Clays and Clay Minerals, Vol. 45, No. 3, 353–364, 1997.

PHOSPHATES IN SOME MISSOURI REFRACTORY CLAYS

ROBERT B. HALL,[1] EUGENE E. FOORD,[2] DAVID J. KELLER[3] AND WALTER D. KELLER[4]

[1] 11280 West 20th Avenue, No. 32, Lakewood, Colorado 80215

[2] US Geological Survey, Box 25046, MS 905, Federal Center, Denver, Colorado 80225

[3] Harbison-Walker Refractories, PO Box 430, Fulton, Missouri 65251

[4] Department of Geological Sciences, University of Missouri-Columbia, Columbia, Missouri 65211

Abstract—This paper describes in detail phosphate minerals occurring in refractory clays of Missouri and their effect on the refractory degree of the clays. The minerals identified include carbonate–fluorapatite (francolite), crandallite, goyazite, wavellite, variscite and strengite. It is emphasized that these phosphates occur only in local isolated concentrations, and not generally in Missouri refractory clays.

The Missouri fireclay region comprises 2 districts, northern and southern, separated by the Missouri River. In this region, clay constitutes a major part of the Lower Pennsylvanian Cheltenham Formation. The original Cheltenham mud was an argillic residue derived from leaching and dissolution of pre-Pennsylvanian carbonates. The mud accumulated on a karstic erosion surface truncating the pre-Cheltenham rocks. Fireclays of the northern district consist mainly of poorly ordered kaolinite, with variable but minor amounts of illite, chlorite and fine-grained detrital quartz. Clays of the southern district were subjected to extreme leaching that produced well-ordered kaolinite flint clays. Local desilication formed pockets of diaspore, or more commonly, kaolinite, with oolite-like nubs or burls of diaspore ("burley" clay).

The phosphate-bearing materials have been studied by X-ray diffraction (XRD), scanning electron microscopy-energy dispersive spectral analysis (SEM-EDS) and chemical analysis. Calcian goyazite was identified in a sample of diaspore, and francolite in a sample of flint clay. A veinlet of wavellite occurs in flint clay at one locality, and a veinlet of variscite–strengite at another locality.

The Missouri flint-clay-hosted francolite could not have formed in the same manner as marine francolite. The evidence suggests that the Cheltenham francolite precipitated from ion complexes in pore water, nearly simultaneously with crystallization of kaolinite flint clay from an alumina–silica gel. Calcian goyazite is an early diagenetic addition to its diaspore host. The wavellite and variscite–strengite veinlets are secondary, precipitated from ion complexes in ground water percolating along cracks in the flint clay. The flint clay host of the variscite–strengite veinlet contains strontian crandallite. All of the phosphates contain significant amounts of strontium. The source of P, Ca and Sr was the marine carbonates. Dissolution of these carbonates produced the argillic residue that became the primordial Cheltenham paludal mud, which ultimately altered to fireclay.

Preliminary firing tests show that the presence of phosphates lowers fusion temperature. However, it is not clear whether poor refractoriness is due to the presence of phosphates, per se, or to Ca, Sr and other alkaline elements present in the phosphates.

Key Words—Calcian Goyazite, Diaspore, Flint Clay, Francolite, Genesis of the Phosphates, Strengite, Strontian Crandallite, Variscite, Wavellite.

INTRODUCTION

The occurrence of phosphate minerals in some Missouri diaspore and kaolinite deposits was reported earlier in an informal note (WD Keller et al. 1992). The relatively rare uranium phosphate, metatorbernite, was reported more than a half-century ago in flint clay from Franklin County, Missouri (Grawe 1943). A related uranium phosphate, torbernite, was identified in thin cracks in a semiflint clay located in the extreme northeastern corner of Callaway County (Keller 1952b). The barium aluminum phosphate, gorceixite, was reported in flint clay from Osage County (Tourtelot and Brenner-Tourtelot 1977, 1978). Phosphate minerals more common in nature than those mentioned above are discussed here. This report represents the 1st recognition of carbonate–fluorapatite (francolite), crandallite, goyazite, wavellite and variscite–strengite in Missouri refractory clays. These occurrences are significant because of implications for their genesis, their paragenetic relationship to the diaspore and kaolinite in which they occur and their possible effect on refractory properties.

GEOLOGIC SETTING

General

Refractory clays and diaspore deposits of east-central Missouri are contained within the Cheltenham Formation of Pennsylvanian age (McQueen 1943; Keller 1952a). These deposits have been the resource base for a high-alumina refractory brick industry since the late 19th century. Merchantable clays have been classified according to their degree of refractoriness (pyrometric cone equivalent, or PCE number), and other properties such as bulk density, fired density, plasticity and shrinkage during drying and firing. These prop-

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Figure 1. Map of Missouri showing location of fireclay districts and of clay pits containing phosphate minerals (adapted from McQueen 1943, Figure 1). See text for distinction between northern and southern districts. 1 = Curley pit, diaspore containing calcian goyazite; 2 = Landwehr No. 1 pit, flint clay containing francolite; 3 = Zeman No. 5 pit, flint clay hosting wavellite veinlet; 4 = Scego No. 7 pit, flint clay containing strontian crandallite and hosting variscite–strengite veinlet.

erties are largely a function of mineral composition. The fireclay categories are: 1) plastic; 2) semiplastic; 3) semiflint; 4) flint; 5) burley; and 6) diaspore (McQueen 1943; Keller et al. 1954). Diaspore deposits in Missouri were virtually exhausted by the 1970s (Keller 1979). Only local remnants of diaspore are accessible for sampling and scientific study.

The geology and characteristics of Missouri refractory clays and diaspore have been well described in earlier publications (McQueen 1943; Keller 1952a; Keller et al. 1954; Keller and Stevens 1983; Stack et al. 1990). A brief summary is given here, as background to discussion of the occurrences of phosphates in the clays.

The Missouri fireclay region is subdivided into 2 districts, northern and southern, separated by the east-flowing Missouri River (Figure 1). The subdivision is based upon differing properties and modes of occurrence. The differences reflect geologic processes, especially degree of leaching, that altered the original paludal Cheltenham mud to kaolinite and diaspore. The Cheltenham overlies a regional unconformity truncating cherty limestones, dolomites and sandstones ranging in age from Cambrian to Mississippian. Deeper erosion and greater karstic development in the southern district determined the difference between materials in the 2 districts.

Northern District

The Cheltenham Formation is an almost continuous claystone blanket north of the Missouri River. It is nearly planar on the top surface but irregular "pockety" at the bottom (Keller et al. 1954). Commercially valuable clays in the northern district are generally less refractory but more plastic than those in the southern district. Accordingly, the main products are plastic, semiplastic and semiflint clays, except for some good flint clay in the southeast corner of the district.

