low crystalline perfection and high Fe contents. In practice, the terms "semi-hard," "flint," and "bauxitic" kaolins have also been used (Stull and Bole, 1926), and variations exist among all five types.

The kaolins or precursor feldspathic sands are believed to have been deposited near the Cretaceousearly Tertiary shoreline in near-shore fluvial, deltaic, or brackish to marine environments (Veatch, 1909; Neumann, 1927; Smith, 1929; Kesler, 1963; Grim and Wahl, 1968; Murray, 1976). Smith (1929) and Murray (1976) suggested that early Tertiary hard kaolins may have been derived from the late Cretaceous soft kaolins by reworking. Hinckley (1965) argued that the textural difference between soft and hard kaolins resulted from their deposition in fresh and saline waters, respectively; however, the effect of electrolyte concentration on particle orientation within the kaolins (Goldschmidt, 1926; Lambe, 1963; Rosenqvist, 1959) is significantly diminished if the unknowns about the effects of postdepositional processes on the size and interparticle geometry of clay platelets are taken into consideration. The significance of post-depositional processes on texture was stressed by Austin (1972) and Hurst *et al.* (1979) who argued that both the Cretaceous and Tertiary kaolins are residual deposits derived by laterization of some unspecified aluminous sediments.

Several types of disorders exist in kaolin crystals (Brindley, 1980), and disorder has been related to structural defects (Plançon and Tchoubar, 1977) and to trace amounts of structural Fe (Mestdagh *et al.*, 1980; Herbillon *et al.*, 1976; Calvert, 1981; Komusinski *et al.*, 1981). The Hinckley (1963) crystallinity index, C.I., is often used as a measure of crystalline perfection, and the C.I. ranges obtained on hard and soft kaolins suggest that they crystallized under different environmental conditions. For a given crystallite size, however, the Tertiary kaolins might be expected to have the same C.I. as the Cretaceous kaolins if the former were weathered from the latter.

Thus, one goal of the present study was to examine crystallinity indexes of hard and soft kaolins as a function of crystallite size. A second goal was to investigate the depositional environment of the Georgia kaolins by means of stable isotope analysis, relying on the fact that O<sup>18</sup>/O<sup>16</sup> ratios of kaolins are sensitive indicators of temperatures of crystallization (Lawrence and Taylor, 1971).

Although most Georgia kaolins are composed of kaolinite, dickite, and nacrite (Hurst *et al.*, 1979), in this

<sup>&</sup>lt;sup>1</sup> Present address: Department of Mining Engineering, University of Tehran, Tehran, Iran.

<sup>&</sup>lt;sup>2</sup> Present address: Cities Service Oil and Gas Corporation, Technology Center, Box 3908, Tulsa, Oklahoma 74102.

Copyright © 1985 The Clay Minerals Society



Figure 1. Location of major Georgia kaolin deposits (hachures) and localities of sampling sites (inset) for this study.

paper "kaolin" is used in a general sense to describe a sample or bed rich in minerals of the kaolin group. No attempt has been made to discriminate among the various kaolin-group minerals.

## SAMPLING AND ANALYTICAL TECHNIQUES

Kaolin samples were collected from mine pits and road cuts. The general locations of these sites are shown in Figure 1, and the specific locations are given in Hassanipak (1980). The hard kaolins were powdered in a Wigglebug for 3–5 min; all other samples were gently crushed with a mortar and pestle. The powdered samples were briefly dispersed in distilled water using an ultrasonic probe, and the <44- $\mu$ m fraction was separated by sieving. The <10-, <5-, 1–2-, 0.5–1-, and <0.5- $\mu$ m size fractions were separated using standard settling techniques (Jackson, 1956).

