Clays and Clay Minerals, 1968, Vol. 16, pp. 113–128. Pergamon Press. Printed in Great Britain

FLINT CLAY AND A FLINT-CLAY FACIES

W. D. KELLER
Department of Geology, University of Missouri, Columbia, Mo. 65201

(*Received* 17 *September* 1967)

Abstract—Flint clay is defined as a sedimentary, microcrystalline to crystalline clay (rock) composed dominantly of kaolin, which breaks with a pronounced conchoidal fracture and resists slaking in water. Additional ceramic (refractory) properties are implied, but not expressed, in the definition. Flint clay first given recognition in the U.S.A., has been observed on all continents; it will probably be found to be more abundant than its occurrences reported to date. It occurs in rocks mainly Carboniferous or Cretaceous in age, and is invariably associated with plant- or coal-bearing measures.

The environment of deposition is commonly lowlying paludal, in basins in either clastic silicate rocks or in karstic carbonates. It is inferred that parent illitic and/or kaolinitic clay colloids were transported into the swamps and there under-went further dialysis, alteration, and eventual crystallization *in situ*, producing a notably homogeneous kaolinite clay possessing interlocking crystallinity. Some occurrences were further desilicated to high-alumina minerals, particularly to diaspore and boehmite.

Flint clay is interpreted as being an intermediate member of a so-called flint-clay facies which is a claystone sequence ranging from high-alumina minerals (or potentially so) formed on the highest part, structurally and/or topographically, of the depositional area, and grading down-structure and/or lower in elevation through flint clay to iliite-kaolinite plastic clay and thence to marine illitic shale, all being equivalent stratigraphically. The geochemical reactions are depotassification of parent clay by substitution of K^+ by H^+, and desilication, especially where high-alumina minerals are formed.

INTRODUCTION

FLINT clay is defined as a sedimentary, microcrystalline to cryptocrystalline clay (rock) composed dominantly of kaolin, which breaks with a pronounced conchoidal fracture and resists slacking in water. This definition, a traditional one, expresses necessary requirements but is not wholly sufficient. To ceramists, who first gave flint clay recognition and distinction on account of its usefulness to them, the term flint clay connotes also certain ceramic properties difficult to described succinctly yet precisely—hence usually left unexpressed, but implied and stringently required in ceramic technology. They will be brought out later in this paper.

Earliest scientific investigations and publications on flint clay were carried out by ceramists, minimal attention being given it by geologists. Two noteworthy geologic papers appeared before 1940, however, and since then the geology of several flint clay districts has been described in considerable detail. Consequently, it is possible now to put together the salient details from the several observations so as to strike a common denominator for flint clay, *per se*, from them. It is the purpose of this paper to do such a synthesis, and to add further geochemical considerations and present a geological and geochemical discussion of flint clay for its own sake, including the proposal of a flint clay facies.

HISTORICAL

Prior to 1890, producers and users of refractory clay (commonly called fire clay) recognized a hard, non-plastic variety of fire clay as a high-quality refractory material (Cook, 1886). Miners of fire clay were impressed by a superficial similarity of this hard clay to flint (or chert) rock and gave it the name "flint clay". Hence basically, miners coined the name, ceramists shaped its meaning as has been indicated, and geologists, following, were left to fit their lithologic description to yield a rock that met the ceramic specifications.

Earliest documented reference to flint clay is in American literature. Wheeler devoted 40 pages (his Chapter IX) to flint clays in Missouri as early as 1896, but the field work on operating clay pits and mines on which this report was based was begun in 1890 so the name must have been used before then. Wheeler wrote (1896, p. 201), "The flint, rock, or non-plastic fire clay of Missouri is unique in mode of occurrence. It usually has a remarkably pure chemical composition, and is devoid of the chief characteristic of clay, or plasticity. The name "flint" clay is very appropriate as regards the appearance as it has a compact, dense, comparatively hard structure, and breaks with a sharp, conchoidal structure that resembles flint" [also chert, or light-colored "flint"], Fig. 1.

Orton wrote in 1893, "Non-plastic fire clays are

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

sometimes known as rock clays and also as flint clays. They exhibit when broken a smooth conchoidal fracture. On exposure to the weather they crumble into small but angular grains, beyond which the disintegration does not advance perceptibly. Their particles, even when finely ground, do not show the ordinary plasticity of clay. In this respect, one of the most important and characteristic of all the clays departs notably from the definition of the very class to which it belongs, but it is held in its place by its chemical composition and behavior. Moreover, by repeated and prolonged grinding, a growing measure of plasticity is imparted to the mass." Orton thus recognized that flint clay will develop appreciable plasticity when ground for considerable time in a wet pan, a fact many later writers have overlooked.

European use of the term lagged somewhat after American documentation. Searle did not list flint clay in his monumental volume on Refractory Materials in 1924, but in 1959 he and Grimshaw included it in their book on clays. In France, Halm reported the presence of flint clays in 1952, stating that, "Until recently [1952] it was generally admitted that flint clays did not occur in France". Slatkine and Heller (1961), and Wurzburger (1963) reported flint clays in Israel as of 1960. Warde described flint clay from South Africa in 1950, and Loughnan reported "tonstein-like" clays (probably flint clays) from Australia in 1962.

FIELD AND LABORATORY WORK

Field work began formally for this study during June and July, 1963. Informally, it began in 1929 with full-time employment (A. P. Green Refractories Co.) in the Missouri flint and diaspore districts, which continued for several years alternating between laboratory research and field geology. During the next 30 years, many of the important Missouri flint clay pits were visited and sampled at one time or another under either industrial affiliation or academic research. Approximately four months in 1963 and 1966 were spent studying in the field the flint and associated refractory clays in Kentucky, Ohio, Illinois, Indiana, Pennsylvania, Maryland, Colorado, and Washington. While on trips abroad, the France Ollieres and Israel Makhtesh Ramon deposits were visited and sampled. African clays were contributed by the Vereeniging Brick and Tile Co., Ltd., and Indian clays by the A. P. Green Refractories Co.

Laboratory facilities at the Department of Geology and Spectrographic and Electronmicrographic Laboratories of the University of Missouri were used part-time of three academic years.

More than 200 specimens were collected specifically for this study, in addition to numerous samples already available. X-ray diffraction and differential thermal analyses were run on most specimens. On some others only X-ray or infrared absorption records were made, and about twenty were subjected to emission spectrographic analysis. From this large file of test data only representative illustrations taken from purposely diversified clay districts will be presented. Repeatedly similar observations on varieties of clay taken from different localities attest conclusively to the same general character of flint clay as a petrologic entity regardless of age or source. The tabulations and illustrations presented are representative of many repetitiously similar diffractograms or thermograms.

DISTRIBUTION

Flint clay has been reported from all continents. The ages of rocks in which it occurs center about Pennsylvanian and Cretaceous, but include one additional occurrence each from the Eocene and Liassic (?). That all of these ages included environments of coal formation, marshes or swamps, and deep weathering is significant. In accord with increasing reports of finds of flint clay and in the opinion of clay geologists, it is believed that flint clay occurs far more widely spread geographically than has been documented, and more reserves for refractory uses will be discovered.

In the U.S.A. it occurs in Pennsylvanian-age rocks in Pennsylvania, Maryland, West Virginia, Ohio, Kentucky, Illinois, and Missouri, in Cretaceous-age rocks in Colorado, and in Tertiary, Eocene (?) rocks in Washington. The French clays are Cretaceous deposits at Ollieres (Var) in southern France (Halm, 1952). Israel flint clays lie on an unconformity that separates late Triassic rocks from the Liassic (?) Ardon formation in Makhtesh Ramon in the Negev Desert (Bentor, 1966). In Argentine, flint clay of probably Cretaceous (?) age occurs near Patquia, and Chile may have deposits of it about 90 km north of Santiago (J. F. Westcott, oral communication, August, 1967). India produces flint clay from Carboniferous rocks about 150 miles northwest of Calcutta. The south Africa flint clays are in lower Permian, coal-measure rocks in Transvaal within 50 miles of Johannesburg (Warde, 1950). The tonstein-like clays of Australia are described from also Permian coal-measure rocks in New South Wales (Loughnan, 1962).

LITHOLOGY, MINERALOGY, AND REFRACTORY PROPERTIES

Texture and structure

Flint clay is characterized by a microcrystalline to cryptocrystalline texture of inter-locking clay-mineral crystals, Fig. 1. Electronmicrographs of clay suspensions obtained by gentle shaking of

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

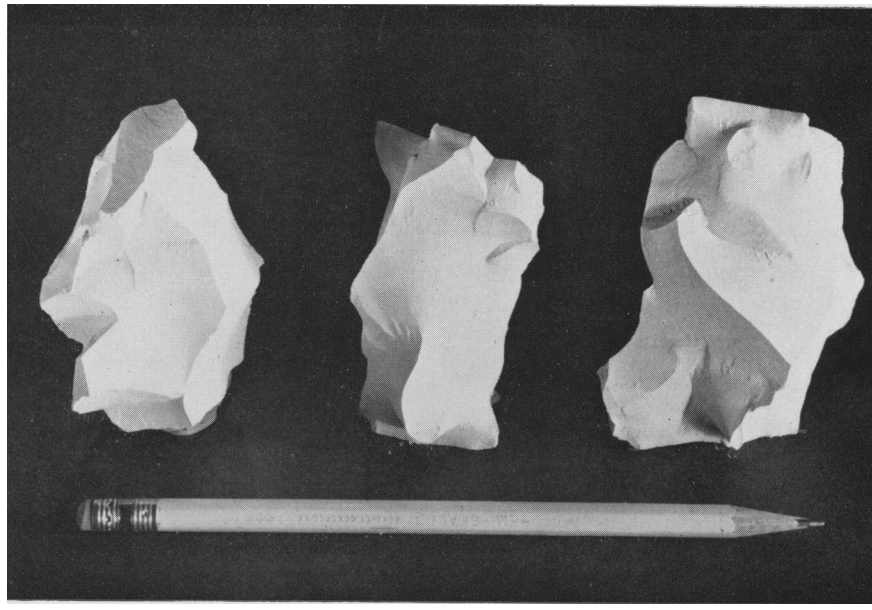


Fig. 1. First-quality flint clay. Note the conchoidal fracture, fine texture, and uniformity of material. Clay from Bueker Pit, near Owensville, Mo., described by Keller (1952) and Keller, Westcott, and Bledsoe (1954).

