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WELL-ORDERED KAOLINITE IN SIDERITE CONCRETIONS FROM THE BRAZIL FORMATION, WESTERN INDIANA

Key Words—Concretion, Crystallinity, Kaolinite, Ordering, Siderite.

Soft, white kaolinite fills many shrinkage cracks in siderite concretions in shale overlying the Upper Block Coal Member of the Brazil Formation (Pennsylvanian). Initial X-ray powder diffraction (XRD) patterns of this white clay showed that it exhibited an extremely high degree of order. Additional samples of the concretions were collected so that a comparative analysis could be made with the Keokuk, Iowa, kaolinite that is found in geodes (Keller *et al.*, 1966). The Keokuk kaolinite is one of the most well-ordered kaolinites that has been described.

The block coal is mined in open pits south of the town of Brazil, Clay County, Indiana. Dark gray to red siderite concretions as large as 50 cm in diameter are relatively common in the shale above the coal. These concretions occur as individual nodules dispersed throughout the shale; some nodules are aligned horizontally along bedding planes in the shale. Many exhibit shrinkage cracks as wide as 8–9 mm which are filled with kaolinite. Sphalerite crystals are locally present in the interior of the concretions and kaolinite is present in shrinkage cracks.

EXPERIMENTAL

Siderite concretions that exhibited shrinkage cracks filled with white kaolinite were collected from the shale in an operating open-pit coal mine. These concretions were cracked open in the laboratory and the white clay scraped off into a small pan. About three dozen concretions were used so that several analyses could be made on the white clay.

X-ray powder diffraction (XRD) patterns were obtained using a Philips-Norelco instrument with CuKα radiation. The diffractograms showed no other minerals to be present other than kaolinite; hence, no particle sizing or orientation procedures were used. Scanning electron micographs were taken using a Cambridge Stereo Scan MK 250 instrument. The specimens were mounted on spindles and coated with carbon. Transmission electron micrographs were taken of gold-coated specimens in Griefswald, D.D.R. Differential thermal-thermal gravimetric analyses were made in Griefswald with units built in the laboratories of Professor Storr.

RESULTS AND DISCUSSION

The kaolinite from the shrinkage cracks in the siderite is similar in crystallinity and crystal size to the kaolinite described by Keller *et al.* (1966) in geodes from Keokuk, Iowa. Hayes (1963) observed for the Keokuk kaolinite that "of the 52 reflections listed by Brindley and Robertson (1946) . . . 49 were observed on the ordinary X-ray patterns of geode kaolinite . . . (which) shows the geode kaolinite to be exceptionally well crystallized and superior to most mentioned in the literature." For the kaolinite from the Brazil Formation, no dickite or nacrite XRD reflections were found, but 46 kaolinite reflections were observed (Ta-

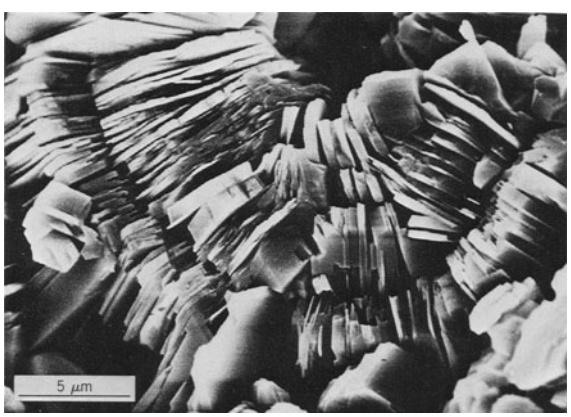

Figure 1. Scanning electron micrograph of highly crystalline kaolinite from cracks in siderite concretions, Brazil Formation, Indiana.

