SCAN ELECTRON MICROGRAPHS OF KAOLINS COLLECTED FROM DIVERSE ENVIRONMENTS OF ORIGIN—II

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Abstract—Scan electron micrographs (SEM) show the textures of ball clay, plastic refractory clay, flint clay, and of kaolins from Cornwall, U.K., and Brittany, France. The texture of ball clay is a swirl and ragged-flake pattern. Plastic refractory clay shows a transition in texture from ball clay to plastic, semi-plastic, to semi-flint, and flint-clay. Flint-clay texture exhibits a matrix of tiny, compactly interlocked clay grains in which may be interspersed small, tight books and sheaves of kaolinite. The plastic to flint clays are interpreted to be sequential components of the flint-clay facies. In one sense they represent elements in clay diagenesis.

Kaolins from the Cornwall district, U.K., and Brittany, France, show more similarity than dissimilarity in texture. Evidence from texture suggests that while hydrothermal action at Cornwall initiated alteration of the granite, the last significant process of kaolinization there was weathering.

BALL CLAY

Ball clay exhibits a distinctive texture in scan electron micrography (SEM). The name "ball clay" was applied in industry to certain sedimentary clays possessing exceptionally high plasticity and good bonding properties. Because of these properties they easily and characteristically formed a cohesive "ball" during factory processing and/or open-pit mining—hence the name. Typical ball clays are dominantly kaolin, although usually they contain accessory illite and/or smectite. Their very high plasticity (necessary, or the clay is not classified as a ball clay) is thought variously to result from very fine particle size, water-holding capacity, some very intimately mixed 2:1 clay, and organic matter (organic colloids). They are secondary deposits, i.e. sedimentary clays.

Ball clays are geologically young clays, occurring primarily in Tertiary-age rocks; no ball clays are reported from Paleozoic rocks. On the other hand, abundant deposits of very plastic, sedimentary refractory clays and underclays do occur in Carboniferous and Mesozoic Cretaceous rocks. Can these be diagenesis products of ertswhile Paleozoic ball clays? The textures of the two types will be compared.

Three samples of ball clays from widely separated localities show quite similar texture: Mayfield, Kentucky, Fig. 1; the Devon Basin, England (Higley, 1975; Freshney, 1970; Bristow, 1968a), Fig. 2; and the Wetro clay, near Bautzen, GDR (Störr and Lasch, 1975), Fig. 3.

Texture of ball clay. Ball clay typically shows a swirl pattern of coalesced flakes on edge, or the flat sides of ragged-edged, overlapping plates when viewed on cleavage faces. One may speculate that the pattern was developed by movement of the clay during sedimentation, dewatering, and compaction.

PLASTIC REFRACTORY KAOLINITIC CLAYS

For more than 70 yr (e.g. see Ries, 1927) ceramists have recognized plastic refractory clays as a major group in classification of clays. They are dominantly kaolinitic but commonly contain some illite, typically of the low-potassium high-hydrogen variety (Keeling, 1961). They are distributed world wide, as the micrographs will show, occurring in large sedimentary deposits found most abundantly in Carboniferous and Cretaceous age rocks. These deposits and clays have been further sub-divided and classified in sequence as plastic, semi-plastic, semi-flint, and soft flint clay leading to hard flint clay. Forward in this sequence, the clays become less plastic and "harder" (not Moh's hardness, but higher crushing strength and resistance to slaking). Several members of the sequence may occur transitionally within one deposit (in Missouri, declining plasticity downward in the deposit). Likewise they may be laterally transitional between near-by deposits within a wide area of connected sedimentary basins (Keller, 1968; McQueen, 1943).

Scan electron micrographs will show a basis for 4 concepts: (1) the similarity of the texture of the geologically older, plastic refractory kaolinitic to younger ball clays, (2) their world-wide distribution, (3) transition in texture toward 'harder" clays, and (4) a basis for inferring diagenesis (diagenetic changes) in clays.

