
Phosphates in Some Missouri Refractory Clays

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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

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