X-ray powder diffractograms were made using Nifiltered CuK $\alpha$  radiation. Preferentially oriented mounts were made to check for the presence of non-kaolin minerals. Randomly oriented mounts were made for X-ray powder diffraction (XRD) of the <44- $\mu$ m fraction and for C.I. measurements of the clay-size fractions, using the Hinckley (1963) technique. C.I. measurements of three replicate traces from each of three separate mounts of both well-crystallized and poorly crystallized kaolinites (samples KGa-1 and KGa-2, respectively, from the Source Clays Repository of The Clay Mineral Society) were made to check precision. The traces of the nine well-crystallized kaolinites had



Figure 2. The effect on crystallinity index of grinding poorly crystallized and well-crystallized kaolinites.

a mean C.I. of  $0.89 \pm 0.023$ , and the traces of the nine poorly crystallized kaolinites had a mean C.I. of  $0.28 \pm 0.025$ . Grinding in a Wigglebug (Figure 2) for as long as 8 min did not substantially reduce the C.I. of the poorly crystallized kaolinite; the C.I. of the well-crystallized kaolinite was significantly decreased by as little as 4 min of grinding. For the poorly crystallized kaolinite, more variation of C.I. was introduced by the method of selecting and measuring peak and background intensities than was caused by the Wigglebug grinding.

Fe<sub>2</sub>O<sub>3</sub> analyses were made on the bulk or the <10µm fraction of most samples using atomic absorption spectrophotometry. Samples were digested to dryness in a 4:1 HClO<sub>4</sub>-HF mixture, and the residue was dissolved in appropriate diluting solutions. The results are reported as Fe<sub>2</sub>O<sub>3</sub>.

Oxygen extractions were made with fluorine in a manner similar to that described by Taylor and Epstein (1962) after desiccation in a drybox and outgassing at 250°C (Savin and Epstein, 1970a, 1970b; Eslinger, 1971). The  $\delta O^{18}$  values of the samples are reported relative to the SMOW standard (Craig, 1961). A blank correction was necessary due to the presence of 20 to 32 moles of oxygen in the fluorine per sample; the  $\delta O^{18}$  of this oxygen was about -4%. For most samples, only one extraction of oxygen was made. Where two extractions were made, the precision (average deviation from the mean) of  $\delta O^{18}$  values was about 0.2%. Hydrogen was extracted using standard techniques (Godfrey, 1962; Friedman, 1953).

### **RESULTS AND DISCUSSION**

#### Mineralogy and chemistry

The samples have a wide range of textures and contain various amounts of minerals other than kaolin. Table 1 lists the depositional age, the rock type based on hand-specimen observation and <44- $\mu$ m XRD mineralogy, and a qualitative measure of the miner-

				Mineralogy <sup>3</sup> (<44 μm)				Crystallinity index and size fraction (µm)			Fe <sub>2</sub> O <sub>3</sub>	
Sample	Site	Age <sup>1</sup>	Rock <sup>2</sup>	к	s	I	Q	1–2	0.5-1	<0.5	Size (µm)	Wt. %
1	1	UK	SK	Mj	T	T	Mn	0.91	0.73	0.79	Bulk	0.56
2	1	UK	SK	Mj	T	T	Mn	1.00	0.90	0.80	Bulk	0.74
5	1	UK	MKS	Mn	T	Mn	Mj	1.36	1.30	1.00	<10	0.58
8	2	ME	KS	Mn	Т	Т	Mj	1.42	1.16	1.00	<10	0.72
11	3	ME	HK	Mj	T	T	T	0.56	0.59	0.42	Bulk	1.32
12	3	ME	HK	Mj	T	T	T	0.64	0.51	0.44	Bulk	1.44
14	3	ME	HK	Mj	T	T	T	0.53	0.52	0.45	Bulk	1.28
15	3	ME	HK	Mj	T	T	T	0.45	0.27	0.27	Bulk	1.48
23	5	UK	SK	Mj	Mn	T	T		0.90	0.83	Bulk	0.34
24	5	UK	SK	Mj	Mn	T	T		0.96	0.92	Bulk	0.22
25	5	UK	SK	Mj	Mn	T	T		1.00	0.84	Bulk	0.16
26	5	UK	SK	Mn	Mj	T	T		0.80	0.80	Bulk	0.42
28 29 30 34	6 6 6	UK-ME UK-ME UK-ME UK-ME	MKS SK MKS PK	Mn Mj Mn Mj	T Mn T Mn	Mn T Mn T	Mj T Mj T	1.30 0.93 1.27 0.61	0.91 0.95 0.98 0.55	1.00 0.80 1.05 0.50	— Bulk — Bulk	0.48 1.81
41	8	UK-UE	SK	Mj	Mn	T	T	1.51	1.56	1.24	Bulk	0.09
42	8	UK-UE	SK	Mj	Mn	T	T	1.15	0.85	0.80	Bulk	0.28
44	8	UK-UE	KS	Mn	Mj	T	Mn	0.74	0.67	0.61	<10	0.96
48	8	UK-UE	KS	Mn	Mj	T	Mn	0.50	0.40	0.30	<10	0.82
50	9	UK	MKS	Mn	T	Mn	Mj	1.28	0.97	0.92		
51	9	UK	SK	Mj	T	T	Mn	0.90	0.86	1.00	Bulk	1.38
52	9	UK	MKS	Mn	T	T	Mj	0.91	0.91	0.79		
54	10	P	HK	Mj	T	T	Mn	0.63	0.60	0.55	<b>Bulk</b>	0.85
56	10	P	MKS	Mn	T	T	Mj	1.00	0.82	0.77	<10	0.45
57	11	P-ME	PK	Mj	T	T	T	0.65	0.58	0.53	Bulk	1.92
58	11	P-ME	HK	Mj	T	T	T	0.67	0.33	0.38	Bulk	1.18
60 61 62 63 65	12 12 12 12 12	UK UK UK UK UK	MKS MKS FK PK MKS	Mn Mn Mj Mj Mn	T T T T T	T T T T	Mj Mj  Mi	1.16 0.92 0.52 0.93 1.29	1.03 0.93 0.33 0.63 1.28	1.12 0.83 0.53 0.86 1.20	 Bulk Bulk <10	 0.30 1.80 0.40