Southern District

South of the Missouri River, much of the Cheltenham was removed by erosion so that only isolated pockets of clay remain filling rudely funnel-shaped karstic sinkholes formed in pre-Pennsylvanian carbonates beneath the regional unconformity. The southern district is the principal source of flint and burley clays. Some karstic pockets yielded diaspore- and boehmite-rich material, prior to depletion (Keller 1979). Flint and burley clays are denser, nonplastic and more refractory than clay in the northern district.

Genesis of the Refractory Clays

The broad basin in which the primordial Cheltenham paludal mud was deposited was low and marshy, much like the Florida Everglades (Keller et al. 1954). The clay residuum, derived from dissolution of pre-Cheltenham carbonate rocks, consisted mainly of illite, with subordinate fine-grained detrital quartz. Minor clay constituents included kaolinite, montmorillonite and chlorite (Robbins and Keller 1952).

Alteration of illite-rich paludal mud to kaolinite-rich fireclay was rapid in the swampy environment, essentially complete by the end of Cheltenham time. Transformation to kaolinite was accomplished by intense hydrolysis in a warm, humid climate favorable to luxuriant vegetation characteristic of the Pennsylvanian period. Organic acids leached alkali and alkaline earth elements from the mud, to be flushed out of the swamp water during frequent tropical rains (Keller et al. 1954).

Land north of the Missouri River was lower than that to the south, and much nearer to sea level. The southern district was elevated by uplift of the Ozark Dome. Consequently, ground water gradient was higher and leaching greater in the southern district than in the northern. This difference in leaching intensity is reflected in the mineral and chemical composition of the several classes of fireclay (Table 1). Note the progressive loss of silica with concomitant gain in alumina, the effect of greater leaching with progression from plastic fireclay to diaspore. Potassium in the plastic clay is attributable to residual illite. The TiO_2 resists leaching and becomes concentrated as anatase in the more thoroughly leached burley clay and diaspore. It is significant that 20 analyses of Missouri refractory materials published in McQueen (1943; Table 25) show P_2O_5 in amounts ranging from 0.01% in a semiflint clay from Audrain County to 0.62% in the burley

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Table 1. Analyses of typical Missouri fireclays (McQueen 1943).

	Plastic†	Flint‡	Burley§	Diaspore¶
SiO_2	50.96	43.32	10.80	6.00
Al_2O_3	29.91	38.18	67.09	72.67
Fe_2O_3	2.69	1.56	1.73	1.93
CaO	0.49	0.39	0.32	0.14
MgO	0.38	0.11	0.17	0.14
Na_2O	0.15	0.08	0.89	0.23
K_2O	2.50	0.49	1.13	0.80
TiO_2	1.68	1.58	3.16	3.16
P_2O_5	0.16	0.10	0.62	0.09
H_2O	10.21	13.62	13.57	14.38
Total	99.13	99.43	99.48	99.52

† Gray plastic clay from Upper Cheltenham, Callaway County, Missouri.

‡ White hard flint clay, Gasconade County, Missouri.

§ High-grade burley clay, Osage County, Missouri. Name comes from oolite-like nubs or "burls" of diaspore in kaolinite matrix.

¶ Fine-grained diaspore rock, Gasconade County, Missouri.

clay analysis listed in our Table 1. Phosphates in small to trace amounts may be more common in fireclays of Missouri (and perhaps elsewhere) than has been previously recognized.

Explaining the formation of flint clay and diaspore is a special problem. Most flint clay is in the southern district where ground water flow was stronger because of the relatively higher gradient off the Ozark Dome. Thus, hydrolysis and leaching of the original mud was rapid and intense, yielding a nearly pure alumina–silica colloidal gel that consolidated into a compact mass of well-ordered, tightly interlocking kaolinite crystallites. A nonplastic clay was formed, resistant to slaking when immersed in water, breaking with a conchoidal flint-like fracture—hence the name.

Some sinkhole clay-filled "pockets" underwent more extreme hydrolysis that removed silica as well as alkali cations, producing burley clay with nubs or "burls" of diaspore in a matrix of flint clay. Further leaching created a bauxite-like, diaspore-rich rock. Contrary to the conventional concept of downward-percolating solutions forming a surficial gibbsitic bauxite blanket (laterization) underlain by kaolinite, the karstic pockets of diaspore commonly show kaolinite *above* the diaspore, suggesting that leaching was accomplished by upward-moving acidic solutions in a swampy, waterlogged environment, the alkali cations and silica being flushed away by periodic rains (Keller et al. 1954).

MATERIALS INVESTIGATED

The following were examined:

1) Diaspore from Curley pit, Osage County, Missouri. Found to contain calcian goyazite.

2) Composite drill-core sample of kaolinite (flint clay) from Landwehr No. 1 pit, Gasconade County, Missouri. Found to contain carbonate fluorapatite (francolite).

3) Wavellite veinlet in flint clay from Zeman No. 5 pit, Gasconade County, Missouri.

4) Veinlet containing mixture of ferrian variscite and aluminian strengite from Scego No. 7 pit, Gasconade County, Missouri. For convenience, this material is designated "variscite–strengite" in this report.

5) Two samples of flint clay, host of the variscite-strengite veinlet, 1 sample immediately adjacent to the veinlet, the other 3 to 5 cm distant from the veinlet. Both were found to contain strontian crandallite.

METHODS

X-ray Diffractometry (XRD)

X-ray patterns were run on a Siemens D-5000 diffractometer in the Denver laboratory of the US Geological Survey (USGS) Water Resources Division. Samples were step-scanned, step 0.02 °2θ, count-time 2 s, lambda value 1.541838 Å Cu$K\alpha$ (alpha 2 not removed). Minerals of the alunite and crandallite groups are isostructural in the hexagonal ditrigonal system and have very similar unit-cell dimensions. Consequently, XRD alone is not definitive. Chemical analyses are essential for unequivocal identification (Botinelly 1976).

SEM and EDS

Scanning electron micrographs and energy dispersive spectra were made on a Cambridge Stereoscan 2000 electron microscope with Kevex EDS analyzer in the USGS Denver laboratory. Concurrently, similar analyses were made on a JEOL-JSM-T330A electron microscope with Kevex EDS analyzer at the University of Missouri, Rolla (UMR).

Chemical Analysis

Analyses were made by the USGS Denver Branch of Analytical Laboratories. Most elements were analyzed by the inductively coupled plasma (ICP) technique. Fluorine was determined by selective ion electrode (SIE). Sulfur (SO_3) was analyzed by LECO combustion.

RESULTS

X-ray Diffractometry

Reflections characteristic of a crandallite-group mineral are clearly evident in the Osage County diaspore (Figure 2a). XRD alone does not identify unequivocally in this case. For example, goyazite, gorceixite, woodhouseite and other minerals isostructural with crandallite yield similar diffractograms. Chemical data (see below) combined with XRD indicated calcian goyazite.