The first clay-SEM example shown is from Breitscheid, Germany (API Reference Clay Minerals, Project 49, 1949–51, designated as kaolinite 129-A) Fig. 4. It serves well as a transition example from ball clay because it is (1) used as a refractory "fire" clay, (2) it is Miocene in age, and (3) its texture is closely similar to that of the designated ball clays. This is followed by 3 SEM's from a single hand specimen



Fig. 1. Ball clay, near Mayfield, Kentucky. 5000 \times (0527). Fig. 2. Ball clay, Devon Basin, U.K. 2000 \times (0419).



 $\label{eq:Fig. 3. Ball clay, We tro deposit, near Bautzen, GDR. 3000 \times (2302).$ Fig. 4. Plastic refractory clay, Breitscheid, Germany, API Reference Clay, 129-A. 3000 \times (2660).



Fig. 5. Plastic refractory clay, Frostburg, Maryland. 2000 \times (2679). Fig. 6. Same specimen as Fig. 5. 1000 \times (2680).



Fig. 7. Same specimen as Fig. 5. $1000 \times (2681)$. Fig. 8. Plastic refractory clay, Mexico, Mo. $3000 \times (2071)$.



Fig. 9. Plastic refractory clay, Mexico, Mo. $1000 \times (2061)$. Fig. 10. Plastic refractory clay, Fulton, Mo. $3000 \times (2065)$.



Fig. 11. Plastic refractory clay, Brierly Hill, England, API Reference Clay, Fire clay 100-A. 3000× (2655).
 Fig. 12. Semi-plastic fire clay, Clearfield County, Pa. 1000× (2678).



Fig. 13. Semi-flint fire clay, Mexico, Mo. $3000 \times (2076)$. Fig. 14. "Soft" flint clay, Bland, Gasconade County, Mo. $4000 \times (0291)$.



Fig. 15. Hard flint clay, Whitesides, Mo. $5000 \times (0304)$. Fig. 16. Hard flint clay, Hammanskrall deposit, Vereeniging, South Africa. $5000 \times (0076)$.



Fig. 17. Hard flint clay, Rock Creek, Colo. $5000\times$ (0114). Fig. 18. Flint clay, Triassic, Garie Member Nat. Park, Australia. $5000\times$ (1307).



Fig. 19. Diaspore clay, near Swiss, Gasconade County, Missouri. 4000 \times (2780). Fig. 20. Cornwall kaolin, Wheal Remfry Pit. 3000 \times (2715).



Fig. 21. Cornwall kaolin, Blackpool Pit. 2000 \times (2705). Fig. 22. Cornwall kaolin, Pentruff Pit. 5000 \times (0587).



Fig. 23. Cornwall kaolin, Imperial Pit. $3000 \times (0011)$. Fig. 24. Cornwall kaolin, after washing and drying, API Reference Clay 114-A. $5000 \times (0312)$.



 $\label{eq:Fig.25.} Fig. 25. Kaolin, Quessoy, Brittany, France. 1000 \times (2684).$ Fig. 26. Incompletely kaolinized granite, Ploemeur, Brittany, France. 2000 \times (2687).

of Carboniferous (Pennsylvanian) plastic fire clay from Frostburg, Maryland, Fig. 5–7. Note the similarity of Figs. 5, 6, to that of ball clay, and the transition toward Fig. 8. The Pennsylvanian Cheltenham Formation of fire clay in Missouri is illustrated in Figs. 8–10 (first two from Mexico, Mo., the last one from Fulton, Mo.). A Carboniferous fire clay from Brierly Hill, England (API Reference Clay, "Fire clay, 100-A") is shown in Fig. 11. Its texture is closely similar to Fig. 10 from Missouri. A Pennsylvanianage, semi-plastic to semi-flint fire clay from the state of Pennsylvania is shown in Fig. 12. Many of the fire clay deposits in Pennsylvania are strongly compacted, presumably due to the mechanical effects of the Appalachian tectonism.

A definitely semi-flint clay but "hard" variety of it, in Missouri, from the same Cheltenham Formation that embodies the full sequence, plastic to semi-flint clay, is shown in Fig. 13. This specimen, which occurred at the bottom of a large clay pit producing primarily plastic and semi-plastic refractory clay (fire clay), is indeed transitional in both physical and ceramic properties, and in texture, toward flint clay.