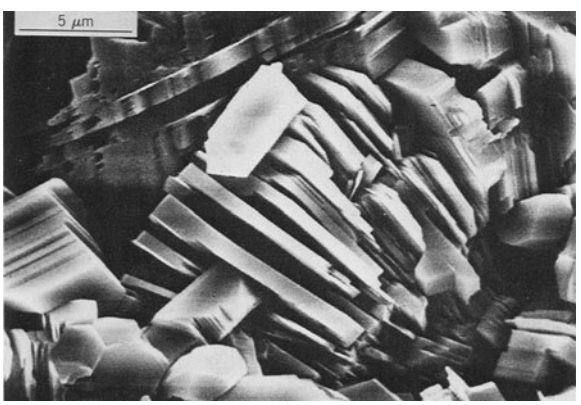

Figure 2. Scanning electron micrograph of highly crystalline, smooth platelets of kaolinite from siderite concretions, Brazil Formation, Indiana.

Table 1. Observed X-ray powder diffraction reflections of highly crystalline kaolinite in siderite concretions, Brazil Formation, Indiana.

d-values	
Brindley and Robinson (1946) d (Å)	Kaolinite (concretions) d (Å)
7.15	7.15
4.45	4.45
4.35	4.35
4.17	4.17
4.12	4.12
3.83	3.83
3.73	3.73
3.56	3.56
3.36	3.36
3.13	3.13
3.09	3.09
2.74	2.74
2.55	2.55
2.52	2.52
2.48	2.48
2.37	2.37
2.33	2.33
2.28	2.28
2.24	
2.18	2.18
2.12	
2.05	
1.98	1.98
1.93	1.93
1.89	1.89
1.86	
1.83	1.83
1.80	
1.77	1.77
1.70	
1.68	1.68
1.66	1.66
1.61	1.61
1.58	1.58
1.54	1.54
1.48	1.48
1.46	
1.45	1.45
1.42	1.42
1.40	1.40
1.36	1.36
1.33	1.33
1.30	1.30
1.28	1.28
1.26	1.26
1.23	1.23
1.19	1.19
1.18	1.18
1.16	1.16
1.12	1.12
1.09	1.09
1.08	1.08
1.02	1.02

ble 1), indicating a kaolinite with essentially as high a degree of order as the Keokuk material.

The large, well-formed kaolinite crystallites shown in the scanning electron micrograph of Figure 1 commonly occur in vermicular stacks and contain relatively smooth basal faces (Figure 2). In the underlying Upper Brazil Block Coal, many of the cleat fractures are coated with soft, white kaolinite, which is similar in habit to the kaolinite in the siderite concretions. In contrast, the kaolinite plates in the underclay of the coal (Figure 3) are thinner and have a micaceous appearance, i.e., thin, flaky aggregates. XRD patterns of the underclay show much less ordering; many of the prism reflections are missing. The shale above the Upper Brazil Block Coal, which contains the siderite nodules, also contains fine, flaky aggregates of kaolinite and illite in a ratio of about 1:2. The underclay contains more or less equal proportions of kaolinite and illite.

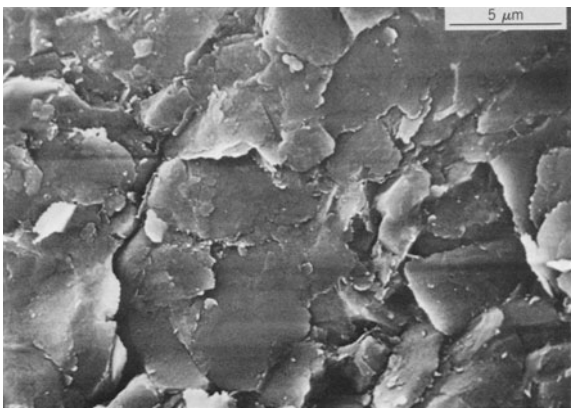

Figure 3. Scanning electron micrograph of kaolinite and illite platelets from Brazil Formation underclay, Indiana.

The kaolinite crystallites in the siderite concretions display smooth basal faces and 2–4-μm straight growth steps (Figure 4). All transmission electron micrographs of this sample showed similar long, straight growth steps.