Table 1. Mineralogy, crystallinity, and Fe<sub>2</sub>O<sub>3</sub> content of samples.

<sup>1</sup> UK = Upper Cretaceous, ME = Middle Eocene, UE = Upper Eocene, P = Paleocene.

 $^{2}$  SK = soft kaolin, HK = hard kaolin, PK = pisolitic kaolin, FK = flint kaolin, KS = kaolinitic sand, MKS = micaceous kaolinitic sand.

 ${}^{3}$ K = kaolin, S = smectite, I = illite, Q = quartz, Mj = major, Mn = minor, T = trace.

alogy of the <44- $\mu$ m fraction. Samples were categorized into: (1) aphanitic masses of soft or hard kaolins, (2) bauxitic kaolins (kaolins with a pisolitic texture), (3) micaceous sands, and (4) micaceous kaolinitic sands. Except for small amounts of smectite, no nonkaolin minerals were detected by XRD in the <2- $\mu$ m size fractions. No consistent variation of smectite content with size fraction was noted.

The C.I. of the 1–2-, 0.5–1-, and <0.5- $\mu$ m fractions are also tabulated in Table 1 and plotted as a scatter diagram in Figure 3. All size fractions of the soft kaolins and micaceous kaolinitic sands have C.I. values >0.74, whereas all size fractions of the hard kaolins have C.I. values <0.74. The C.I. values of the pisolitic kaolins and the kaolinitic sands vary widely from 0.30 to 1.42. The distinct difference between the C.I. of the soft and hard kaolins indicates that the hard Tertiary kaolins could not have been simply derived from the soft Cretaceous kaolins by winnowing during erosion and transportation unless subsequent recrystallization of one or both occurred.

The relationship between  $Fe_2O_3$  content and C.I. is shown in Figure 4. The logarithmic axis for C.I. is used after Mestdagh *et al.* (1980) who showed a correlation ( $r^2 = 0.75$ ) between the logarithm of C.I. and the percentage of total  $Fe_2O_3$  in the structure of the kaolins. The data from the study herein are shown as rectangles and, except for the pisolitic kaolins, the samples define the same general trend as the data of the other four studies. There is considerable scatter in the data, but



Figure 3. Crystallinity index vs. size fraction. Abscissa position of data points within a given size-fraction range has no significance. Fields of hard kaolins and soft kaolins are delineated by dashed lines and solid lines, respectively. Sample numbers are indicated.

consideration must be given to the fact that total Fe in each sample, not just structural Fe, is plotted for the samples in this study.