Figure 2b shows reflections of an apatite-group mineral that was identified by chemical analysis as car-

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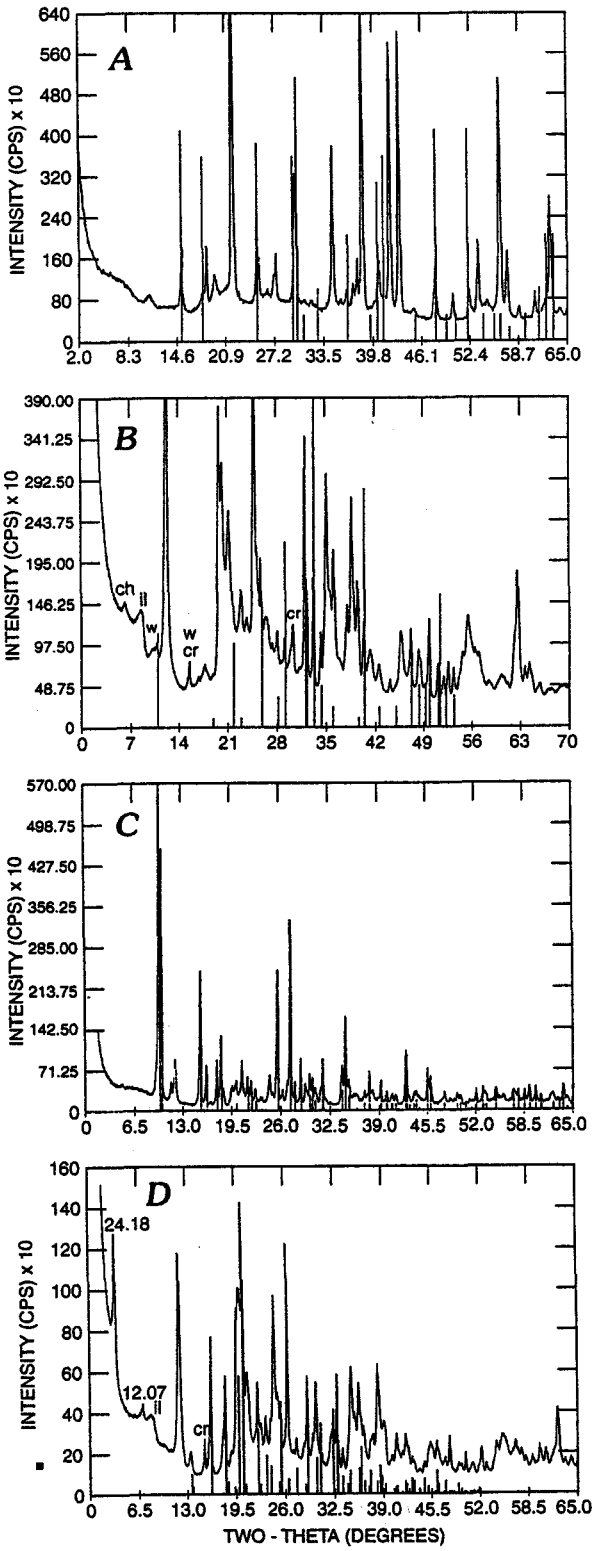


Figure 2. X-ray diffractograms showing phosphate minerals in diaspore and flint clay. A) Crandallite-group reflections ("sticks") in diaspore from Curley pit, Osage County, Missouri. Unmarked peaks are diaspore. Chemistry proved the mineral to be calcian goyazite. B) Carbonate–fluorapatite (francolite), indicated by "sticks", in "high alkali junk clay", from Landwehr No. 1 pit, Gasconade County, Missouri. Unmarked peaks mostly kaolinite; minor accessories include chlorite (ch), illite (il), crandallite (cr) and wavellite (w). C) Wavellite ("sticks") occurs as veinlet in drill-core sample of flint clay from Zeman No. 5 pit, Gasconade County. Unmarked peaks mostly kaolinite. D) Variscite ("sticks") in drill-core sample of flint clay from Scego No. 7 pit, Gasconade County. Particles of the veinlet have variscite interiors with outer rims of aluminan strengite. X-ray cannot distinguish the Fe from the Al phase in this mixture. See text for discussion of variscite–strengite relationship, and the 24-Å constituent. The 12.07-Å peak is 2nd-order basal reflection of 24-Å mineral. Minor accessories include illite (il) and crandallite (cr).

bonate–fluorapatite (francolite) in the flint clay composite drill-core sample. XRD alone does not always clearly distinguish carbonate–fluorapatite from other apatites, such as the fluorapatite found in igneous and metamorphic rocks, or hydroxyapatite, carbonate–hydroxylapatite (dahllite) and chlorapatite. Carbonate–fluorapatite is the form of apatite found almost universally in a sedimentary milieu (JB Cathcart, USGS, personal communication, 1992).

Wavellite is dominant in Figure 2c. The wavellite veinlet is relatively free of contaminants other than kaolinite.

Figure 2d shows variscite (perhaps better designated as variscite–strengite) as the principal phosphate. Petrographic microscope examination (DJ Keller 1992) revealed that the variscite veinlet is not homogeneous; rather, microsize aggregates have light-yellowish interiors, interpreted as ferrian variscite, with darker-colored brownish outer rims, interpreted as aluminian strengite. An XRD of this mixture cannot discriminate between the Al and Fe members of the variscite–strengite series. The presence in the Scego veinlet sample of a small amount of illite and crandallite is not surprising, but sharp basal *d*-spacings at 24.18 Å (001) and 12.07 Å (002) were unexpected. The 24-Å material was first thought to be rectorite. However, the 24-Å basal spacing did not expand to 27 Å after overnight glycolation, as is diagnostic of true rectorite (Brindley and Brown 1980). Dennis Eberl (personal communication, 1991) has suggested that the 24-Å mineral may be 1:1 (Reichweite 1) regularly stacked illite-chlorite. Confirmation would require further investigation, but the amount of sample is too small to allow separation of the several constituents. The 24-Å clay may not have formed in the veinlet simultaneously with the variscite–strengite.

An XRD of the flint clay adjacent to the veinlet (not included in Figure 2) showed no trace of the 24-Å clay, and only a bare trace of variscite–strengite. A crandallite group mineral was subsequently identified by chemical analysis as strontian crandallite.