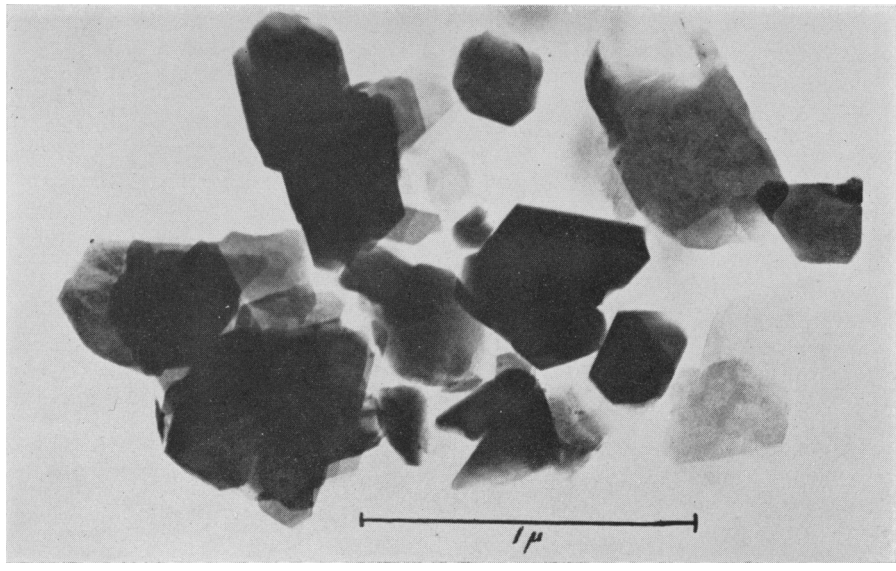


Fig. 2. Electronmicrograph of crystals from a suspension of flint clay shaken gently in water. Clay from Bueker Pit, near Owensville, Mo.

[*facing page* 114]

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

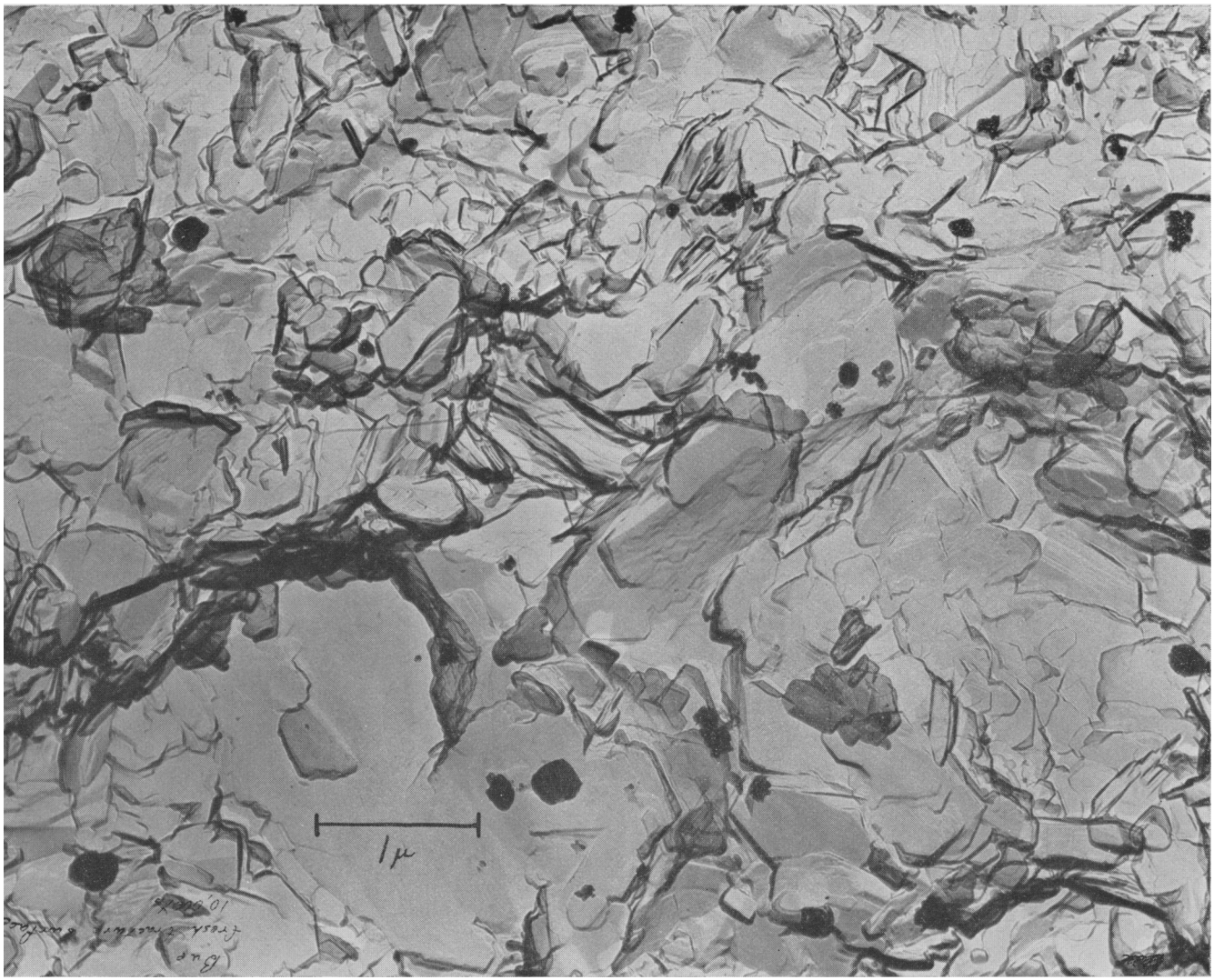


Fig. 3. Replica electronmicrograph of freshly fractured surface of flint clay. Note similarity to Fig. 2. Bueker Pit. Charles B. Roth, microscopist.

flint clay particles in water show most commonly subhedral to euhedral, stacked hexagonal kaolinite plates, ranging in size up to about 1 μ in cross section, but most of them are about 0·2–0·5 μ dia., Fig. 2. Some of the softer flint clays contain elongate shapes up to 1·5 μ in length which appear to be rolls of overlapping plates rather than rolls or scrolls of single sheets or a thin stack of more than one equi-dimensional sheets.

Carbon–metal replicas of surfaces of fresh fractures of flint clay show stacked crystals of the same general dimensions as those deposited from suspension, as cited above, Fig. 3. The thickness of the stacked aggregates is approximately the same general magnitude as their diameters. Because of this approach to equi-dimensionality, and because the angularity of step-wise stacking potentially dovetails with the basal hexagonal angularity of the plate, the kaolinite crystals in the flint clay can, and do, develop a close-packed and tightly interlocking texture. This texture resembles that of a monomineralic igneous rock, such as a syenite. This kind of texture is interpreted to contribute significantly to at least four attributes of flint clay: (1) its notable isotropic macro-properties in the clay rock, (2) high homogeneity in chemical composition, (3) resistance to slaking in water, and (4) relationship to the chemical system in which it originated.

Although flint clay is a variety of mudstone, just as shale also is, structurally flint clay is the antithesis of shale. Whereas fissility is the essential structural characteristic of shale, the typical flint clay is completely devoid of lamination, and reaches almost the ultimate in isotropism in texture, hardness, resistance to fracture and crushing, permeability, thermal properties, and even electrical resistance. Such isotropism is manifested by the clay fracturing conchoidally equally well in all directions, a property likewise consistent with fineness and complete randomness of crystals. Typical lack of fissility is extended into large-scale clay bodies, such as beds, large lenses and irregular masses that are outlined and delimited by parting planes, random or curved-surface joints, and incipient tension cracks developed during consolidation, syneresis, and dewatering. Freshly exposed surfaces, as in pits and mines, may spall into rounded forms. Even in thin section most flint clay shows random orientation of crystals and uniformity across the section—except, of course, where the fine-grained matrix is interrupted by oolites, flecks of carbonaceous matter, or grains of quartz, pyrite, or siderite.

Clay mineralogy

The essential and dominating clay mineral in flint clay is kaolinite. This arises from and reflects its original, ceramic functional requirement of refractoriness (flint fire clay). Bentonitic (montmorillonite) clays may also be as fine grained and develop conchoidal fracture surfaces as well as does kaolinitic flint clay, but the bentonite fuses below refractory requirements (below PCE 28 to 30) and may slake vigorously and swell forcibly and voluminously in water. Likewise, not all kaolin-rich clay is flint clay, e.g. ball clay, china clay, or "kaolins" of the ceramic and paper-coating technologies have different physical, slaking, and high-temperature maturing properties than does flint clay and therefore are not flint clay although they may contain 90-plus per cent kaolinite.

Although kaolinite is the main mineral, and ideally the only clay mineral in the "purest", and "hard" flint clay (rock), the "soft" and semi-flint varieties contain increasing amounts of illite, up to perhaps 25 per cent illite. Toward the other end of the flint clay sequence, high-alumina minerals increase in amount, e.g. approximately 5–10 per cent diaspore or boehmite in "burley" or nodular flint clay, and thence higher in quantity into Al-richer burleys, nodular, second-grade diaspore, and first-grade diaspore (or boehmite) clays.