 $\delta O^{18}$ 

Isotopic data are tabulated in Table 2. Figure 5 shows crystallinity index plotted against  $\delta O^{18}$ . The  $\delta O^{18}$  range of hard kaolins is +19.8 to +22.1‰ and that of the other kaolin types is +18.5 to +23.3‰. Thus,  $\delta O^{18}$ 



Figure 4. Crystallinity index vs. weight percent Fe<sub>2</sub>O<sub>3</sub> for bulk or <10- $\mu$ m kaolins. Height of the rectangles encompasses the C.I. range for all size fractions analyzed. Data of Mestdagh *et al.* (1980) fall within the broken line, and the straight line is their best fit line through their data. Diamonds are from Komusinski *et al.* (1981), the upright triangles ( $\Delta$ ) from Calvert (1981), and the inverted triangles ( $\nabla$ ) from Herbillon *et al.* (1976). Numbers are sample numbers from the present study.

Table 2. $\delta O^{18}$ and $\delta D$ of kaolin samp	les
--------------------------------------------------------	-----

Sample <sup>1</sup>	Size (µm)	δO <sup>18</sup>	Sample ∂O <sup>18</sup> average	δD
1	<0.5	+21.2	+21.2	
2 2	<0.5 0.5 <b>-</b> 1	+21.8 +21.6	+21.7	-41.3 (1-2 μm)
5	< 0.5	+20.7		-44.5
5	0.5-1 1-2	+19.8 +20.3	+20.4	-46.6
5	<10	+20.6		40.0
8	1–2	+19.7	+19.7	
11	<0.5	+20.7	<b>*</b> 0 (	
11	0.5 - 1	+20.5 +10.0	+20.4	-11 5
11	<10	+20.5		
12	0.5-1	+20.9	+20.5	
12	1–2	+20.0		
14	< 0.5	+19.8		-46.2
14	1-2	+20.9	+20.6	-48.6
14	< 10	+ 21.0	1016	
15	<0.5 0. <b>5</b> –1	+21.8 +21.3	+21.0	
23	<10	+22.7	+22.7	
24	1–2	+21.8	+21.8	-52.0
28 28	0.5–1 1–2	$^{+22.1}_{+21.6}$	+21.9	
29	1-2	+23.3	+23.3	
30	1-2	+21.8	+21.8	
34	0.5-1	+23.2	+23.2	
41	<0.5	+23.0	+22.3	-56.1
41	<10	+21.5		
42 42	0.5–1 1–2	+22.5 +21.8	+22.2	-44.8
50	1–2	+20.2	+20.2	
51	< 0.5	+20.2	+19.5	(2.7
51	1-2	+18.9	1.21.6	-63.7
50	0.5-1	+21.5	+21.5	-49.0
)   E0	0.5-1	+ 22.2	+22.2	-33.1
58 58	0.5–1 <10	+22.1 +21.5	+21.8	
60	<10	+20.8	+20.8	
61	1–2	+20.8	+20.8	
62	<0.5	+22.6		
62 62	0.5-1	+21.6	+21.8	-44.9
62	-1-2 	121.2 18.5	±18.5	-526
65	1.0	+ 10.3	+ 10.3	-52.0
05	1-2	±23,1	±23.1	-33.0

<sup>1</sup> Sample numbers are the same as those given in Table 1.

values do not discriminate between the hard and soft kaolins. The overlap in  $\delta O^{18}$  ranges does not necessarily mean that all kaolin types crystallized under identical conditions, but that the two variables which govern the kaolin  $\delta O^{18}$ , i.e., the crystallization temperature and





Figure 5. Crystallinity index vs.  $\delta O^{18}$ . Sample numbers are inside symbols. Numbers above symbols are wt. % Fe<sub>2</sub>O<sub>3</sub>. S, M, and L below symbols denote 0–0.5-, 0.5–1.0-, and 1.0–2.0- $\mu$ m size fractions, respectively (=small, medium, and large). Bold line is the wt. % Fe<sub>2</sub>O<sub>3</sub> = 1.0 isoline. Samples collected at sites 1, 3, and 6 are delineated by fields.

the  $\delta O^{18}$  of pore waters present during crystallization, resulted in overlapping ranges. The fairly wide range of  $\delta O^{18}$  values for the kaolins is too large to be attributed to known impurities (Sayin and Jackson, 1975) such as rutile, anatase, and iron oxides. The solid line labeled 1.0% Fe<sub>2</sub>O<sub>3</sub> in Figure 5 separates high-Fe kaolins from low-Fe kaolins. It is evident that there is no significant relationship between  $\delta O^{18}$  and Fe content.