The textures of ball clay, plastic fire clay, and thence toward flint clay, support an hypothesis that they can be genetically related (within a flint-clay facies, Keller, 1968). The parent material in Missouri deposits was kaolinitic and/or illitic (low K, high-H) residuum from chemically weathered carbonate rocks that was transported into low-lying basins lush with vegetation. Alkali and alkaline-earth elements were removed from the clay in the basins by action of plants, their residues, and dialysis via the Donnan effect, leading to enrichment in kaolin minerals. The clay appears to have been "digested" to a thick gellike mud from which neoformed kaolinite crystallized. When the reaction goes this far the clay enters the flint-clay stage.

A stage of "digestion" of clay appears to be characteristic and essential to the formation of clays in the flint-clay facies. Source material for such clays, other than the Carboniferous examples from Missouri and eastern USA, includes volcanic ash (Spain, Australia, Colorado), and winnowed fine kaolin flakes.

As seen in the example from Pennsylvania, mechanical (tectonic) pressure on refractory clay contributes to compacting and lithifying it.

FLINT CLAY

The name flint clay originated in industry, as did the names ball- and fire-clay, by miners who applied it to certain refractory clay which superficially resembled flint (chert) rock (Keller, 1968). Flint clay is a very fine-grained clay composed dominantly of kaolinite (ordinarily moderately to fairly well ordered) that breaks with a characteristic conchoidal fracture (flint-like), resists slaking, and has a high bulk density, typically 2.2–2.5 (Baumann and Keller, 1975–76). It is sedimentary in origin—one exception of hydrothermal alteration was reported in Mexico, but the precursor rock was significantly also sedimentary (Hanson and Keller, 1971). It is world-wide in occurrence (on every continent), commonly being associated with coal-bearing sediments, as in Carboniferous, Trias– Jurassic, and Cretaceous rocks.

Flint clay is a middle member of the flint-clay facies which ranges from highly plastic refractory clays to high-alumina "burley" clays grading into diaspore clay (Keller, 1968). Texture likewise shows a gradational change from semi-flint clay, Fig. 13, to soft flint clay, Fig. 14, to "harder" flint clay, more fully regenerated kaolinite, Fig. 15. The preceding examples were taken from Missouri where a flint-clay facies is well developed. First-quality, hard flint clay (Carboniferous) from Africa, Fig. 16, is indistinguishable from Missouri or Pennysylvania flint clay, either in hand specimen or texture. Cretaceous flint clay from Colorado is shown in Fig. 17, Triassic flint clay from Australia in Fig. 18.

The texture of flint clay is invariably fine-grained, usually requiring magnification of $5000 \times$ or higher to resolve individual grains or crystals. The matrix is tightly compacted of fine flakes, sheaves, and interspersed tight, thin books of kaolinite, all closely intergrown and interlocked. This produces the high bulk density previously cited for flint clay.

Typically, flint clay has undergone a stage of complete "digestion", previously described, in which the texture of parent rock has been essentially obliterated. Ordinarily the loss of original texture cannot be demonstrated, but it can be followed step-wise and dramatically with the hydrothermal alteration of a calcareous, silty mudstone to flint clay in Mexico (Hanson and Keller, 1971. Some border-line examples of flint-like clay, usually having a lower bulk density, may preserve some relic texture of parent material, such as that of smectite, if the original rock was volcanic ash and conversion has not been complete (example, clay from Oregon and Australia not shown here). An incompletely digested, flint-like sedimentary clay was observed from Cserszegtomaj, Hungary (courtesy of G. Bardossy, 1962).

Further desilication of flint clay commonly produces oolites of diaspore, less commonly boehmite. These structures and minerals are mined in the highalumina burley and diaspore clay in Missouri (Keller, Westcott and Bledsoe, 1954), the "shotty and burnt" clay in Pennsylvania (Williams, 1960), the oolitic and pisolitic flint clay in Israel (Bentor) and in some of the flint clay in France (Halm, 1952). A SEM of Missouri diaspore is shown in Fig. 19.