The kaolinite in hard, scantily slaking, flint clay is commonly very well ordered crystallographically, yielding X-ray diffraction peaks that are as symmetrical, sharp, and numerous as in diffractograms that characterize reference kaolin minerals. The (020) and (002) reflections are clearly resolved. In thin section, the somewhat monotonous cryptocrystalline matrix of some flint clays may be interspersed with small oolite-like bodies or partially filled nearly spherical cavities that contain pockets of tiny but microscopically resolvable kaolinite flakes. These are interpreted as having been secondarily recrystallized, presumably well after the flint clay body had been consolidated. Galpin (1912) reported also high-birefringent clay plates interspersed with the kaolinite in some of the "ribs" (Galpin's term); these may have been illite, and are more likely to have occurred in "softer" flint clay matrices than in what is now categorized as "hardest" flint clay.

Kaolinite in soft flint clay and in semi-flint clays is commonly modified in several ways from that in hard flint clay. (Soft flint clay is more easily crushed and slakes more readily in water than does hard flint clay; semi-flint clay is a flint-like variety associated closely with plastic clay deposits and may overlap soft flint clay properties.) The high-spacing, low-angle side of the 001 basal reflection of soft clay may broaden asymmetrically to a considerable extent indicating mixed layering probably with water, but possibly with illite. Ceramic and chemical properties suggest illite, but

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

crystallographic precedence suggests water. Other peaks that are sharply resolved in well-ordered kaolinite may lose resolution and blend into bands in soft flint clay (See Fig. 4). A 10 Å bulge, or a fairly sharp 10 Å peak, may appear in the less "pure" varieties. No sharp distinction has been made between definitions of flint, semi-flint, and semi-plastic fire clays but a maximum of probably 20 per cent illite occurs in soft and semi-flint varieties of flint clay.

Differential thermal analyses of flint clays run under atmospheric pressure and at a heating rate of 12°C/min show endothermic peak temperatures characteristically 600–630°C from hard flint clays (lump samples), but below 600°C from soft flint clays, Fig. 5. As is well known, grinding kaolin clays tends to reduce the endothermic peak temperature (Keller, Pickett, and Reesman, 1966). Correspondingly, the endothermic peak temperature of hard flint clay lumps may be reduced approximately 100°C by powdering specimens of the same clays, Fig. 5. In general, but subject to some other variables, higher ordering of crystals tends to correlate with higher dehydroxylation peak temperatures, Fig. 6.

Halloysite that was identified in flint clay by the polarizing microscope before X-ray diffraction and electron microscopy became widely available has not generally been confirmed by the latter techniques. In the present investigation no electron micrographs of flint clay samples from either domestic or foreign deposits showed significant amounts of well-developed scrolls or tubes ordinarily attributed to halloysite morphology (halloysite nomenclature and speciation is still under review: Brindley and de Souza Santos, 1966; Chukhrov and Zvyagin, 1966).

A 14 Å clay mineral, presumably Al-chlorite has been observed in flint clay from the Olive Hill, Kentucky, district by Patterson and Hosterman (1962) and from a Missouri diaspore-boehmite clay pit (Hahn, 1954; Keller, 1964, p. 143). Attempts to recover and isolate this clay mineral in sufficient purity to characterize it have thus far been unsuccessful.

Non-clay "light" minerals

Quartz, in grains ranging from sand to clay size is very common in flint clay, although in some highest quality clays no quartz is detectable. Any silica present in flint clay, in addition to that in chemical combination in kaolinite, tends to lower the fusion temperature of the clay (because it moves the chemical composition of the clay system toward the SiO_2-Al_2O_3 eutectic). Users of flint clay for refractory purposes reject without further observation or study, therefore, highly "sandy" or "siliceous" flint clay. Consequently, quantitative data on the amount of sandy flint clay relative to that useful for refractories is not recorded, but from experience with clay mining operations, the amount of sandy flint clay is known to be large. The amount of quartz to kaolin in any occurrence may range from zero to one hundred per cent going from clay to a sandstone rim or roof rock.

Siderite in sand-size rhombs and particles is well known in flint clays of the Appalachian district, where it has been referred to by miners as "red lice" in the clay. Since it lowers the fusion, leaves gas pockets, and discolors the fired product, it is a cause for quality rejection of flint clay. On exposed surfaces of clay the siderite may have dissolved, leaving tiny white spots, also known as "white lice".

Pyrite (and marcasite) is a deleterious mineral in flint clay. Where present, it is commonly associated with carbon-rich varieties of clay.

Carbon and carbon compounds color flint clay through shades of gray to coal-black. The darkness of color is not a reliable indicator of the amount of carbon present. Some compact black clays fire to a nearly white, high-quality ceramic product, whereas lighter gray, "smutty" clay may be unacceptable.

Iron oxides, which may color clay purple, red, or brown, are as common, perhaps, as quartz in flint clay. Because iron is a fluxing element with aluminum silicate, amounts above about three per cent Fe_2O_3 cause the clay to be "irony", and suspect for refractory purposes. It may still be perfectly good "geologic" hematitic flint clay (analogous to good geologic sandy, pyritic, or carbonaceous flint clay), and must be given full attention in an exhaustive geologic consideration of the processes and environments of origin of flint clay, although it is "junk" clay to the ceramist.

Similarly "alkali" flint clay, although rejected by the refractories ceramist, is a part of the geologic record of flint clay origin. Alkali clay refers to low-fusion clay that is fluxed by the presence of alkali, or less commonly, alkaline earth metals. One to two per cent RO in a clay devoid of free silica may not affect the refractoriness, but if fine-grained quartz is associated with the alkali a small amount of alkali-silicate glass thereby generated melts down the clay. "Alkali" minerals are most commonly high-alkali illite, a sedimentary (sodic) or possible proto-alunite (the diffractogram deviates slightly from hydrothermal alunite: Keller, Gentile, and Reesman, 1967), secondary gypsum, and rarely calcite or dolomite.

Secondary torbernite was observed along a few partings in Missouri flint clay (Keller, 1952).

Heavy minerals

Owing to the fineness of crystals in flint clay and

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

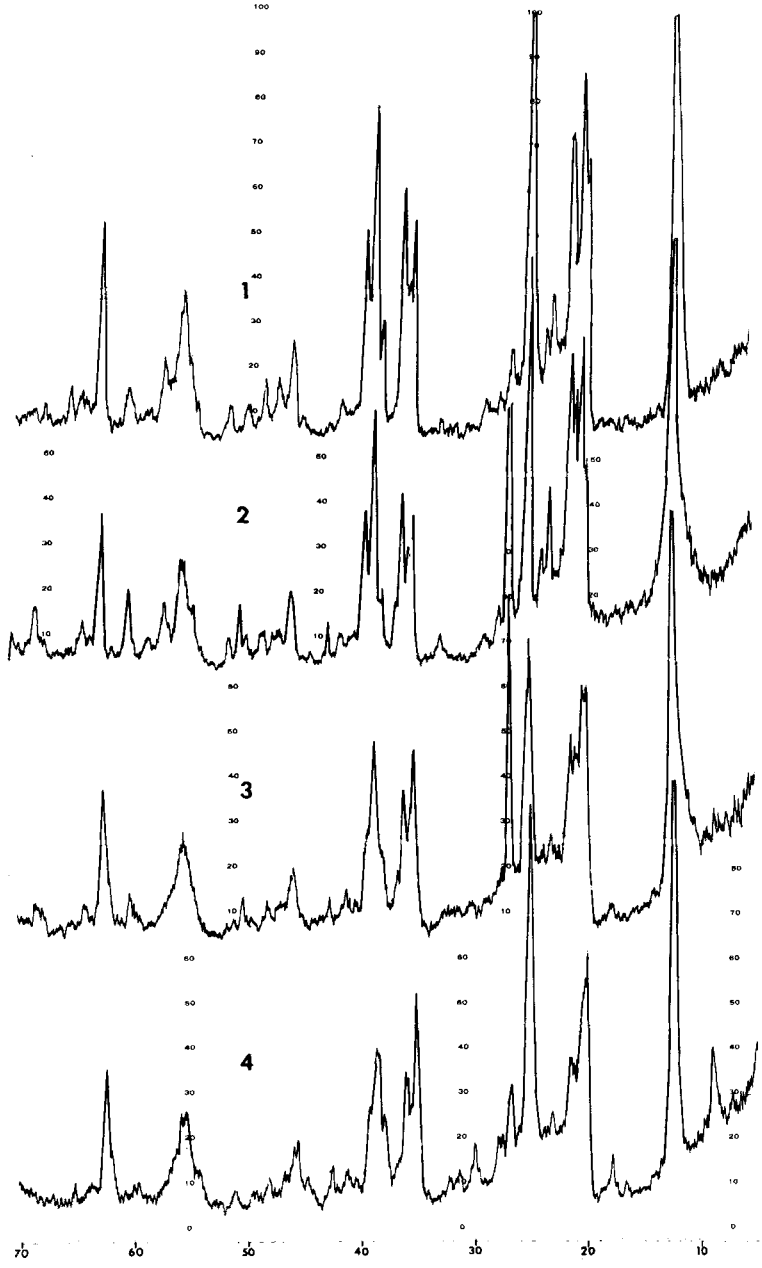


Fig. 4. X-ray diffractograms of flint clays.

No. 1 is a hard flint clay from the Farnberg pit, near Owensville, Mo. Reflections are sharp, symmetrical and well resolved, a lTc diffractogram.

No. 2. is a soft flint clay from Mt. Savage, Maryland. The 7 Å basal reflection shows expanded development on the low-angle, high-*d* side. Some quartz is also present.

No. 3 is a semi-flint clay – in effect a soft flint clay in association with plastic clays in a dominantly plastic clay deposit at Mexico, Mo. Note the expanded 7 Å spacing.

No. 4 is an illite – containing flint clay – note the 10 Å peak. From a deposit near Bland, Mo.

Copper Kα radiation.