Figure 6. Plot of size fraction vs.  $\delta O^{18}$ . Sample numbers are indicated.

Envelopes have been drawn in Figure 5 around samples from the three collecting sites from which three or more samples were studied. The geometry of these three fields indicates that  $\delta O^{18}$  generally decreases with increasing C.I. for samples collected within each of these sites. Also, the range of  $\delta O^{18}$  values for sites 1 and 6 are distinct from one another. Further, for a given sample,  $\delta O^{18}$  usually decreases with increasing size fraction (Figure 6). Thus,  $\delta O^{18}$  generally varies with size fraction, crystallinity index, and collecting site regardless of kaolin type. A possible explanation for this



Figure 7. Plot of  $\delta D$  vs.  $\delta O^{18}$ . A = calculated kaolinite in oceanic sediments (Savin and Epstein, 1970b); B = weathering or sedimentary kaolinites from quarries and outcrops in temperate climates (Savin and Epstein, 1970a); C = kaolinite from Recent Georgia soil profile developed on granite (Lawrence and Taylor, 1972); D = kaolinites from soils and saprolites (Lawrence and Taylor, 1971; only their analyses with error bars  $\leq 1.0\%$  are used here); E = kaolinite from portions of ore deposits dominated by supergene alteration (Sheppard *et al.*, 1969). Sample #62 (dashed square) is a very hard "flint" kaolin which has not been included in the previous discussion because it was powdered in a Wigglebug for 5–10 min, and thus its measured C.I. (cf. Table 2) is subject to error.

variation is that post-sedimentation recrystallization resulted in larger average crystallite sizes having higher C.I. values, and that this recrystallization occurred in a warmer environment and/or in the presence of ground waters with a lower  $\delta O^{18}$  relative to that in which the original kaolin crystallized. This explanation for the  $\delta O^{18}$  variation is consistent with the genetic model of Austin (1972) and Hurst *et al.* (1979) in which soft kaolins are interpreted to be highly leached and recrystallized, with the formation of large vermicular kaolin booklets and etched quartz grains.

## $\delta D$ - $\delta O^{18}$ relationships

 $\delta D$  vs.  $\delta O^{18}$  of the kaolins is plotted in Figure 7 along with data for other low-temperature kaolins reported in the literature. The kaolinite line (Savin and Epstein, 1970a) is a best fit line through kaolins interpreted to be in isotopic equilibrium with meteoric waters at earthsurface temperatures. The dashed line (Sheppard et al., 1969) arbitrarily divides kaolins of undoubted supergene origin (those to right of line) from those of possible hypogene origin (those to left of line). The general distribution of kaolins sub-parallel to the kaolinite line is due to the geographic variation in  $\delta O^{18}$  and  $\delta D$  of meteoric waters in the presence of which the kaolins crystallized. Thirteen of the fifteen kaolins from this study fall in a small field which trends oblique to the kaolinite line, suggesting that the isotopic composition of the waters with which the Georgia kaolins are in equilibrium varied over only a small range, and that the variation in  $\delta O^{18}$  and  $\delta D$  of the kaolins is due mostly to the temperature of equilibration. The  $\delta D$ - $\delta O^{18}$  trend of the 13 Georgia kaolins, although not strongly defined  $(\delta D = -2.24 \delta O^{18} + 0.07; r = -0.56)$ , is compatible with a model in which both oxygen and hydrogen kaolinite-water isotope fractionations decrease with increasing temperature within the temperature range of crystallization. Assuming a constant water  $\delta O^{18}$ , the kaolin  $\delta O^{18}$  variation of about 3‰ is equivalent to about a 15°C temperature range in the 20° to 35°C temperature range (from the extrapolation to low temperatures of hydrothermal fractionation data of Kulla, 1979).

The 13 kaolins in the outlined field are on the high  $\delta D$ -high  $\delta O^{18}$  side of Lawrence and Taylor's (1972) recent Georgia kaolin position ("C" diamond, Figure 7). Assuming that this Recent kaolin point is representative of kaolins now forming in Georgia, most of the late Cretaceous and early Tertiary kaolins formed at a slightly lower latitude, because  $\delta D$ - $\delta O^{18}$  positions of kaolins generally plot above and to the right of the kaolinite line with decreasing latitude of formation (Lawrence and Taylor, 1971). This geographic shift is compatible with plate tectonic data which places southeastern North America at lower latitudes in the late Cretaceous and early Tertiary (Bambach and Scotese, 1979).