CORNWALL AND BRITANNY KAOLIN

The kaolin from Cornwall England (Bristow, 1968b), accompanied by the Brittany, France, (Esteoule and Esteoule-Choux, 1974) kaolin, is described in this paper in a separate section for 2 reasons: (1) their huge size and importance, and (2)

the diversity in interpretation of origin of the Cornwall kaolin. As stated in Part I of this paper (Keller, 1976) many of the most experienced clay (kaolin) mineralogists-geologists from Europe (and overseas) attended the 1974 Exeter Conference of the Committee on Correlation of Age and Genesis of Kaolin. They heard the same lectures at the Conference, which included discussion on kaolin genesis by weathering in generality, and hydrothermal alteration specifically, e.g. Bristow's "Trinities" concept. They next visited the same Cornwall pits and outcrops in one another's presence. At the conclusion of the excursion an informal expression of genetic interpretation was surveyed. True to the traditional individuality of geologists, the interpretations of origin were well divided between the "end-member" theories: hydrothermal genesis vs wholly weathering, and a combination of hydrothermal premeation followed by intense weathering.

Will texture of the kaolin favor one interpretation or the other? Let each reader inspect the following SEM's, compare them with others of clays whose origins are known from independent evidence (Part I, Keller, 1976) and draw his own conclusions.

Clay from the western area, the Wheal Remfry Pit, is shown in Fig. 20, at $3000 \times$. Note the large, loosely packed books which are lightly coated with tiny flakes of kaolinite. Moving to the central district, clay from the large Blackpool Pit is shown in Fig. 21, at $2000 \times$. These books are about the same size as in Wheal Remfrey, two-thirds the magnification of Fig. 20, but there are fewer small flakes. From the eastern area, Pentruff Pit, Fig. 22, at $5000 \times$, the clay again shows prominent books and abundant small flakes. The long-productive, old Imperial Pit furnished Fig. 23, at 3000×. An API sample, 114A, collected at the drier after the washing process, is shown in Fig. 24. Note that kaolin crystals are remarkably durable, resisting disaggregation despite considerable factory processing. The same type of durability has been observed in Georgia kaolin, to be discussed in a later paper.

Across the English channel in Brittany near Quessoy, the kaolin occurs in coarse books, Fig. 25, $1000 \times$. This deposit was described by Esteoule and Esteoule-Choux (1974) as either an in situ deposit or one that has not been transported far. This texture accords with that of other in situ kaolins previously described (Keller and Hanson, 1975; Keller, 1976). "Incompletely kaolinized granite" (a muscovite leucogranite) is shown in Fig. 26, at 2000×. This micrograph shows well the typical, shattered appearance and dissolved micro-pores of kaolinizing feldspar as may be observed also on the surface of a weathering boulder. Books of kaolinite are observed in the process of formation. As to origin, Esteoule and Esteoule-Choux (1975, p. 10) follow the interpretation of J. Nicolas that "pneumatolytic and hydrothermal processes (were) responsible for kaolinization of the granite." Field evidence for hydrothermal alteration is manifestly open to question, in the opinions of the writer and several of the field-trip participants. Any present-day alteration obviously is by weathering. The texture in Fig. 26 is typical as has been said, of the weathering process.

Since 1960, the time of my first visit to Cornwall and Brittany kaolins, it has logically seemed to me that the kaolins of the two districts have likely originated by the same process(es). There are many geologic similarities, i.e. granitic parent rocks, topographic expression, kaolin bodies, mineralogy, and slight geographic separation (only by the English Channel, which is not much in terms of plate tectonics). Dissimilarities seem insignificant in comparison to similarities.

More formidable is the present separation (Atlantic Ocean) of the Carboniferous plastic refractory clays of North America (Missouri, Ohio, Kentucky, Maryland, Pennsylvania) from very closely similar Carboniferous plastic refractory clays in Scotland and England. They are so similar petrographically and ceramically they could be interpreted as geologic evidence of continental continuity before the time of break up with Atlantic spreading.