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

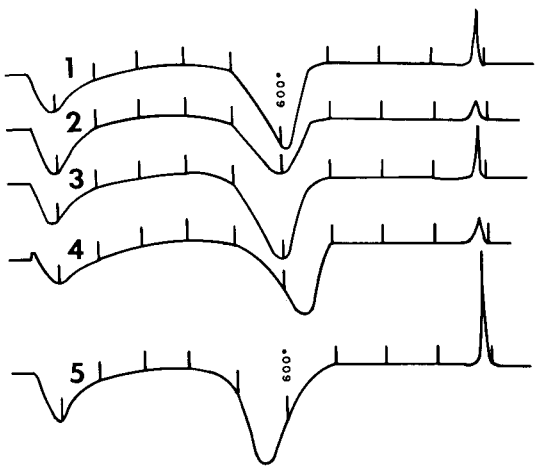


Fig. 5. Differential thermograms of flint clays run on single lumps (50 mg) of clay, except for No. 5. Temperature rise, 12·5°C/min.

No. 1 is hard flint clay from the Scego pit, near Owensville, Mo. Note dehydroxylation peak temperature is above 600°C.

No. 2 is a soft flint clay from the same pit as No. 1. Note the dehydroxylation peak temperature is slightly below 600°C.

No. 3 is a medium-hard flint clay from India.

No. 4 is a hard flint clay, run in a single lump (53 mg). from Hammanskraal, South Africa. This is one of the highest dehydroxylation peak temperatures for flint clay observed in our laboratory.

No. 5 is from the same hand specimen as No. 4 except that the clay was pulverized, 51 mg Note how the dehydroxylation peak temperature has lowered almost 100°C from No. 4.

The 980°C exothermic peak in flint clay tends to be more subdued in lump samples than in powdered samples.

sorbent properties of clay particles in suspension, the separation of heavy minerals from the clay and their subsequent identification is rarely easy. Ordinarily the whiter, and "purer" flint clays contain minimal amounts, both qualitatively and quantitatively, of heavy minerals – perhaps only a few grains of anatase, leucoxene(?) or zircon(?) recoverable from 5 g of clay. Despite a poor recovery of heavy minerals from these clays, in thin section at high magnification abundant very fine "dust" having high relief (and probably high index of refraction) appears uniformly and abundantly disseminated in the clay matrix. The expectation that this comes from high-index mineral crystallites or nuclei containing "high-index elements" such as Ti, Zn, V, B (tourmaline), or even Pb and Zn is supported by finding these elements in emission spectrographic analyses of the clays (tabulated under chemical composition).

Warde's work (1950) on African flint clays yielded a relatively rich variety of heavy minerals, namely: zircon, rutile, tourmaline, garnet, leucoxene, iron ores, and monazite. A possible granite parent source for part of these clays may account for the relatively extensive development of heavy minerals in them. It is noteworthy that the heavy minerals in flint clay are strongly resistant to chemical weathering.

CHEMICAL COMPOSITION

Major chemical elements

The chemical composition of flint clay may be thought of basically as that of theoretical kaolinite diminished by some titania, iron oxide, small amounts of alkali and alkaline earth metals, possibly minor phosphate, sulphate, carbon, and extra water. Titania is always present, usually from one to three per cent. The amounts of other elements present are functions of non-kaolin minerals that were deposited in association with the kaolinite in the flint clay sedimentational basins.

Typical chemical analyses of flint clays are assembled in Table 1.

Spectrographic analysis

Arc emission spectrographic semi-quantitative analyses run on 10 representative flint clays are shown in Table 2. Greatest value among elements determined spectrographically are attached to those in trace amounts at the right of the table beginning with Ti, which is likely to be present in anatase, rutile, leucoxene or their precursor minerals. V is a common substituent of Al in the octahedral sheet of 2 : 1 (micaceous) clay minerals but independent evidence as to whether it proxies for Al or is accessory in the flint clays is lacking. Zr is probably present in zircon. Cu, Ni, Zn, Ga, and Cr could possibly substitute for Al, but whether they do is not known. B probably represents tourmaline.

In any case, recalling that high-relief dust is found uniformly dispersed across the thin sections of flint clay, it is presumed that these trace elements are likewise uniformly dispersed through the clay.

Desirable refractory properties

Clean or relatively "pure" flint clay possesses a rare combination of many desirable refractory properties: high PCE (Pyrometric Cone Equivalent, a test of fusion under standard heating conditions), good bond and high structural strength maintained with refractory bond clays, low spalling loss due to thermal or structural stress, firing to a high density and low porosity, and maintenance of permanent volume over the entire life of high-heat service. Furthermore, flint clay presents no serious difficulties to processing and fabrication during manu-

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

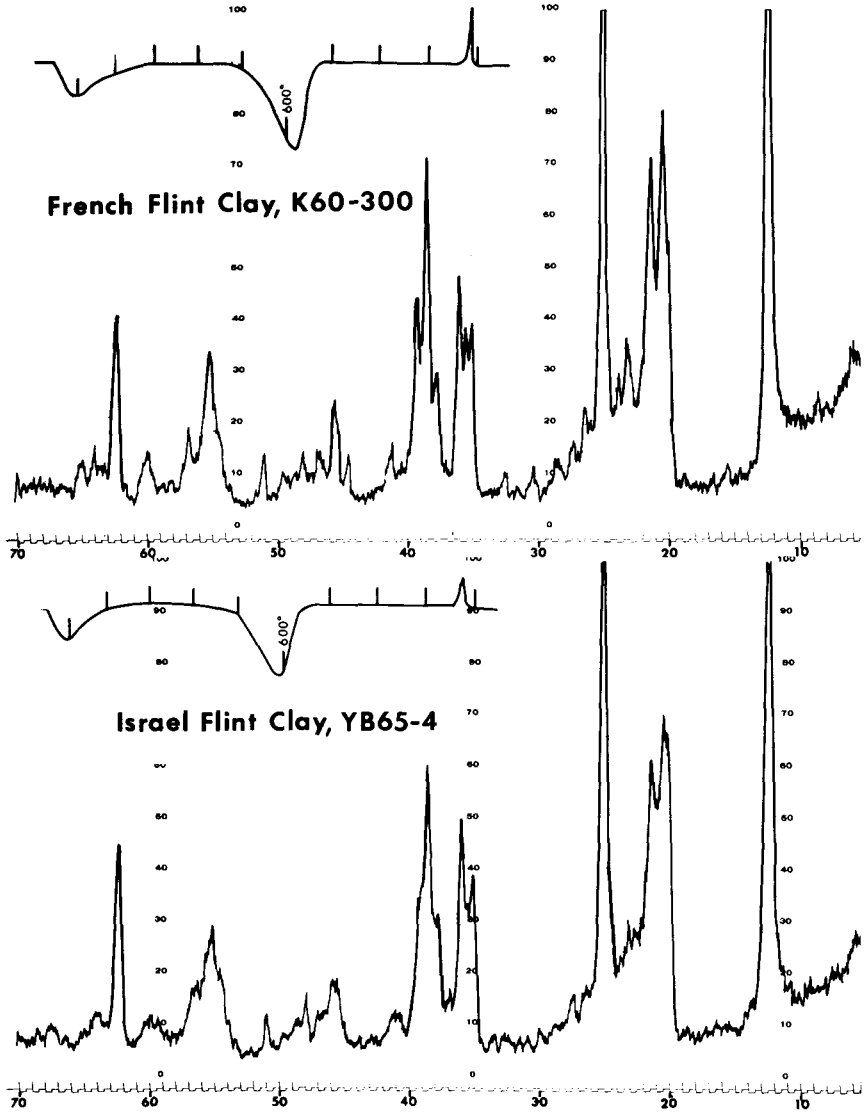


Fig. 6. The sample of better-ordered variety French flint clay dehydroxylates at a higher peak temperature than does the sample of softer, poorer-ordered variety of Israel clay.

facture into finished refractory products. As has been implied, not all kaolin-rich claystones possess these same ceramic and physical properties.

The mineralogic and lithologic bases for the desirable properties of flint clay appear to be the interlocked crystal texture of relatively well ordered kaolinite in stacked plates, completely homogenized, and "uniformitized" in three dimensions, with the small amount of impurities located probably interstitially to the kaolinite. This produces material of high natural density, uniformity in all directions, and the possibility of complete ceramic compatibility with bond-type clays, enabling the fabrication of a "monolithic" clay refractory essentially devoid of particular directions of weakness in service conditions.

High resistance to thermal spalling, i.e. resistance to breaking or cracking of the refractory when heated or cooled suddenly, early distinguished flint clay as raw material. This spalling resistance is probably due to the isotropism of the clay matrix and the purity of the kaolinite so that the mullite

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

Table 1. Chemical analyses of flint clays

	(1)	(2)	(3)	(4)	(5)	(6)
SiO_2	45·1	42·68	46·86	48·03	44·13	42·44
Al_2O_3	37·8	38·49	38·22	36·10	39·32	36·69
Fe_2O_3	0·45	1·55	1·19	0·30	0·60	2·13
FeO	0·48					
MgO	0·09	0·08	–	–	–	0·28
CaO	0·16	–	–	–	0·23	0·20
Na_2O	0·09	0·28	tr.		0·55	0·72
K_2O	0·64	0·49	tr.			
TiO_2	2·1	2·90	0·41	0·74	1·45	4·00
P_2O_5	0·01					
MnO	·01					
H_2O	·4	14·07	13·59	14·56	13·88	13·37
CO_2	0·07					
SO_3	0·03					
Sum	100·50	100·54	100·18	99·73	100·16	99·83

(1) Kentucky flint clay (Patterson and Hosterman, 1962). (2) Missouri flint clay (Thornberry, 1925, p. 34). (3) African flint clay (Warde, 1950). (4) Colorado flint clay (Waage, 1953). (5) French flint clay (Halm, 1952). (6) Pennsylvania flint clay (Greaves-walker, 1939).