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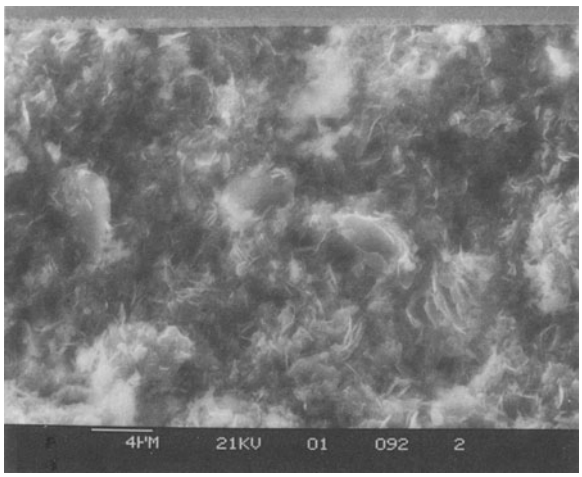


Figure 3. Wispy platelets of diaspore with sparse flakes of illite. Curley pit, Osage County, Missouri. Calcian goyazite is present but cannot be isolated in the photo.

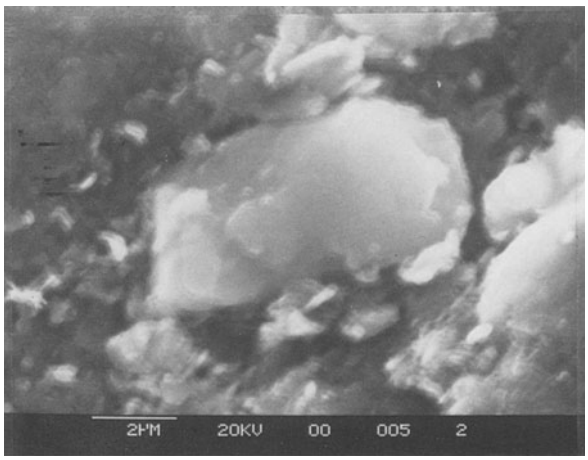


Figure 5. Crystallites (large white particles) of sylvite (KCl) in francolite-bearing flint clay from Landwehr No. 1 pit.

SEM and EDS

CALCIAN GOYAZITE IN DIASPORE. Figure 3 shows diaspore dominating the field. Individual goyazite crystallites are so finely dispersed as not to be discernible. However, the EDS spectrum showed peaks of P, Sr and Ca, elements characteristic of calcian goyazite, as well as a strong Al peak from goyazite and diaspore.

FRANCOLITE IN FLINT CLAY. Figure 4 shows crystallites of francolite in a kaolinite matrix. An EDS spectrum of a carbonate–fluorapatite crystallite showed only Ca and P peaks. During the SEM-EDS investigation of the francolite in the flint clay, several crystallites of sylvite (KCl) were discovered in the clay serendipitously (Figure 5). So far as is known to the authors, this is the first identification of sylvite in Missouri fireclay.

WAVELLITE IN FLINT CLAY. Figure 6 shows stubby orthorhombic crystallites of wavellite dominant in the field, with subordinate subhedral flakes of kaolinite. The EDS spectrum showed a prominent peak of P with a strong Al peak common to both wavellite and kaolinite.

VARISCITE–STRENGITE IN FLINT CLAY. A particle of the Scego veinlet consists of capsule-shaped aggregates of crystallites (Figure 7). The EDS spectrum showed Fe stronger than Al, suggesting strengite. However, the electron beam activates only the outer surface of the veinlet particles; interiors of the capsules were determined by petrographic microscope at UMR to be ferrian variscite. The 24-Å clay and other minerals identified in XRD are not distinguishable in this SEM.

The flint clay host immediately adjacent to the variscite-strengite veinlet contains a fairly high concentration of strontian crandallite.



Figure 4. Crystallites of francolite in kaolinite matrix. Flint clay from Landwehr No. 1 pit, Gasconade County, Missouri.

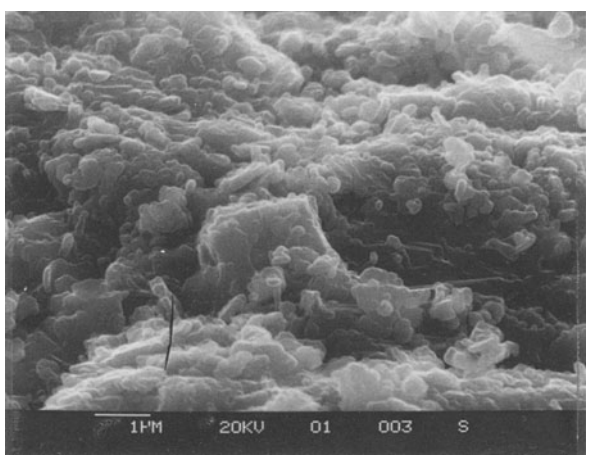


Figure 6. Stubby orthorhombic prisms of wavellite, accompanied by sparse subhedral platelets of kaolinite. Veinlet from Zeman No. 5 flint clay pit, Gasconade County, Missouri.

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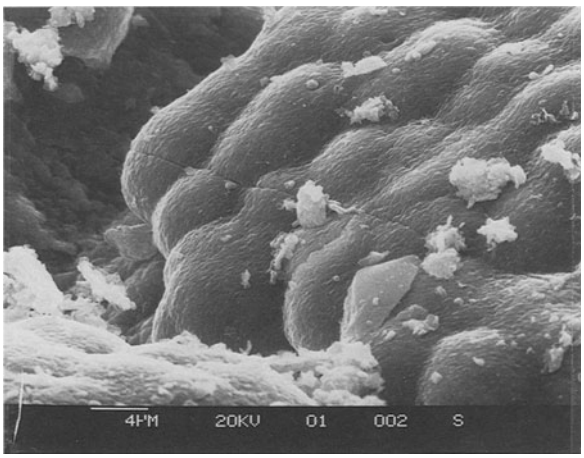


Figure 7. Capsule-like aggregates of variscite–strengite showing numerous tiny crystallites oriented subparallel to long axes of the capsules. Veinlet from Scego No. 7 flint-clay pit, Gasconade County, Missouri.

Chemistry

ANALYSES. Table 2 presents major and trace element analyses of the phosphate-bearing fireclays and fireclay-hosted phosphate veinlets. All samples are mixtures of 4 or more minerals, so that major chemical components are shared by several minerals.

ESTIMATED PROPORTIONS OF MINERAL CONSTITUENTS. XRD allows a first approximation of the weight percent of individual minerals in the sample. The "ideal" or theoretical composition of each mineral was used to calculate each mineral content and chemistry. The calculated total of each major component is compared to the laboratory analysis. The process then becomes one of trial and error until a reasonable match is attained between the chemistry calculated by estimated proportions of mineral constituents and the chemical analysis reported by the laboratory.

Table 3 lists for each sample the minerals identified in X-ray, a "best estimate" proportion of each mineral and the calculated composition (major components only) compared to the values in Table 2. Table 3 results range from fair to good, but give a reasonable idea of the mineral composition of each sample.