### ACKNOWLEDGMENTS

This work was funded by NSF Grant EAR-7904148. We thank J. Hetrick for help with sample collecting, J. Lawrence for access to his D/H isotope facilities, and S. Savin and R. Suchecki for valuable editorial comments. Cities Service Oil and Gas Corporation facilitated the preparation of this manuscript.

#### REFERENCES

- Austin, R. S. (1972) The origin of the kaolin and bauxite deposits of Twiggs, Wilkinson, and Washington Counties, Georgia: Ph.D. dissertation, Univ. Georgia, Athens, Georgia, 185 pp.
- Bambach, R. K. and Scotese, C. R. (1979) Paleogeographic reconstruction: the State of the Art: Short Course, Southeastern Section, Mtng., Geol. Soc. Amer., Geol. Soc. Amer., Boulder, Colorado, 58 pp.
- Brindley, G. W. (1980) Order-disorder in clay mineral structures: in Crystal Structure of Clay Minerals and their X-ray Identification, G. W. Brindley and G. Brown, eds., Monograph 5, Mineralogical Society, London, 125–195.
- Calvert, C. S. (1981) Chemistry and mineralogy of ironsubstituted kaolinite in natural and synthetic systems: Ph.D. dissertation, Texas A&M Univ., College Station, Texas, 224 pp.
- Craig, H. (1961) Standard for reporting concentrations of deuterium and oxygen 18 in natural water: Science 133, 1833-1834.
- Eslinger, E. V. (1971) Mineralogy and oxygen isotope ratios of hydrothermal and low-grade metamorphic argillaceous rocks: Ph.D. dissertation, Case Western Research Univ., Cleveland, Ohio, 205 pp.
- Friedman, I. (1953) Deuterium content of natural water and other substances: *Geochim. Cosmochim. Acta* **4**, 81–103.
- Godfrey, J. D. (1962) The deuterium content of hydrous minerals from the east-central Sierra Nevada and Yosemite National Park: Geochim. Cosmochim. Acta 26, 1215–1245.
- Goldschmidt, V. M. (1926) Undersøkelser over lersidimenter: Nord. Jordbrugsfors. No. 407, 434-445.
- Grim, R. E. and Wahl, F. M. (1968) The kaolin deposits of Georgia and South Carolina, USA: in Proc. 23rd Int. Geol. Cong., Prague, Symposium 1, Genesis of Kaolin Deposits (Rept. vol. 14), Prague, Academia, 9–21.
- Hassanipak, A. A. (1980) Isotopic geochemical evidence concerning the origin of Georgia kaolin deposits: Ph.D. dissertation, Georgia Inst. Tech., Atlanta, Georgia, 198 pp.
- Herbillon, A. J., Mestdagh, M. M., Vielvoye, L., and Derouane, E. G. (1976) Iron in kaolinite with special reference to kaolinite from tropical soils: *Clay Miner.* 11, 201– 220.
- Hinckley, D. N. (1963) Variability in "crystallinity" values among the kaolin deposits of the Coastal Plain of Georgia and South Carolina: in *Clays and Clay Minerals, Proc. 11th Natl. Conf., Ottawa, Ontario, 1963, Ada Swineford, ed.,* Pergamon Press, New York, 229–235.
- Hinckley, D. N. (1965) Mineralogical and chemical variations in the kaolin deposits of the Coastal Plain of Georgia and South Carolina: *Amer. Mineral.* **50**, 1865–1883.
- Hurst, V. J., Kunkle, A. C., Smith, J. M., Pickering, S. M., Shaffer, M. E., Smith, R. P., Williamson, M. E., and Moody, W. E. (1979) Field Conference on Kaolin, Bauxite, and Fuller's Earth: Field Guide, Ann. Meet. Clay Min. Soc., Macon, Georgia, 107 pp.
- Jackson, M. L. (1956) Soil Chemical Analysis-Advanced Course: Univ. Wisconsin, Dept. of Soils, Madison, Wisconsin, 894 pp. (publ. by author).