Table 2. Spectrographic analysis of flint clays

Clay No.	Si	Al	Fe	Mg	Ca	Ba	Sr	Ti	V	Zr	Mn	Cu	Co	Ni	Zn	Ga	Mo	Cr	B
(1)	M	M	m	m	m	t	t	m	m	tm	t	t		t	t	t		m	t
(2)	M	M	m	m	m	t	t	m	m	tm	m	t		t	t	t		m	t
(3)	M	M	m	m	m	t		m	m	tm	m	t		t	t	t	t	t	t
(4)	M	M	m	m	m	t		m	m	tm	t	t	t	t	t	t		m	t
(5)	M	M	m	m	m	t		m	m	tm	t	t	t	t	t	t	t	m	t
(6)	M	M	m	m	m	t		m	m	tm	m	t		t	t	t		m	t
(7)	M	M	m	m	m	t		m	m	tm	m	t		t	t	t	t	m	t
(8)	M	M	m	m	m	t		m	m	tm	m	t		t	t	t	t	m	t
(9)	M	M	m	m	m	t		m	m	tm	t	t	t	t	t	t		m	t
(10)	M	M	m	m	m	t	t	m	m	tm	t	t		t	t	t		m	t

M > 1% m 0·01–1% t < 0·01%

(1) Missouri hard flint clay, Bueker pit, Owensville, Mo. (2) Missouri soft flint clay, Gleize pit, Bland, Mo. (3) Colorado hard flint clay. H&W Pit, Good pasture, Colo. (4) French medium flint clay, Ollieres (Var), France. (5) Israel hard flint clay, Makhtesh Ramon, Negev Desert, Israel. (6) India hard-med. flint clay, 150 mi. N.W., Calcutta, India. (7) African hard flint clay, Hammanskraal Deposit, Transvaal, Africa. (8) Pennsylvania hard flint clay, Chase Pit, near West Decatur, Penna. (9) Missouri hard flint clay, Maher Pit, Whitesides, Mo. (10) Missouri med.-soft flint clay, Independent pit, near New Florence, Mo.

Analyses by Spectrographic Laboratory, University of Missouri.

and glass (high temperature Al_2O_3-Si_2 phases) formed in it have uniquely favorable characteristics. The mullite needles formed in hard flint clay, as shown in thin section, are notably tiny, abundant, and matted into a three-dimensional, interlocking network that imparts uniformly high strength. The tininess of the mullite needles is probably a function of very high viscosity of the glass phase (low in alkali flux because of the purity of the kaolinite which crystallized from a parent colloidal gel). Even at high temperature of incipient fluxing the glass is viscous, tough, and "stringy", and does not shatter profusely when thrust into water or cold air.

The property of flint clay refractories to maintain constant, or "permanent", volume while in service at sustained high temperatures contributes vastly to their value. They do not deteriorate as does a shrinking refractory, which opens or cracks inward permitting flame, gas or fluids to enter and erode it.

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

The probable basic cause for flint clay's resistance to in-service shrinkage is its origin by crystallization in place from clay colloids, which builds into the clay a high internal density, compactness, and mineral purity—properties of stability that persist through high temperature. For these same reasons, high strength and low porosity and permeability are also developed in flint clay refractories. It is the combination of these refractory properties available in one clay material that distinguishes flint clay, and which the ceramist identifies as being mandatory, but not expressed, in flint clay and its definition.

STRUCTURAL AND STRATIGRAPHIC OCCURRENCE

Flint clays are invariably sedimentary deposits. They occur in discontinuous beds, lenses, or downward pointing cone or funnel-shaped bodies, whose diameters typically range from 5 to 500 m dia. or length. The discontinuity in clay layer results from deposition in haphazardly joined basins and channels of irregular depths.

Two major types of depositional basins for flint clay include those (1) underlain by relatively soluble carbonate rocks as in Missouri, France, and Israel, and by possibly gypsum in Israel, and (2) depressions within clastic sediments such as sandstone or mudstone, e.g. in the Appalachian and Appalachian-flanking provinces, Colorado, and Washington, Argentine, and Australia. In the African flint clay district both types were developed: "sinkholes and collapse valleys . . . underlain by pre-Karroo dolomite" and "depressions by . . . ancient drainage systems" (Warde, 1950, p. 257).

Basins in limestone are eroded dominantly by irregular dissolution, many being karstic and leading to caverns or collapse structures. In Missouri occurrences they may show downward relief up to 20 or 25 m across a short horizontal distance, but the upper surface of the clay filling them may not vary more than one or two meters in elevation over a hundred square km. The thickness of the clay deposited in this Missouri district is then largely a function of the depth of the basins eroded in the limestones of the Mississippian, Devonian, and Ordovician ages below the Pennsylvanian unconformity. A 20-m thickness of clay may pinch out to practically zero within the same horizontal distance, or it may maintain several m thickness over an irregular dia. of 100 m (for details see McQueen, 1943, or Keller, Westcott, and Bledsoe, 1954). Deposition of clay and occasional collapse of a solution structure beneath may have taken place simultaneously in the Missouri district. Typically, a basal chert conglomerate that grades up through sandstone intervenes the older limestone and flint clay above. Commonly, but not always, the sandstone, and sandy clay grade through iron-oxide stained clay into cleaner flint clay deposits, but sandstone (Keller, 1938) and shale (Keller, 1952) have been observed overlying the clay in several deposits. Sandstone covers the flint clay in France (Halm, 1952).

Whereas flint clay deposits in limestone country rock tend to be basin or funnel shaped, those within sandstone or mudstone tend to occur more nearly bedded, or in flatter lenses. Their depositional basins in clastic rocks are interpreted to have been channels in sandstone (in Colorado, Waage, 1953), low-lying coastal swamps (in Kentucky, Patterson and Hosterman, 1962), or channels and basins (in Pennsylvania, Foose, 1944) some of which were on topographic highs on a sandstone, the Lower Connoquenessing (Williams, 1960). The thickness of the flint clay in these basins ranges commonly from 0 to 10 ft. usually not more than 5 ft, but locally possibly up to 20 ft. No single unique sequential relationship between flint clay and plastic clay, sandstone, or shale prevails across all of the producing regions or localities, although in one particular district, for example, sandstone may predominantly overlie, or underlie, the clay.

Lateral gradation between flint clay and plastic clay, or flint clay and high-alumina clay characterized by diaspore or boehmite is the rule rather than the exception. Of the Mercer clay in Pennsylvania, Foose (1944, p. 568) wrote, "Lateral variation and gradation of the physical character of the clay itself is very common. An almost solid section of combined block and flint clay may change within 100 ft to a "representative" section, or even to a dominantly nodule clay." Likewise in Missouri clay, one boulder may show complete gradation from flint clay (39% Al_2O_3) to first-grade diaspore (70% Al_2O_3, trade usage, but analyses are run on raw, field samples of clay). The French and Israel occurrences show similar short-distance gradation.

ORIGIN OF FLINT CLAY

A rational theory of origin for flint clay in general may be synthesized logically by coordinating the similarities in interpretations made by investigators of individual flint clay districts plus addition of some principles of geochemistry.

(1) Depositional sites were lowlying coastal swamps and marshes, stream channels from which the more vigorous currents had been diverted, and solution-eroded depressions in regions of carbonate rocks which still stood high enough that ground water could move through and dissolve the rock. Present day examples of these environments are South Atlantic, vegetation-filled coastal rivers and swamps (Greaves-Walker, 1939), and carbonate

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

regions in the cenote region of Yucatan (Urbina, 1910).

(2) The occurrence of plant remains, coal beds in close association, or clay-casted wood (Keller, 1938) in flint clay attests that vegetation was present in all flint clay districts, and must have been lush in some of them. Upright roots preserved in certain Kentucky and Pennsylvania clays indicate that the clay mud served as a soil. It is interpreted as a transported soil, based on the observation that in present-day deltaic, coastal, or alluvial swamps the mud serves as a fertile substrate for vegetation although it displays no A-B-C horizons as in the parent upland soil from which it was eroded. Parenthetically, various underclays may have similar histories.

The vegetation contributed to flint clay formation in several ways. Mechanically, it may have served as a filter that lined the marshes and held out coarser clastics but allowed colloidal clay suspensions to pass. Plants growing in the clay extracted alkali and alkaline earth metals from the clay for growth and metabolism. These metal ions are easily leached out of leaves and stems after they fall from the plants, thus mobilizing the flux ions for removal by solution. Silica likewise will be mobilized, thereby enriching the clay residue in alumina. Silica accumulating plants, such as reeds and bull rushes, live in this type of environment. If *Equisetum* was present, the aqueous solubility of silica could have been more than doubled relative to its value in fresh water, as observed by Lovering (1959). Chelation by organic compounds, and complexing by CO_2 from decaying organic matter could enhance the removal of fluxes and silica from the clay colloids and mud in the swamps. H^+ ions from organic acids would react with the silicates present to accelerate kaolinization.

(3) The parent clay material deposited in the entire lowlying area was derived from the regolith of the low-relief land mass adjacent. Sand, silt, and coarser clay fractions of the stream load were dep sited on interfluves and in stream fills outside the quietest, plant-fringed basins. Much of the parent clay must have been illite as shown by the illitic plastic clay associated laterally, above, or below the flint clay. In the Missouri locality, illite is the main clay mineral in Paleozoic limestones that were exposed and weathered in the paleogeographic areas around the Pennsylvania-age sedimentation (Robbins and Keller, 1952). Limestone-derived detritus also was available in the French, Israel, and part of the African districts. Illitic clay from weathering Silurian limestone in Kentucky has been observed to be readily susceptible to endellization by virtue of endellite-halloysite nodules forming in the residue (Keller, McGrain, Reesman, and Saum, 1966). Presumably higher susceptibility of it to kaolinization arises because the clay is in a second (or more) cycle of weathering. Likewise, the clay residue in Missouri caves, derived from weathering limestone, is commonly rich in kaolin minerals. Where the source rock of clay parental to flint clay was clastic, as may have been the case in the Appalachian regions, apparently it was mineralogically similar to the limestone-derived clay because the plastic clay and shales of these two regions are similar.