CALCIAN GOYAZITE IN DIASPORE. Several trace elements are present in sufficiently high amount as to merit comment. Lithium, 850 ppm Li, equivalent to 0.18% Li_2O, would suggest, if assigned to cookeite, the presence of about 6% of that chlorite, enough to show in XRD. However, no chlorite is evident (Figure 2a). Lithium probably is incorporated in a phase other than cookeite.

Barium, 760 ppm Ba, and cerium, 240 ppm Ce, probably are in substitution for Sr and Ca in the goyazite structure. Chromium, 350 ppm Cr, probably is in substitution for Fe.

FRANCOLITE IN FLINT CLAY. Comparison of chemical characteristics of the Landwehr francolite with typical francolites is shown below:

	CaO/P_2O_5	CO_2/P_2O_5	F/P_2O_5
Typical francolites	1.4–1.6	~0.086	0.082–0.106
Landwehr francolite	1.25	0.014	0.110

The Landwehr francolite F/P_2O_5 ratio is slightly higher than the normal range for most francolites. The CaO/P_2O_5 and CO_2/P_2O_5 ratios indicate a deficiency of Ca^{2+} and CO_3^{2-} ions in the Landwehr francolite. The Sr^{2+} ion shares the Ca^{2+} position in the francolite structure (Bliskovskiy et al. 1967). The Landwehr analysis shows 0.31% SrO. If Sr is converted to equivalent weight CaO, the Landwehr *equivalent* CaO/P_2O_5 ratio then becomes about 1.4, closer to typical francolites.

The low CO_2/P_2O_5 ratio of the Landwehr francolite can be explained if the observation of McClellan (1980) is considered: "weathering alters francolites such that their composition changes toward fluorapatite". Mildly acidic ground waters percolating slowly through Cheltenham clay could have partially decarbonated the Landwehr francolite. Such waters also could have leached Ca^{2+} ions, thus accounting for both the low CaO/P_2O_5 and CO_2/P_2O_5 ratios in the Landwehr francolite.

Partial substitution of SO_3^{2-} for PO_4^{3-} is common in apatites, including francolites (McConnell 1937; Vasileva 1958; McArthur 1978). The Landwehr analysis shows 0.25% SO_3, the greater part if not all of which is probably in the francolite structure. Furthermore, small amounts of Na, Mg and rare earth elements (REE) share the Ca^{2+} position (McArthur 1978). At least part of the alkali and alkaline earth elements reported in Table 2 as well as the greater part of the REE are probably incorporated in the Landwehr francolite structure.

Table 2 shows 260 ppm Li, equivalent to about 2% cookeite if all of the lithium is attributed to cookeite. An XRD (Figure 2b) suggests the presence of a small amount of chlorite, but it is not certain that this chlorite is cookeite.

WAVELLITE VEINLET IN FLINT CLAY. The most striking feature among major components in Table 2 is the fluorine content, 2.21% F. The sample is estimated to contain about 69.5% of wavellite. If all of the fluorine is in wavellite, its F content is calculated to be 3.18%. Palache et al. (1951) list 5 wavellite analyses, 2 of which show F greater than 2%. Apparently, the wavellite structure can accommodate considerable F^- ion, much of it probably in substitution for OH^- (Palache et al. 1951).

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Table 2. Major elements (in wt%) and trace element (ppm) analyses of phosphate-bearing refractory clays and fireclay-hosted phosphate veinlets.

	Curley diaspore with calcian goyazite	Landwehr flint clay with francolite	Zeman wavellite veinlet	Scego variscite–strengite veinlet	Scego flint clay host adjacent to variscite–strengite veinlet	Scego flint clay host 3–5 cm distant from variscite–strengite veinlet
SiO_2	10.9	38.8	11.7	19.7	40.5	44.0
Al_2O_3	62.6	31.8	33.4	28.5	33.4	33.6
Fe_2O_3	0.91	0.69	1.58	6.57	0.68	0.65
MgO	0.24	0.43	0.17	0.14	0.20	0.23
CaO	0.59	6.22	0.18	0.35	1.22	0.78
SrO	1.42	0.31	0.06	0.37	1.54	0.89
Na_2O	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
K_2O	1.56	2.25	0.33	0.63	0.91	0.96
P_2O_5	2.44	4.98	24.6	23.9	4.31	2.68
TiO_2	2.73	1.46	0.50	0.63	1.23	1.32
F†	0.15	0.55	2.21	0.31	0.22	0.20
LOI 925 °C	14.9	11.3	24.4	18.5	14.0	13.7
H_2O^+	13.0	10.1	19.5	5.79	11.9	11.7
H_2O^-	1.17	0.7	3.02	12.6	0.67	1.01
Total H_2O	14.2	10.8	22.5	18.4	12.6	12.7
Total C	0.22	0.53	0.37	0.22	0.53	0.49
CO_2	<0.01	0.07	<0.01	<0.01	<0.01	<0.01
SO_3†	1.43	0.25	0.14	0.26	0.80	0.63
Total	99.47	99.17	99.74	100.18	99.69	100.24
Ag (0.07)‡	<8	<4	<4	<4	<4	<4
As (1.3)	41	<20	<20	560	44	38
Au (0.004)	<30	<20	<20	<20	<20	<20
B (10)	NA	NA	NA	NA	NA	NA
Ba (707)	760	630	310	430	1500	970
Be (2.3)	10	6	130	32	5	4
Bi (0.17)	<40	<20	<20	<20	<20	<20
Cd (0.2)	<8	<4	<4	<4	<4	<4
Ce (57)	240	220	64	81	200	170
Co (25)	<4	30	3	<2	<2	<2
Cr (56)	350	190	74	86	160	170
Cu (55)	37	110	170	7	11	9
Eu (1.1)	<8	4	62	<4	<4	<4
Ga (15)	89	40	11	16	36	36
Ge (1.5)	NA	NA	NA	NA	NA	NA
Ho (1.2)	<20	<8	310	<8	<8	<8
La (28)	150	130	<4	50	120	100
Li (20)	850	260	35	74	170	190
Mn (950)	<20	22	8	11	23	26
Mo (1.5)	<8	<4	<4	7	<4	<4
Nb (13)	48	23	32	8	17	18
Nd (23)	140	120	21	34	85	69
Ni (35)	83	77	13	8	13	16
Pb (15)	53	25	<8	20	43	39
Sc (22)	50	33	71	99	22	23
Sn (2)	NA	<10	<10	<10	<10	<10
Ta (2)	<200	<80	<80	<80	<80	<80
Th (5.7)	45	27	<3	11	26	23
U (1.3)	<400	<200	<200	<200	<200	<200
V (135)	370	120	66	70	97	100
W (1.5)	NA	NA	NA	NA	NA	NA
Y (1.4)	180	150	13,000	57	63	58
Yb (1.5)	17	9	1100	6	4	4
Zn (70)	28	7	28	<4	<4	5
Zr (210)	NA	NA	NA	NA	NA	NA

† Figures for F and SO_3 are averages of results from USGS Denver Analytical Laboratories and from Skyline Labs, Inc., Wheat Ridge, Colorado.