105

- Kesler, T. L. (1963) Environment and origin of the Cretaceous kaolin deposits of Georgia and South Carolina: Ga. Min. Newslet. 16, 3–11.
- Komusinski, J., Stock, L., and Dubiel, S. M. (1981) Application of electron paramagnetic resonance and Mössbauer spectroscopy in the investigation of kaolinite-group minerals: *Clays & Clay Minerals* 29, 23-30.
- Kulla, J. B. (1979) Oxygen and hydrogen isotopic fractionation factors determined in experimental clay-water systems: Ph.D. dissertation, Univ. Illinois, Urbana, Illinois, 98 pp.
- Lambe, T. W. (1953) The structure of inorganic soils: Proc. Amer. Soc. Civ. Eng. 79, 1-49.
- Lawrence, J. R. and Taylor, H. P., Jr. (1971) Deuterium and oxygen-18 correlation: clay minerals and hydroxides in quaternary soils compared to meteoric waters: *Geochim. Cosmochim. Acta* 35, 993-1003.
- Lawrence, J. R. and Taylor, H. P., Jr. (1972) Hydrogen and oxygen isotope systematics in weathering profiles: *Geochim. Cosmochim. Acta* 36, 1377–1393.
- Mestdagh, M. M., Vielvoye, L., and Herbillon, A. J. (1980) Iron in kaolinite: II. The relationship between kaolinite crystallinity and iron content: *Clay Miner*. 15, 1–13.
- Murray, H. H. (1976) The Georgia sedimentary kaolins: in *Proc. 7th Symp. Congress of Kaolin Inter. Geol. Correlation Program*, Committee on correlation of age and genesis of kaolin, Tokyo, Japan, Univ. Tokyo (publ.), 114–125.
- Neumann, F. R. (1927) Origin of the Cretaceous white clays of South Carolina: *Econ. Geol.* 22, 380–386.

Plançon, A. and Tchoubar, C. (1977) Determination of

structural defects in phyllosilicates by X-ray powder diffraction—I. Principle of calculation of the diffraction phenomenon: *Clays & Clay Minerals* **25**, 436–450.

- Rosenqvist, I. Th. (1959) Physico-chemical properties of soils-soil-water systems: in *Proc. Amer. Soc. Civil Engineers*, vol. 85, Paper 2000, J. Div. Soil Mechanic and Found. No. SM 2, pt. 1, 31-53.
- Savin, S. and Epstein, S. (1970a) The oxygen and hydrogen isotope geochemistry of clay minerals: Geochim. Cosmochim. Acta 34, 25-42.
- Savin, S. and Epstein, S. (1970b) The oxygen and hydrogen isotope geochemistry of ocean sediments and shales: *Geochim. Cosmochim. Acta* 34, 43–63.
- Sayin, M. and Jackson, M. L. (1975) Anatase and rutile determination in kaolinite deposits: *Clays & Clay Minerals* 23, 437-443.
- Sheppard, S. M. F., Nielsen, R. L., and Taylor, H. P. (1969) Oxygen and hydrogen isotope ratios of clay minerals from porphyry copper deposits: *Econ. Geol.* 64, 755-777.
- Smith, R. W. (1929) Sedimentary kaolins of the Coastal Plain of Georgia: Ga. Geol, Surv. Bull. 44, p. 474.
- Stull, R. T. and Bole, G. A. (1926) Benefication and utilization of Georgia clays: U.S. Bur. Mines Bull. 252, 72 pp.
- Taylor, H. P., Jr. and Epstein, S. (1962) Relationship between O<sup>18</sup>/O<sup>16</sup> ratios in coexisting minerals of igneous and metamorphic rocks. Part I. Principles and experimental results: *Bull. Geol. Soc. Amer.* 73, 461–480.
- Veatch, O. (1909) Second report on the clay deposits of Georgia: Ga. Geol. Survey Bull. 18, 453 pp.
  - (Received 5 February 1984; accepted 4 September 1984)