(4) Given now that clay colloids of illite, accompanied by some kaolin fractions, plus dissolved alumina and silica, are contained in a vegetation-fringed swamp. By what processes is this clay transformed into flint clay, and when does the alteration take place?

The mechanism is clearly one of depotassification and desilication by way of dissolution, hydrolysis, and dialysis. Clay minerals dissolve, incongruently and releasing silica at first at least, in fresh water as was shown by Reesman's extensive experiments (Reesman, 1966; Reesman and Keller, 1967; Reesman and Keller, in press, 1967), Table 3.

Stability relations between kaolinite and mica with respect to K^+/H^+ and H_4SiO_4, as shown graphically by Garrels and Christ (1965, p. 361), are applicable to the illite–kaolinite system in the colloidal clay mud in flint-clay producing swamps. Fig. 7. Fresh rainwater at pH 7 to below 5 (Carroll, 1962) is a source of H^+ ions, augmented by organic and carbonic acids. Straight-forward dissolution of K^+, and substitution of K^+ by H^+ to achieve Donnan equilibrium (Bolan, 1932) between the colloidal clay and fresh, or especially acidified, water are the mechanisms by which typical, K-rich illite becomes progressively H-rich illite and then kaolinite. Each colloidal clay particle suspended in water, because of the structure of clay, furnishes it own semi-permeable membrane through which K^+-H^+ dialysis occurs, Fig. 8.

The K^+/H^+ ratio plotted in Fig. 7 may be expressed as pK minus pH. From distilled-water solutions (presumably equilibrated) representative clays of the plastic to flint series, the pK-minus-pH values show a corresponding monotonic decrease, as below (Keller, 1967, data from Reesman, 1966).

This transition in chemical properties was accompanied by a mineralogical transition from illite-containing, kaolinite plastic refractory clay to illite-free or low-illite, soft and/or semi-flint clay in which mixed-layering occurred, Fig. 4. This mixed layering is shown on X-ray diffractograms by an asymmetrical widening of the 7 Å peak on the high-d, low-θ angle side, whereas the relatively pure kaolinite in the harder varieties of flint clay is usually better ordered. Thus, the record seems

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

Table 3. Aqueous dissolution of representative flint clays and associated clays

Clay No.	Si	Al	K	Na	Ca	Mg	pH
			(Dissolved ppm)				
(1)	3·82	0·007	0·18	0·11	0·04	0·03	5·3
(2)	3·22	0·0005	0·21	0·05	0·65	0·10	6·8
(3)	5·90	0·01	0·37	0·72	1·14	0·26	7·0
(4)	3·74	0·011	3·7	2·61	31·1	7·8	5·0
(5)	7·9	0·90	11·4	0·85	5·0	3·7	4·0
(6)	0·68	0·0007	0·12	0·01	0·80	0·26	6·0

(1) Maryland hard flint clay, Mt. Savage. (2) Missouri hard flint clay, Bueker pit. (3) Missouri medium flint clay, New Florence. (4) Missouri semi-flint clay, Mexico, Mo. (5) "Grundite" illite, Illinois. (6) Diaspore surface boulder, Swiss, Mo.

Data from Reesman (1966).

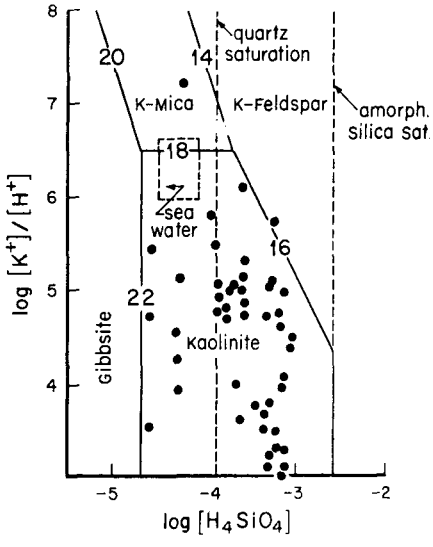


Fig. 7. Stability relations in the system K_2O-Al_2O_3-SiO_2-H_2O at 25°C and 1 atm, as functions of $[K^+]/[H_4SiO_4]$. Solid circles represent analyses of waters in arkosic sediments (from Garrels and Christ, 1965).

clear that kaolin clay evolved from illite in a colloidal system stabilized somewhere in the kaolinite field represented in Fig. 7. If desilication continued, diaspore and boehmite, or possibly their precursor gibbsite, began to form, usually in oolites, yielding burley or nodular high-alumina clays.

Although emphasis has been placed on alteration of illite to kaolinite in the swamp, there is no question but that colloidal kaolin can and may have formed to a large extent in the regolith that contributed colloidal mud to the swamp. Insofar as this occurred, extensive chemical and mineral alteration possible in the quiet swamps has simply been preceded by pedologic weathering. Criteria are not known to differentiate how much alteration to kaolin composition occurred in either of the places.

The kaolinite stability field is wide, permitting a wide variation in composition of the chemical system, and considerable time, for alteration of the colloidal clay to take place and still produce kaolinite. The colloidal mud may be envisaged as slowly being compacted under its own weight and later also that of overlying sediments. During most of the compaction and de-watering process it was a homogeneous colloidal body—acting as a low-

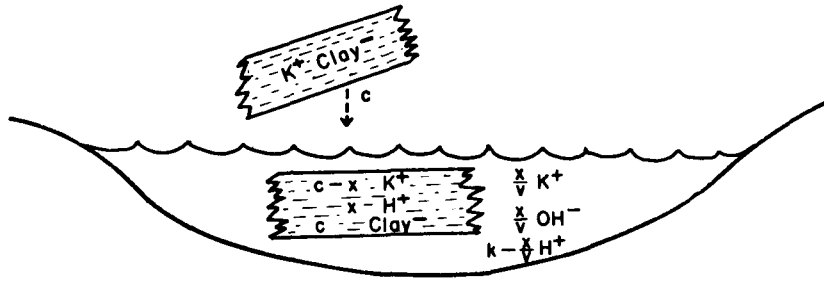


Fig. 8. Schematic illustration of a K-containing illite clay particle losing K^+ for H_+ by dialysis via the Donnan effect from water in a swamp, (from Keller, 1957).

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

Typical K^+/H^+ ratios of Missouri refractory clays

Clay	pK minus pH (mean values)*
Plastic fire clay, Mexico, Mo.	−3·15
Soft flint clay, New Florence, Mo.	−2·07
Semi-flint clay, Mexico, Mo.	−1·90
Hrad flint clay, Owensville, Mo.	−1·38

*Reesman, 1966.

temperature, silicate "magma"—having essentially a kaolinite composition plus minor and trace amounts of such elements as Ti, Zn, Ga, Zn, etc. either dissolved, sorbed, or in colloidal mixture. From the colloidal kaolinite "magma" crystallized a homogeneous, tightly interlocking monomineralic kaolinite rock, through which "impurities" were uniformly dispersed interstitially or possibly sorbed on the clay crystals. The uniform, non-swelling kaolinite packets having crystallized (not compacted) into an interlocking texture developed a rock which is resistant to slaking, isotropic in properties, and fractures conchoidally. Its crystallization from a viscous, colloidal, low-temperature kaolin silicate "magma", closely parallels the crystallization of, say a syenite, from a viscous, high-temperature feldspar silicate magma. In contrast, a kaolin rock that was compacted by pressure (not crystallization), or one that contains montmorillonite or illite (this includes many "kaolins" as well as soft flint clays), are susceptible to slaking in various degrees.

The time in its petrologic history that the flint clay evolves is significant. There is no question but that in the Missouri district kaolinization and major high-alumina mineralization took place in the depositional basin or within a small fraction of the Pennsylvanian Period thereafter. Observation of fresh, green, illitic thin Excello shale (under thick, well-developed Ft. Scott limestone) overlying oxidized, *weathered*, otherwise hard, fresh flint clay and diaspore in the Bueker clay pit (Keller, 1952*a*; Keller, Westcott, and Bledsoe, 1954) shows unequivocally that clay formation had been completed well before Excello time in the Cheltenham–Excello interval. This interval includes not more than the Atokan and part of the Des Moinesian Series and possibly less than that; these are only the lower two of four series comprising the Pennsylvanian Period (Howe and Koenig, 1961). No doubt secondary solution and possibly some recrystallization has occurred later in the flint clay, but the major episode of flint clay formation dates back to essentially one of syngenesis.

Question has been raised as to the direction in which silica and potassium were removed during alteration. Traditionally in geologic observation and thinking, the direction of leaching by meteoric water in geologic systems has been downward, but this also traditionally implies sufficient relief to allow circulation–otherwise, waterlogging is specified. Four considerations negate downward leaching during flint clay formation: (1) the land was lowlying, (2) usually impermeable clay (flint or plastic underlies the flint clay or upper part of it, tending to seal off downward leaching, (3) the most highly leached clay is rarely at the top of the flint clay section as it should be if leaching was downward, and (4) flint clay deposits rarely, if ever, show a concentration of silica and/or potassium in the lower part of the clay or in the rock beneath. Foose (1944) commented in regard to the Pennsylvanian clays, "there is little field evidence at this time to indicate what became of all the leached silica".

Where kaolins are formed by hydrothermal leaching, upward of course, of silicate rocks, as in Mexico, huge "gossans" of silica, useful as visible guides to ore, are developed above the clay (Hanson and Keller, 1966; Keller and Hanson, 1967). The Missouri clay pits definitely do not show significant silicification in either basal clay layers or rocks below the clays. To explain the disposition of silica during flint clay formation in Missouri, Keller, Westcott, and Bledsoe (1954) proposed that it was flushed off by fresh water moving across the top of the swamp, having risen, with potassium and other fluxing ions, by upward dialysis. I have seen no evidence of downward silicification in any American, French, or Israel flint clay deposits–indeed nothing that suggests even to a miniscule degree the silica deposits I have observed above hydrothermally formed clays in Mexico. It seems strongly compelling that the only way these lowlying, hydrolyzing basins of clay minerals could lose silica would be to the water upward—upward dialysis—and that it was then flushed away by rain water or any other movement of water on top, Fig. 8.