Most kaolinites dehydroxylate upon heating in a conventional differential thermal apparatus at 550°–

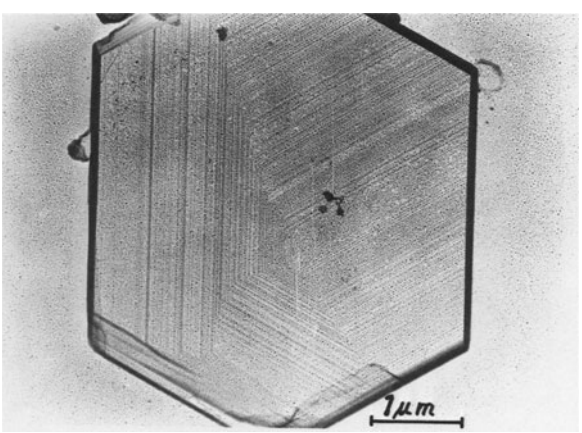

Figure 4. Transmission electron micrograph of kaolinite platelet showing long and straight growth steps.

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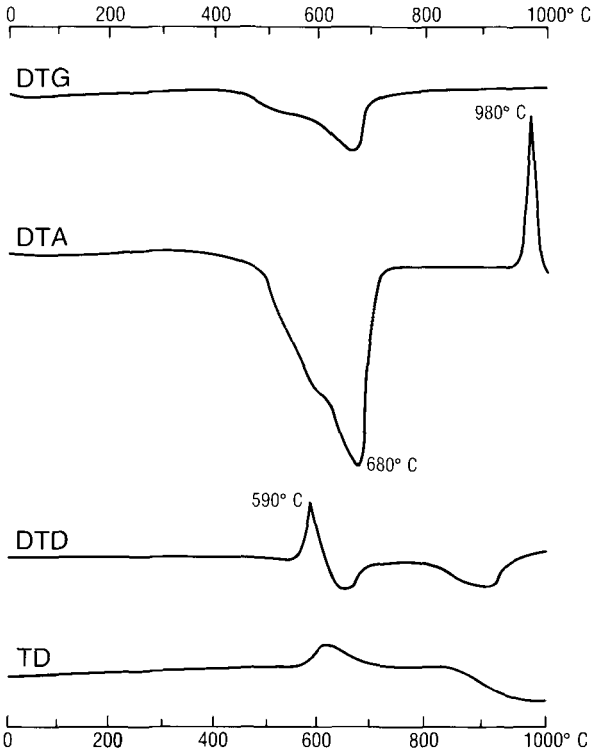

Figure 5. Differential thermogravimetric, differential thermal, differential thermodilatometric, and thermodilatometric curves of kaolinite in Brazil Formation siderite nodules.

625°C. Keller *et al.* (1966) observed that the Keokuk kaolinite dehydroxylated at 690°–695°C and suggested that the true dehydroxylation temperature of very well ordered or highly crystalline kaolinite was 690°–695°C. The dehydroxylation endotherm of the kaolinite from the siderite concretion is 680°C, considerably higher than the dehydroxylation endotherm of most reference kaolinites. Figure 5 shows the differential thermogravimetric (DTG), differential thermal (DTA), differential thermodilatometric (DTD), and thermodilatometric (TD) patterns of the kaolinite from the siderite concretion. The shape of the DTA curves is similar to that reported by Keller *et al.* (1966), Logvinnenko *et al.* (1977), and Stoch and Waclawska (1981). The kaolinite from the siderite nodules shows an expansion between 580° and 620°C, as shown on the DTD and TD curves (Figure 5). Storr *et al.* (1979) and Schomburg and Storr (1984) showed that dickite expands in this range, and stated that such an expansion was characteristic of dickite. Thermodilatometric data for the kaolinite from both the siderite nodules and the Keokuk geodes, however, indicate that these well-ordered kaolinites also expand between 580° and 620°C, but about 8–10 times less in this temperature range than dickite.

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