‡ Number in parentheses represents average abundance of the element in the continental crust. Numbers for most elements from Taylor (1964). Numbers for Ba, Ce, Cr, Eu, La, Nb, Nd, Ni, Pb, Th, U, Y, Yb and Zr from Weaver and Tarney (1984).

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Table 3. Calculated composition of samples based on estimated proportions of mineral constituents, compared to laboratory analyses.

Mineral	Estimated proportion	Major component	Calculated contribution from estimated mineral proportion	Amount in Table 2
A. Calcian goyazite-bearing diaspore				
Diaspore	69.7	SiO_2	9.96	10.9
Illite	20.0	Al_2O_3	70.16	62.6
Calcian goyazite†	7.6	P_2O_5	2.45	2.44
Anatase	2.7	CaO	0.44	0.59
		SrO	0.97	1.42
		TiO_2	2.70	2.73
B. Francolite-bearing flint clay				
Kaolinite	75.0	SiO_2	39.46	38.8
Illite	6.0	Al_2O_3	34.46	31.8
Chlorite	4.0	P_2O_5	4.96	4.98
Crandallite	3.0	CaO	5.02	6.22
Wavellite	2.0	H_2O	12.71	10.80
Francolite	8.5	CO_2	0.29	0.05
Anatase	1.5	TiO_2	1.50	1.46
C. Wavellite veinlet in flint clay				
Wavellite	69.5	SiO_2	11.64	11.7
Kaolinite	25.0	Al_2O_3	37.52	33.4
Crandallite	5.0	P_2O_5	25.67	24.6
Anatase	0.5	CaO	0.68	0.18
		H_2O	24.00	22.5
		TiO_2	0.50	0.50
D. Variscite–strengite veinlent in flint clay				
Variscite molecule	30.0	SiO_2	19.87	19.7
Strengite molecule	17.4	Al_2O_3	28.65	28.5
Kaolinite	32.0	Fe_2O_3	7.86	6.57
2:1 clays	10.0	P_2O_5	23.52	23.9
Crandallite	10.0	H_2O	17.04	18.4
Anatase	0.6	TiO_2	0.60	0.63
E. Strontian crandallite-bearing flint clay immediately adjacent to D				
Quartz	3.5	SiO_2	40.75	40.5
Kaolinite	72.5	Al_2O_3	36.08	33.4
Illite	4.7	P_2O_5	4.78	4.31
Chlorite	3.0	CaO	1.18	1.22
Strontian crandallite‡	15.0	SrO	1.31	1.54
Anatase	1.3	H_2O	12.85	12.6
		TiO_2	1.30	1.28
F. Same as E, but 3 to 5 cm distant from D				
Quartz	4.5	SiO_2	43.45	44.0
Kaolinite	73.0	Al_2O_3	35.86	33.6
Illite	7.0	P_2O_5	3.03	2.68
Chlorite	5.3	CaO	0.71	0.78
Strontian crandallite§	8.9	SrO	0.76	0.89
Anatase	1.3	H_2O	12.90	12.70
		TiO_2	1.3	1.32

† Calcian goyazite formula calculated as $(Sr_{0.56}Ca_{0.42}Ba_{0.02})Al_3(PO_4)_2(OH)_5{\cdot}H_2O$.

‡ Strontian crandallite formula calculated as $(Ca_{0.58}Sr_{0.39}Ba_{0.03})Al_3(PO_4)_2(OH)_5{\cdot}H_2O$.

§ Strontian crandallite formula calculated as $(Ca_{0.59}Sr_{0.38}Ba_{0.03})Al_3(PO_4)_2(OH)_5{\cdot}H_2O$.

Another striking feature of the wavellite veinlet analysis is the extraordinarily high content of yttrium, 13,000 ppm Y, that is, 1.3%. An SEM/EDS analysis strongly suggests that xenotime, YPO_4, is the source of the anomalous yttrium.

Beryllium, 130 ppm Be, is anomalously high. Be is commonly associated with F in nature; therefore, a positive correlation of Be with F in the wavellite veinlet is likely.

Holmium, 310 ppm Ho, and ytterbium, 1100 ppm Yb, also are anomalously high. The anomalous Ho and Yb correlate with the high Y content because yttrium is associated with the "heavy" (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) REE group. The "light" REE—La, Ce and Nd in the wavellite veinlet—are present only in normal nonanomalous amounts.

VARISCITE–STRENGITE VEINLET IN FLINT CLAY. The chemistry indicates that the variscite molecule is present in greater proportion than the strengite molecule.

High arsenic content, 560 ppm As, is understandable when one considers that the variscite–strengite pair is isostructural with mansfieldite, $AlAsO_4{\cdot}2H_2O$, and scorodite, $FeAsO_4{\cdot}2H_2O$, which form a diadochic series like variscite and strengite. The AsO_4^{3-} ion in Cheltenham ground water entered the variscite–strengite structure in substitution for PO_4^{3-}.

Trace elements other than As are not remarkably high. Scandium, 99 ppm Sc (0.01% Sc_2O_3) is greater than any other Sc analysis in Table 2. Small amounts of scandium are common in variscites and other aluminous phosphates. The Sc^{3+} substitutes for Al^{3+} as a minuscule amount of kolbeckite ("sterrettite"), $ScPO_4{\cdot}2H_2O$ molecule in solid solution with $AlPO_4{\cdot}2H_2O$ (Frondell et al. 1968).

STRONTIAN CRANDALLITE-BEARING FLINT CLAY, HOST OF VARISCITE–STRENGITE VEINLET. Columns 6 and 7, Table 2, list analyses of the flint clay that hosts the variscite–strengite veinlet (column 5). These 2 flint clay samples are discussed together because they are very similar, separated in the drill core by only 1 or 2 cm. Column 6 gives the analysis of flint clay immediately adjacent to the veinlet; column 7 lists the analysis of the clay 3 to 5 cm distant from the veinlet. An XRD showed mere traces of variscite–strengite; instead, crandallite is the dominant phosphate. Strontium is in sufficient concentration as to dictate the modifier "strontian" crandallite.

Clay immediately adjacent to the variscite–strengite veinlet contains appreciably more P_2O_5 than the sample 3 to 5 cm from the veinlet.

The paragenetic relationship between the crandallite in the host flint clay and the variscite–strengite veinlet filling the fissure in the clay is not clear.