FLINT CLAY FACIES RELATIONSHIPS

Facies relationships of flint clay to associated clays, which are evidenced on bases of clay mineralogy and physical stratigraphy, have been worked out in greatest detail in the Missouri occurrences. Mineralogically, flint clay stands in an intermediate position. In the direction of higher alumina (and lower silica) kaolinitic flint clay grades, by way of burley and nodular clays, into diaspore and boehmite. In the opposite direction, toward higher silica and lower alumina, kaolinitic flint clay grades into kaolin-illite plastic clays,

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

and thence to marine illitic shales. These trends are well illustrated in the Missouri clays.

Stratigraphically and structurally, the Missouri diaspore clay (with minor amounts of boehmite) occurs highest on and closest to the center of the Ozark dome, see Fig. 9. Down slope and down structure, but in the same stratigraphic interval, the Cheltenham formation, occur progressively the flint-clay dominant band, thence plastic fire clay, and farthest down, covered by younger Pennsylvanian-age sedimentary rocks, are non-refractory, high-silica shales (illitic and fissile).

In the Colorado refractory clay district, Waage showed a source for the clay from the land masses to the west (Waage, 1953, Fig. 8 p. 21, and p. 49). He inferred that as deposition in a "large swamp area with a coastal plain"... "progressed the swampy vegetation may have encroached on the bodies of open water [with the result that the flint clay bed in the marginal areas is not as thick as in the areas that remained in open water]". He emphasized the cyclothemic character of the deposits, but did not discuss a facies possibility. During a reconnaissance field survey of the Colorado refractory clay district, I found flint clay on the west giving way to more plastic clay toward the east, which is in a direction away from the higher western source and land area. Therefore, I interpret a facies relationship here, but not so clearly developed as in Missouri.

Both the French and Israel flint clays are associated with plastic clays, either laterally, vertically, or both. Stratigraphic information has not been published that either confirms or denies a facies relationship at these localities. It is entirely possible, therefore, that a facies sequence might be found here if looked for from that point of view.

From the North American occurrences as indicators, I propose 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. If this concept is valid, possibly it will

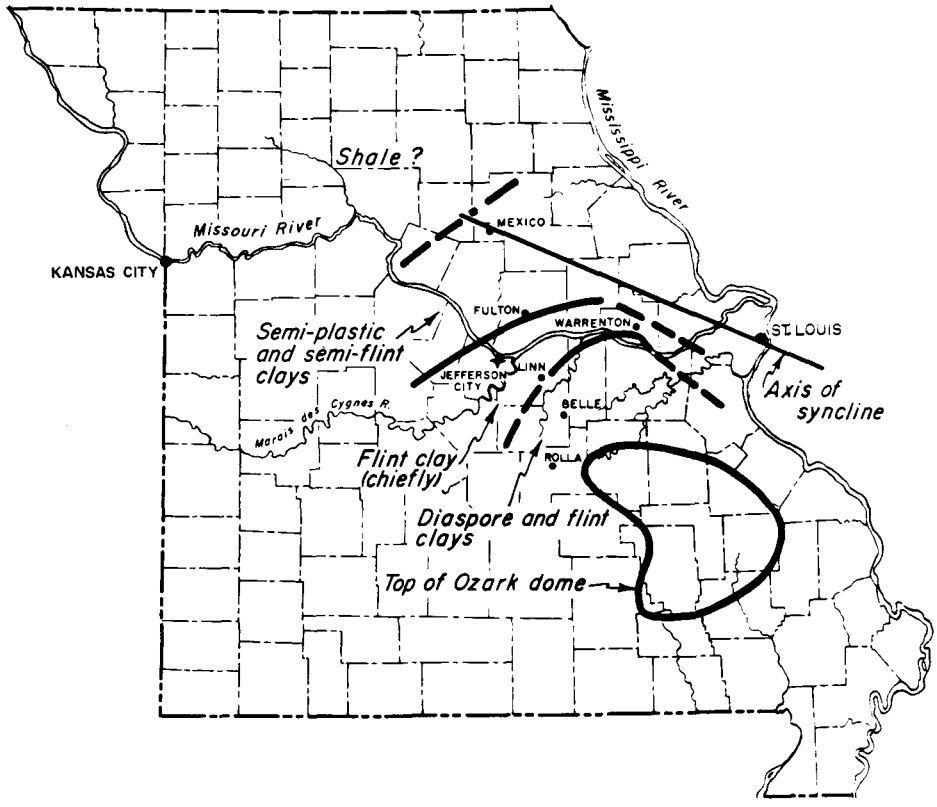


Fig. 9. Map of Missouri showing the distribution of bands of high-alumina clays, flint clays, plastic clays, and shales of Pennsylvanian age in progressively down-structure position of the Ozark dome. This is a relatively complete development of the flint-clay facies.

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

help unravelling additional geologic history, and may aid in locating additional reserves of refractory clays.

Acknowledgments—Support for this study was received from National Science Foundation Grant GP-1057. Personal time and help during field studies was given by many persons, including Rudolph Valenti, Goldman Foreman, Lee Courson, George Pace, Bert Johnson, A. O. Bledsoe, J. F. Westcott, and Lester Stallings. N. M. Saum and R. S. Reddy assisted with laboratory testing. The writer is grateful for all of this help, without which the study could not have been made.

REFERENCES

Bolam, T. R., (1932) *The Donnan equilibrium*: Bell, London, 232 pp.

Bolger, R. C., and Weitz, J. H. (1952) Mineralogy and origin of the Mercer fire clay of north-central Pennsylvania: *AIME Symp. Volume, Problems of Clay and Laterite Genesis*, 81–93.

Brindley, G. W., and de Souza Santos, P. (1966) New varieties of kaolin-group minerals and the problem of finding a suitable nomenclature: *Proc. Int. Clay Conf.* 1966, Israel, 1, 3–10, *Israel Program for Sci. Translations*, Jerusalem.

Carroll, D. (1962) Rainwater as a chemical agent of geologic processes—a review: *U.S. Geol. Survey Water Sup. Paper* **1535-G**, 18 pp.

Chukhrov, F. V., and Zvyagin, B. B. (1966) Halloysite, a crystallochemically and mineralogically distinct species: *Proc. Int. Clay Conf.* 1966, Israel, **1**, 11–26, *Israel Program for Sci. Translations*, Jerusalem.

Cook, R. A. (1886) The manufacture of fire-brick at Mt. Savage, Maryland: *Trans. AIME*, **14**, 698–706.

Erickson, E. S., Jr. (1963) Mineralogical, petrographic, and geochemical relationships in some high-alumina and associated claystones from the Clearfield Basin, Pennsylvania: Unpublished Ph.D. thesis, *Pennsylvania State University*, University Park, Pennsylvania, 190 pp.

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

Galpin, S. L. (1912) Studies of flint fire clays and their associates: *J. Am. Ceram. Soc.* **14**, 301–346.

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

Greaves-Walker, A. F. (1939) The origin, mineralogy, and distribution of the refractory clays of the United States: *N. Carolina Eng. Exp. Sta. Bull.* **19**, Raleigh, North Carolina, 87 pp.

Hahn, G. W. (1954) Clay mineral relationships in the Ocheskey fire clay pit: Unpublished M.A. thesis, *Univ. of Missouri Library*, Columbia, Missouri, 90 pp.

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. (1966) Genesis of refractory clay near Guanajuato, Mexico: *Clays and Clay Minerals*, Pergamon Press, New York, **14**, 259–267.

Howe, W. B., and Koenig, J. W. (1961) The stratigraphic succession in Missouri: *Missouri Geol. Surv. Water Resources, Rep. Invest.*, **40**, 2nd Series, 185 pp.

Howell, J. V. (1957) Glossary of geology and related sciences: *NAS-NRC Publ.* **501**, pp.

Keller, W. D. (1938) Diaspore clay cast of fossil wood in a Missouri disapore pit: *Am. Mineralogist* **23**, 461–463.

Keller, W. D. (1938) A sandstone-covered Missouri flint clay pit: *J. Am. Ceram. Soc.* **17**, 322.

Keller, W. D. (1952) Observations on the origin of Missouri high-alumina clays: *AIME Symp. Vol., Problems of Clay and Laterite Genesis*, 115–135.

Keller, W. D. (1952) Torbernite in Missouri fire clay: *Am. Mineralogist* **37**, 125–28.

Keller, W. D. (1957) *The Principles of Chemical Weathering*, Lucas Bros., Columbia, Missouri, 113 pp.

Keller, W. D. (1964) Processes of origin and alteration of clay minerals: *Soil Clay Mineralogy Symposium Vol.*, North Carolina Press, Raleigh, North Carolina, 3–76.

Keller, W. D. (1967) Geologic occurrences of clay minerals: Layer-silicate short course, *Geol. Soc. Am.*, 1967 meeting.

Keller, W. D., Gentile, R. J., and Reesman, A. L. (1967) Allophane and Na-rich alunite from kaolinitic nodules in shale: *J. Sediment Petrol.* **37**, 215–220.

Keller, W. D., and Hanson, R. F. (1967) Hydrothermal refractory clay near San Luis Potosi, Mexico: *Abstr. Clay Min. Soc. Meeting*, Denver, Aug. 1967.

Keller, W. D., Pickett, E. E., and Reesman, A. L. (1966) Elevated dehydroxylation temperature of the Keokuk geode kaolinite—a possible reference mineral: *Proc. Int. Clay Conf.* 1966, Jerusalem, **1**, 75–85.