Резюме — Были определены минералогия, степень кристаллизации каолина, содержание Fe,  $\delta O^{18}$ , и  $\delta D$  для "мягкого" позднемелового и "твердого" раннетретичного джорджийских каолинов. Кристальность фракций мягких каолинов размером <0,5-, 0,5--1,0-, и 1,0--2,0- $\mu$ m была выше, чем кристальнось эквивалентных по размеру фракций твердых каолинов.  $\delta O^{18}$  и  $\delta D$  мягких и твердых каолинов колебались от 18,5 до 23,1% и от 64% до 41% соответственно и не могли быть использованы для распознавания мягких каолинов от твердых. Характер зависимости кристальности от  $\delta O^{18}$  был разный для каолинов, отобранных из разных мест, и для данного образца  $\delta O^{18}$  в основном уменьшается при увеличении размера кристаллитов. Эти данные указывают на то, что третичные каолины не могли просто формироваться из меловых каолинов путем механического фракционирования пока не произошла послеседиментационная перекристаллизация одного типа или обоих.  $\delta D$  в зависимости от  $\delta O^{18}$  показывают и температуры около 15°C в присутствии вод, незначительно отличающихся по составу изотопов. [E.G.]

**Resümee**—Es wurde die Mineralogie, die Kaolinkristallinität, der Fe-Gehalt, die  $\delta O^{18}$ - und  $\delta D$ -Werte an "weichen" Georgia-Kaolinen aus der späten Kreide und an "harten" Georgia-Kaolinen aus dem frühen Tertiär untersucht. Die Kristallinität der weichen Kaoline der Fraktionen <0,5; 0,5-1,0, und  $1,0-2,0 \mu m$  war besser als die der entsprechenden Kornfraktionen der harten Kaoline.  $\delta O^{18}$  und  $\delta D$  der weichen und harten Kaoline lag zwischen 18,5 und 23,1% bzw. zwischen -64 bis -41% und konnte nicht zur Unterscheidung zwischen weichem und hartem Kaolin verwendet werden. Wurde die Kristallinität gegen  $\delta O^{18}$  aufgetragen, so waren die Trands für Kaoline von verschiedenen Vorkommen verschieden, und—bei einer gegebenen Probe—nahm der  $\delta O^{18}$ -Wert im allgemeinen mit zunehmender Kristallinität und mit zunehmender Kristallgröße ab. Diese Daten deuten darauf hin, daß die tertiären Kaoline nicht einfach durch Sortierung aus den Kaolinen der Kreide entstanden sein können, ohne daß eine postsedimentäre Rekristallisation des einen oder beider Kaoline eintrat. Darstellungen von  $\delta D$  gegen  $\delta O^{18}$  zeigen, daß die spätkretazischen bis frühtertiären Georgia-Kaoline über einen Temperaturbereich von etwa 15°C in Gegenwart von Wässern kristallisierten, die in ihrer Isotopenzusammensetzung in geringem Maße variierten. [U.W.]

**Résumé** – On a déterminé la minéralogie, la cristallinité de Kaolin, le contenu en Fe,  $\delta O^{18}$ , et  $\delta D$  pour des kaolins de Georgie "mous" du bas Crétacé et "durs" du haut Tertiaire. La cristallinité de fractions de taille <0,5, 0,5–1,0 et 1,0–2,0 µm de kaolins mous était plus élevée que celle de fractions de tailles equivalentes de kaolins durs.  $\delta O^{18}$  et  $\delta D$  des kaolins mous et durs s'étendaient entre 18,5 à 23,1‰, et –64 à –41‰ respectivement, et ne pouvaient pas être employés pour discriminer entre les kaolins mous et les kaolins durs. Les tendances de cristallinité vs.  $\delta O^{18}$  étaient différentes pour les kaolins rassemblés à des localités différentes, et, pour un échantillon donné,  $\delta O^{18}$  diminuait généralement proportionnellement à une augmentation de cristallinité et à une augmentation de la taille de la cristallinité. Ces données indiquent que les kaolins Tertiaires ne peuvent pas être simplement dérivés des kaolins Crétacés, par ruissellement à moins que la recristallisation de l'un ou l'autre ne se soit produite. Les systématiques de  $\delta D$  vs.  $\delta O^{18}$  indiquent que les kaolins de Géorgie du bas Crétacé au haut Tertiaire se sont cristallisés sur une étendue de températures d'à peu près 15°C en la présence d'eaux qui ont varié peu de composition isotopique. [D.J.]