Among trace elements, barium, 970 to 1500 ppm Ba, and cerium, 170 to 200 ppm Ce, are noteworthy. These 2 elements probably occur as minute amounts

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of gorceixite (Ba) molecule and florencite (Ce) molecule in solid solution with the strontian crandallite.

GENESIS OF THE PHOSPHATES

General

The fact that francolite, calcian goyazite and strontian crandallite are thoroughly dispersed and intimately intermixed with their clay host suggests that the phosphates were formed penecontemporaneously with, or during very early diagenesis following conversion of the nonrefractory primordial Cheltenham mud to refractory clay. The wavellite and variscite–strengite veinlets obviously formed later. Phosphorous is a common minor element in marine carbonates, averaging about 400 g t^{-1} (Rankama and Sahama 1950). Phosphorous remained in the argillic residue left by dissolution of pre-Pennsylvanian carbonates. The small amount of phosphate in marine limestone is accounted for by Ames (1959), who proposed that the low concentration of P in seawater (approximately 0.09 ppm, mainly as HPO_4^{-2} ion) reacts with limestone at the seafloor–water interface, resulting in gradual replacement of calcite by francolite. This concept is supported by others (Pevear 1966; Cook 1970; Altschuler 1973; Gaudette and Lyons 1980).

THE NEW GUINEA EXAMPLE. A phosphate-rich soil blanket lies above karstic Tertiary limestone terrain in western New Guinea (Schroo 1963). The phosphatic soil is residual from tropical weathering and leaching during development of the karst, just as the Cheltenham mud was residual from dissolution of pre-Pennsylvanian carbonates. The analogy is striking, despite the considerable difference in time and geographic location.

The New Guinea limestone is not notably rich in P, ranging from 0.02 to 0.70 wt% P_2O_5, and averaging about 0.20 wt% P_2O_5 (Schroo 1963). By contrast, the soil residuum from the limestone is remarkably rich in P, ranging from 0.08 wt% P_2O_5 in phosphate-poor soil, to 28 wt% P_2O_5 in phosphate-rich soil. A suite of 25 New Guinea soil samples held an average P_2O_5 content of 14.93 wt%, extraordinarily high for any soil (Schroo 1963).

PHOSPHOROUS CONTENT OF PRE-PENNSYLVANIAN CARBONATES. We lack data on pre-Pennsylvanian carbonates in east-central Missouri underlying Cheltenham fireclays. However, published analyses of Ordovician and Mississippian limestones and dolostones in northeast Missouri (Rueff and Hays 1991) are believed to fairly represent comparable carbonates that underlie the Cheltenham. The average P_2O_5 content of 141 analyses is 0.07 wt%, ranging between 0.02 and 0.38 wt% (Rueff and Hays 1991).

PHOSPHOROUS CONTENT OF CHELTENHAM CLAYS. The P_2O_5 content of Cheltenham fireclays ranges from 0.03 wt% in semiplastic clay from the northern district to 0.62 wt% in a burley clay from the southern district (McQueen 1943). Local concentrations of phosphate in some Missouri fireclays must be considered as anomalies, not typical of Missouri refractory materials generally. Small to trace amounts of phosphate are likely to be found in Missouri fireclays, if P_2O_5 is looked for during chemical analysis.

BIOLOGICAL PHOSPHOROUS. Sporadic coaly pockets and thin discontinuous lenses of poor quality coal are fossil evidence that phosphorous was sufficiently abundant in the original Cheltenham mud to support plants (DJ Keller 1992). As plants died and decayed, "organic" P again became "inorganic", available either to biota, or to local formation of phosphate minerals.

Francolite

At present the only fireclay in Missouri known to contain francolite is that at the Landwehr No. 1 pit in Gasconade County. Sedimentary marine phosphate rock (phosphorite) deposits are composed mainly of francolite. The difference in environment of deposition—shallow marine for commercial phosphorites, paludal swamp for the francolite in Cheltenham fireclay—clearly suggests that the francolite in Landwehr pit flint clay could not have formed in the same way as marine francolite. Francolite in Landwehr flint clay occurs as small crystallites interspersed in a matrix of kaolinite crystallites (Figure 4). This contrasts with marine phosphorite concentrations of francolite granules and nodules, exemplified by deposits in Florida (Altschuler et al. 1964) and North Carolina (Rooney and Kerr 1967).

The association of francolite with kaolinite is common in nature. Deans (1940) described small crystallites of francolite, presumably of freshwater origin, dispersed in kaolinite "oolites" and crack-fillings in siderite overlying a coal seam in the Coal Measures (Upper Carboniferous) of Yorkshire. The only common characteristic shared by the Yorkshire occurrence and the Missouri occurrence is the intimate intermixture of francolite in a kaolinite matrix. Deans offered no explanation for genesis of either the francolite or the kaolinite "oolites".

Nriagu (1976) has shown that clay minerals, including kaolinite, coexist with apatite in a pH range between 6 and 8. Kaolinite and other clay minerals occur in the matrix of phosphorite beds worldwide (Nriagu 1976). The coexistence boundaries between clays and apatite fall in the range of most soils and sediments, given appropriate activity of $H_2PO_4^-$ ions. According to Altschuler (1973), the F^-ion causes apatite to precipitate at lower pH and lower CaO concentration than if fluorine were absent. Marine phosphorites are thought to have formed under mildly alkaline conditions. By contrast, the Missouri fireclays were formed

https://doi.org/10.1346/CCMN.1997.0450306 Published online by Cambridge University Press

by hydrolysis under mildly acid conditions. The presence of F^- ion in pore water, together with $H_2PO_4^-$, CO_3^{2-} and Ca^{2+} ions, would have allowed francolite to precipitate during the transformation of the Cheltenham silica–alumina colloidal gel into kaolinite. This process occurred only at the Landwehr deposit, so far as is now known. It is not known why conditions favored formation of francolite at this particular locality. XRD analysis of so-called "junk" clays may reveal francolite in other locales. The small amount of sylvite in the Landwehr clay may have precipitated either simultaneously with francolite, or later. The K^+ ion was available from dissolution of illite in the primitive Cheltenham mud; Cl^- ions are common in ground water.

Strontian Crandallite and Calcian Goyazite

Direct precipitation of crandallite from pore water is a likely process. Crandallite-group minerals are common in soils and sediments, although pure end members are rare or nonexistent in nature. Crandallite, the Ca member and most common species, occurs in solid solution with goyazite (Sr), gorceixite (Ba) and florencite (Ce, REE). Such combinations have been reported in Australian soils and flint clays (Sweatman 1961; Norrish 1968; Loughnan 1970), in Eocene marl in Alabama (Milton et al. 1958) and in Cretaceous tonstein in Colorado (Triplehorn and Bohor 1983). The New Guinea P-rich soil contains abundant crandallite (Schroo 1963). A triclinic form of crandallite occurs in a Guatemalan swamp in a montmorillonite–halloysite matrix (Cowgill et al. 1963).