Keller, W. D., Westcott, J. F., and Bledsoe, A. O. (1954) The origin of Missouri fire clays: *Clays and Clay Minerals, Proc. 2nd conf.* Nat'l Acad. Sci-Nat'l Res. Coun. Publ. **327**, 7–46.

Loughnan, F. C. (1962) Some tonstein-like rocks from New South Wales, Australia: *N. Jahrbuch f. Mineral.*, Stuttgart, **99**, no. 1, 29–44.

Lovering, T. S. (1959) Significance of accumulator plants in rock weathering: *Bull. Geol. Soc. Am.* **70**, 781–800.

McQueen, H. S. (1943) Fire clay districts of east central Missouri: *Missouri Geol. Surv. Water Resources Rep. Invest.*, 2nd Ser., **23**, 250 pp.

Orton, E. (1893) The clays of Ohio, their origin, composition, and varieties: *Rep. Geol. Surv. Ohio* **7**, 45–68.

Patterson, S. H., and Hosterman, J. W. (1962) Geology and refractory clay deposits of the Haldeman and Wrigley Quadrangles, Kentucky: *U.S. Geol. Surv. Bull.* **1122-F**, 113 pp.

Popoff, C. C. (1955) Cowlitz clay deposits near Castle Rock, Washington: *U.S. Bur. Mines, Rep. Invest.* **5157**.

Reesman, A. L. (1966) A study of clay mineral dissolution: unpublished Ph.D. thesis, *Library, Univ. of Missouri at Columbia*, 163 pp., 3 appendices 49 pp. Extracts in press.

Reesman, A. L., and Keller, W. D. (1967) Chemical composition of illite: *J. Sediment Petrol.* **37**, 592–596.

Reesman, A. L., and Keller, W. D. (In press) Aqueous solubility studies of high-alumina and clay minerals: *Am. Mineralogist*.

Ries, H. (1909) *Economic Geology of the United States*, MacMillan, New York, p. 99, 451 pp.

Robbins, C., and Keller, W. D. (1952) Clay and other

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

non-carbonate minerals in some limestones: *J. Sediment Petrol.* **22**, 146–152.
Searle, A. B., 1924, *Refractory materials: their manufacture and uses*: Griffin, London, 730 pp.
Searle, A. B., and Grimshaw, R. W. (1959) *The chemistry and physics of clays and other ceramic materials*: Inter-science, New York, 942 pp.
Slatkine, A., and Heller, L. (1961) A petrological study of the flint clays from Makhtesh Ramon, Israel: *Proc. Int. Comm. Study Clays, Int. Geol. Cong.*, **24**, 88–107.
Thornberry, M. H. (1925) Treatise on Missouri clays: *Tech. Ser. Bull. School Mines and Metallurgy*, Univ. of Missouri, Rolla, Missouri, **8**, 69 pp.
Urbina, J. E. (1910) Informe acerca de una excursion geologica preliminar efectuada en el Estado de Yucatan: *Parergones del Inst. de Mexico*, Tomo III, No. 7.
Waage, K. M. (1950) Refractory clays of the Maryland coal measures: *Maryland Geol. Surv. Bull.* **9**, 182 pp.
Waage, K. M. (1953) Refractory clay deposits of south-central Colorado: *U.S. Geol. Surv. Bull.* **993**, 104 pp.
Warde, J. M. (1950) Refractory clays in the Union of South Africa: *J. Am. Ceram. Soc.* **29**, 257–260.
Wheeler, A. A. (1896) Clay Deposits of Missouri: *Missouri Geol. Surv.* **11**, 622 pp.
Williams, E. G. (1960) Relationship between the stratigraphy and petrography of Pottsville sandstones and the occurrences of high-alumina Mercer clay: *Econ. Geol.* **55**, 1291–1302.
Wurzburger, V. (1963) The flint clay of Makhtesh Ramon: *Israel J. Earth Sci.* **12**, 1.

Résumé—L'argile réfractaire se définit comme une argile (roche) sédimentaire, microcristalline à cristalline, composée surtout de kaolin, dont la cassure est fortement conchoïdale et n'absorbe pas l'eau. Les autres propriétés céramiques (réfractaires) sont sous-entendues, mais non exprimées dans la définition. Reconnue pour la première fois aux Etats-Unis, l'argile réfractaire a été découverte dans tous les continents, et on en trouvera probablement en quantité plus abondante que celles observées jusqu'ici. On la rencontre surtout dans les roches carbonifères et crayeuses, et elle s'associe invariablement aux zones plantifères et gisements houillers.

Le dépôt se trouve généralement dans un milieu marécageux à faible niveau, en bassins de roches clastiques de silicate ou de carbonates karstiques. On en conclut que des colloûdes de parenté illitique et/ou d'argile kaolinitique furent transportés dans les marais et y subirent encore une dialyse, une altération et éventuellement une cristallisation in situ, produisant une argile kaolinitique notablement homogène et possédant une cristallinité solide. D'autres dépôts subirent une désilicatisation qui les transorma en minéraux à haute teneur d'alumine, en particulier en diaspore et boehmite.

L'argile réfractaire est considérée comme étant un intermédiaire entre ce quel'on appelle les facies d'argile réfractaire, qui sont une succession d'argiles allant des minéraux à haute teneur d'alumine (ou potentiellement tels) formés sur la partie la plus élevée de la zone de dépôt, du point de vue structurel et/ou topographique, et s'échelonnant des structures basses et/ou plus inférieure en élévation à travers l'argile réfractaire jusqu'à l'argile clastique illite-kaolin et ainsi au shale marin illitique, tous étant équi-valents du point de vue stratographique. Les réactions géochimiques sont la dépotassification de l'argile mère par substitution de K^+ par H^+, et la désilicatisation, surtout là où sont formés les minéraux à haute teneur en alumine.

Kurzreferat—Schieferton wird definiert als sedimentärer, mikrokristalliner bis kristalliner, vorwiegend aus Kaolin bestehender Ton (Stein), mit ausgesprochenem Muschelbruch und Löschwiderstand gegnüber Wasser. Die Definition deutet ferner, wenn auch nicht ausdrücklich, auf keramische (feuerhemmende) Eigenschaften hin. Der erstamalig in den USA namentlich erwähnte Schieferton wird auf sämtlichen Kontinenten angetroffen; es darf angenommen werden, das er in weit grösseren als den bisher bekannt gewordenen Mengen aufgefunden wird. Er tritt hauptsächlich in Gestein aus dem Karbon und der Kreide auf und ist immer mit pflanzen-oder kohleführenden Lagern verbunden.

Die Umgebung der Lagerstätte ist im allgemeinen tiefliegendes Sumpfland in Becken von entweder klastischen Silikatgesteinen oder karstischen Karbonaten. Es wird vermutet, dass illitische bzw. kaolinitische Tonmutterkolloide in die Sümpfe verbracht wurden und dort Gegenstand weiterer Dialyse, Veränderung und schliesslich Kristallisierung an Ort und Stelle waren, wobei es zur Bildung eines ausgesprochen homogenen, verkettete Kristallinität aufweisenden Kaolinittones kam. Manche der vorkommenden Gebilde wurden weiter zu tonerdereichen Mineralen entsilikatisiert und zwar besonders zu Diaspor und Boehmit.

Schieferton wird als Zwischenglied einer sogennanten Schieferton-Fazies angesehen, die eine Tonsteinfolge darstellt, welche sich von den an tektonisch bzw. topographisch höchster Stelle der Lagerstätte gebildeten (oder bildungs-fähigen) tonerdereichen Mineralen tektonsich oder höhenmässig über Schieferton bis zu illit-kaolinischem, plastischem Ton und von da zu illitischen Meeresschiefern erstreckt, wobei alle diese Gebilde stratigraphisch gleichwertig sind. Die geochemischen Reaktionen bestehen aus der Entfernung des Kaliums aus dem Mutterton durch Ersatz des K^+ durch K^+ und Entsilikatisierung, besonders dort, wo tonerdereiche Minerale gebildet werden.

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press

Резюме—Твердая огнеупорная глина определяется как осадочная микрокристаллическая до кристаллической глина (порода), состоящая главным образом из каолина, который когда ломается дает отчетливо конхоидальный излом и сопротивляется отслаиванию в воде. В определении подразумеваются (но не выражаются) добавочные керамические (огнеупорные) свойства. Твердая огнеупорная глина была впервые признана в США, но уже обнаружена на всех материках и, по всей вероятности, более изобильна, чем в залеганиях известных по настоящее время. Встречается глина эта главным образом в породах углесодержащего или мелового периода и всегда связана с растительными или каменноугольными отложениями.

Окружающая среда отложений обычно низменная, болотистая и находится в бассейнах в обломочных силикатных породах осадочного происхождения или в карстовых карбонатах. Подразумевается, что исходные иллитовые и/или каолинитовые глинистые коллоиды были перенесены в болота и там подверглись дальнейшему диализу, изменению и последующей кристаллизации на месте, что дает заметно гомогенную каолинитную глину, обладающую взаимносоединяющей кристалличностью. Некоторые залегания подверглись дальнейшему удалению силикагов, преобразовываясь в минералы с высоким содержанием глинозема, особенно в диаспор и бёмит.

Твердая огнеупорная глина определяется, как промежуточный член т.наз. фаций твердых огнеупорных глин, являющихся аргиллитовой последовательностью, простирающейся от высокоглиноземных минералов (или потенциально таковых) образуемых в наиболее высокой как структурно; так и (или топографически) части на участке отложений и нисходя по структуре и/или ниже по уровню через огнеупорную глину до иллито-каолинитовой пластичной глины, а затем до морских иллитовых сланцев, причем все они стратиграфически эквивалентные.

Геохимическая реакция это удаление калия из исходной глины замещением H^+ вместо K^+, а также удаление силикатов, особенно там, где образуются минералы с высоким содержанием глинозема.

https://doi.org/10.1346/CCMN.1968.0160202 Published online by Cambridge University Press