Assuming that Cornwall and Brittany kaolins were once connected, it is not unexpected that the interpretations of origin would be similarly controversial. In Cornwall, field evidence shows that tourmalinization, greisenization, and action by fluorine and boron took place in the granite bodies. At the time of the Exeter Conference (1974), no longer was accessible to view a sill reportedly beneath which, but not above, kaolin was found. The texture, by SEM, of Cornwall and Britanny kaolins bears closer similarity, in the opinion of this writer, to that of kaolin known to be formed by weathering than that known to be hydrothermally altered. Texture appears to indicate that the last significant process or stage of kaolinization in Cornwall and Brittany was supergene weathering.

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REFERENCES

- API Reference Clay Minerals, 1949–51) Research Project
 49: Preliminary Reports R.P. 49, Am. Petrol. Inst., P.
 F. Kerr, Editor, Columbia University, N.Y.
- Bardossy, G. (1962) Contributions to the knowledge of the kaolinitic refractory clay deposits of Cserzegtomaj: Ann. Inst. Geol. Pub. Hungary, 49 (fasc. 4), 1029–1052.
- Baumann, D. and Keller, W. D. (1976) Bulk densities of selected dried natural and fired kaolin clays: Clays & Clay Minerals 23, 424-427.
- Bentor, Y. K. (1966) *The Clays of Israel*: Guide-book to the excursions, Int. Clay Conf., Jerusalem, 1966, 121 pp.
- Bristow, C. M. (1968a) The derivation of the Tertiary sediments in the Petrockstow Basin, North Devon: Proc. Ussher Soc. 2, (1), 29–35.

- Bristow, C. M. (1968b) Kaolin deposits of the United Kingdom of Great Britain and Northern Ireland: XXIII Int. Geol. Cong. 15, 275–288.
- Bristow, C. M. (1974) The trinities associated with primary deposits of hydrothermal origin: *Proc. Symp. Int. Geol. Correlation Program, Exeter*, in press.
- Esteoule, J. and Esteoule-Choux, J. (1974) Guidebook, III Symposium International sur le Kaolin, Exeter-Rennes, INSA and Univ. de Rennes, Rennes, France.
- Freshney, E. C. (1970) Cyclical sedimentation in the
- Petrockstow Basin: Proc. Ussher Soc. 2, (3), 179–189. Halm, L. (1952) Comparative study of American and
- French flint clays: J. Am. Ceram. Soc. 31, 79-84. Hanson, R. F. and Keller, W. D. (1971) Flint clay by hydrothermal alteration of sedimentary rock in Mexico: Clays & Clay Minerals 19, 115-119.
- Highley, D. E. (1975) Ball Clay: Min. Dossier No. 11, U.K. Min. Resrcs. Consultative Committee, London, 33pp.
- Keeling, P. S. (1961) A new concept of clay minerals; geochemistry of common clay minerals: *Trans Br. Ceram.* Soc. 60, 449–475; 678–689.
- Keller, W. D. (1968) Flint clay and a flint-clay facies: Clays & Clay Minerals 16, 113–128.
- Keller, W. D. (1976) Scan electron micrographs of kaolins

collected from diverse origins—I: *Clays & Clay Minerals* **24**, 107–113.

- Keller, W. D. and Hanson, R. F. (1975) Dissimilar fabrics by scan electron microscopy of sedimentary vs hydrothermal kaolins in Mexico: Clay & Clay Minerals 23, 201-204.
- Keller, W. D., Wescott, J. F. and Bledsoe, A. O. (1954) The origin of Missouri fire clays, Clays and Clay Mins. Proc. 2nd Conf., Nat. Acad. Sci-Nat. Res. Coun. Pub. No. 327, 7-46.
- McQueen, H. S. (1943) Fireclay districts of east central Missouri: Mo. Geol. Surv. and Water Res., 2nd series, 23.
- Störr, M. and Lasch, G. (1975) The kaolinite clay deposit "Wetro," north of Bautzen. In Kaolin Deposits of the GDR in the Northern Region of the Bohemian Massif (edited by Störr M.), pp. 127–132. Sektion Geol. Wissenschaften, Ernst-Moritz-Arndt-Universitat Greifswald, Greifswald, GDR.
- Williams, E. G. (1960) Relationship between the stratigraphy and petrography of Pottsville sandstones and the occurrences of high-alumina clay: *Econ. Geol.* 55, 1291–1302.