Alunite (solid-solution) and aluminum–phosphate–sulfate minerals of the woodhouseite group with subordinate amounts of gorceixite, florencite and goyazite are present in zones of silicification and advanced argillic alteration in the hypogene La Vanguardia kaolinite deposit near Illapel, Chile (Dill et al. 1995).

Although aluminum has low solubility relative to other elements in aluminous minerals, organic acids have the capacity to dissolve and transport Al (Huang and Keller 1972). Humic and fulvic acids derived from plants in the Cheltenham swamps were capable of taking Al into solution. The PO_4^{3-} ion combines readily with Al ion complexes to form aluminous phosphates (Huang and Keller 1972). Local concentrations of Al, P, Ca and Sr ions in pore water would permit precipitation of crandallite-group minerals in kaolinite host. The crandallite in Missouri fireclays contains strontium in substitution for calcium in sufficient amount as to merit the designation "strontian" crandallite, having a mean Ca/Sr atomic ratio of 59/41. The New Guinea soil crandallite has a Ca/Sr ratio of about 87/13. The Guatemalan swamp triclinic crandallite has a Ca/Sr ratio of 74/26. The tendency of crandallite to take up strontium was noted by Frondel (1958), who considered crandallite to be a scavenger of strontium.

Calcian goyazite in the Curley diaspore has the calculated formula $(Sr_{0.55}Ca_{0.42}Ba_{0.03})Al_3(PO_4)_2(OH)_5 \cdot H_2O$. Strontium became sufficiently concentrated in pore water to allow gradual exchange of Sr^{2+} for Ca^{2+} so that the goyazite molecule superseded the crandallite molecule in the solid solution. The primary source of both Ca and Sr was the Paleozoic carbonates that yielded the Cheltenham residual mud. ("Calcium carbonate formed in the sea always contains some Sr", per Krauskopf 1967).

Variscite–Strengite

The veinlet of variscite–strengite occurs in a crack in a drill-core sample of flint clay about 20 m below surface at Scego No. 7 pit (DJ Keller 1992). Composition of the veinlet and the reason for the designation "variscite-strengite" have been presented already. Variscite and strengite are likely to be found in acid soils (Chang and Jackson 1958; Hsu and Jackson 1960; Bache 1963). Reducing conditions favor variscite over strengite (Hsu and Jackson 1960). However, low pH values favor precipitation of strengite over variscite (Bache 1963). Interiors of the Scego veinlet crystallite aggregates are ferrian variscite, while the exteriors are aluminian strengite (Figure 7), which suggests that the veinlet-forming fluids became more acidic as precipitation progressed. Ground water percolating along cracks or joints and carrying Al^{3+}, Fe^{3+} and $H_2PO_4^-$ ions formed the veinlet.

Wavellite

In an argillaceous environment, as in the Cheltenham Formation, acid ground water is not well-buffered. Consequently, acid alteration of Ca-bearing phosphates such as francolite and crandallite results in formation of simple aluminum phosphates, particularly wavellite (Altschuler 1973). As in the case of the Scego variscite–strengite veinlet, ground water carrying ion complexes of P and Al formed the wavellite veinlet.

EFFECT OF PHOSPHATES ON REFRACTORY PROPERTIES

Further research is needed to more fully determine the effects of phosphates on the refractory properties of Missouri fireclays. A few qualified comments are given here, based on limited and preliminary firing tests (DJ Keller 1992; Keller and Bolter 1993).

According to C.E. Stack of A.P. Green Industries, Inc. (personal communication, 1991), the francolite-bearing flint clay from the Landwehr pit melted at about 1480 °C (PCE cone 17), and was rejected as "high alkali junk clay". It is not clear whether or not PCE test failure is attributable to the combined effect of P and Ca in the francolite or to Ca alone. Phosphorous in the form of $Al(HP_2O_4)_3$ is added to some alumina refractories as a bonding agent (Baumgart 1984).

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This use of phosphorous suggests that P free of alkaline associates may not degrade refractoriness.

Crandallite contains less Ca and P than francolite. Limited test firing showed that increasing P and Ca lowered the PCE number (DJ Keller 1992). Because crandallite, including strontian crandallite, contains less Ca and P than does francolite, its adverse affect on firing properties should be less than that caused by francolite present in an equivalent weight amount. Moreover, crandallite contains Al, a desirable refractory element not present in francolite.

Firing tests were not made on materials containing the wavellite and variscite–strengite veinlets. Such veinlets are not likely to affect firing properties significantly unless present in inordinately high concentrations. The Fe-bearing strengite would be a more deleterious contaminant than variscite.

SUMMARY AND CONCLUSIONS

The Lower Pennsylvanian Cheltenham Formation in east-central Missouri is mostly claystone, a significant portion of which is valuable refractory clay. Kaolinite-rich fireclays were formed by leaching and hydrolytic alteration of illite-rich mud, residual from dissolution of pre-Pennsylvanian carbonates underlying the Cheltenham.

Local concentrations of phosphates in the refractory clays include calcian goyazite, francolite, wavellite, variscite–strengite and strontian crandallite. These materials were examined by XRD, SEM/EDS and chemical analysis. The francolite in flint clay precipitated from P-bearing pore water during or shortly after crystallization of colloidal alumina–silica gel into kaolinite. Calcian goyazite is an early diagenetic precipitate in a diaspore host. Wavellite and variscite–strengite veinlets are secondary, precipitated by P-bearing ion complexes in ground water percolating along cracks in the host flint clay. Strontian crandallite precipitated from pore water in the flint-clay host of the variscite–strengite veinlet.

Limited firing tests show a clear correlation between phosphate content and poor refractoriness. However, it is not clear whether failure is attributable to phosphates, per se, or to alkaline elements associated with phosphorous.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the cooperation of D. Eberl and D. McCarty, USGS Division of Water Resources, in providing the X-ray diffractograms of Figure 2. P. Modreski and D. Allerton, USGS Branch of Central Mineral Resources, and K. Esposito, Branch of Sedimentary Petrology, also helped with X-ray data on several occasions. C.E. Stack, A.P. Green Industries, Mexico, Missouri, provided the Landwehr francolite-bearing flint clay. The USGS Branch of Analytical Laboratories supplied the chemical analyses of Table 2. M. Clemensen, P. Drouillard and M. Keithly, USGS Branch of Central Mineral Resources, prepared the final manuscript. A. Hall typed the preliminary version. The manuscript was greatly improved following comments by USGS geologists R. Pollastro and G. Whitney and 2 reviewers.

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(*Received 30 August 1995; accepted 3 July 1996; Ms. 2688*)

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