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ANALOGUES OF FLINT CLAYS IN SOVIET LITERATURE

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Abstract—The term "flint clay" used in USA and several other countries, corresponds very closely to the term "toasted bread (sukhar) clay". In both USA and U.S.S.R., the typical occurences of "toasted clays" are confined to deposits of the lower Carboniferous. In their properties and occurrence the well-studied toasted clays of the Borovichy deposit (Novgorod province) are highly similar to the flint clays of Missouri, differing significantly only in having lower bulk specific gravity and higher porosity than do Missouri flint clays. Varieties with excess free alumina (diaspore, boehmite) are observed both among "toasted" and flint clays. The author suggests the term "toasted complex" (sukharnii kompleks) which corresponds to W. D. Keller's term "flint clay facies". The clays of the "toasted complex" are sediments of ancient swamps and lakes which contained rich vegetation. Their source material was finaly dispersed silicate particles transported from dry land. The structure and properties of toasted clays are explained by the precipitation of kaolinite as colloidal clumps in which crystallization occurred with formation of intimate intergrowths and variously oriented segregations.

THANKS to the kindness of Professor W. D. Keller, the author had the opportunity to familiarize himself with the peculiarities and occurrence of clays designated as flint clays, directly in the quarries where such clays are mined. These observations and the results of new investigations by American and Soviet authors served as a basis for concluding that there is a close similarity between the clays called "flint clay" in the American literature and "toasted bread clay" in the Soviet literature.

The name "toasted bread clay" or "toasted clay" in Soviet literature is used to designate sedimentary substantially kaolinitic refractory clays which do not yield plastic masses even after prolonged submersion in water. Such clays are not laminar. They are cryptocrystalline, possess greater hardness (up to 3 Mohs), are lithoidal, split into angular fragments on impact, and frequently exhibit conchoidal fracture. American flint clays have analogous characteristics.

We do not know precisely when the terms "toasted bread clay" or "toasted clay" first appeared in the Russian literature. It is known, however, that as early as 1855 this name was applied to the refractory clays of the Borovichy deposit. The Russian name "toasted clay" reflects peculiarities not characteristic of typical clays, e.g. absence of plasticity and lithoidal appearance.

It is characteristic of both Soviet and American deposits that there are observed transitions ranging from typical lithoidal non-slaking clays ("toasted clays" or flint clays) to plastic clays through the so called "semi-toasted clays" which can be considered as equivalent to semi-flint clays; some varieties of toasted clays, as well as of flint clays contain greater amounts of free alumina (e.g., diaspore and, less frequently, boehmite).

In the Soviet Union the most widely known and investigated toasted clays are those of the Borovichy deposit in Novgorod province which have long been used in manufacture of refractories. The modes of occurrence, composition and properties of these clays are collated in Table 1 according to data of various investigators (Balbashevsky *et al.*, 1941; Goncharov, 1952; Ageeva, 1967; Vikulova, 1967; Vikulova, Shusterova, 1940).

A comparison of the data for the refractory clays of the Borovichy deposit (Table 1) with the description of the refractory clays from the state of Missouri (USA) studied in detail by Keller (1954, 1968) enables drawing the conclusion that these clays are very similar in respect to their detailed characteristics of occurrence, composition, structure and properties. It is characteristic of both the Missouri and Borovichy deposits that they are confined to the Lower Carboniferous (in Missouri—the Cheltenham formation; in Borovichy—the Nizhnetulskaya stratum) and in some places trend to varieties containing free-alumina minerals (diasporic clays in Missouri and "kremnyovkas" in Borovichy). In addition to the Borovichy clays, the literature shows (Balbashevsky *et al.*, 1941) that toasted clays occur

Table 1. Modes of occurrence and characteristics of refractory clays of the Borovichy deposit

Salient features of the ancient relief in region of deposit		Uneven relief in the region of gradual uplift
Character of sedimentary basins		Small continental basins with rich vegetation (bogs, lakes) not far from sea
Stratigraphic position of refractory clays		Nizhnetulskaya sand-argillaceous stratum (Bolrikov horizon) of the Lower Carboniferous
Underlying rocks		Lower-Carboniferous continental variegated sandstones, plastic clays and coastal marine sands of the Bobrikov horizon, less frequently sand-clay deposits of the Likhvin horizon
Overlying rocks		Coal or coaly shales of Lower Alexinsky age of the Lower Carboniferous
Mineral composition	Toasted clay	Main mineral – kaolinite, much pyrite, rare orthoclase, carbonates, diaspore, zircon, tourmaline, disthene, staurolite
	Plastic and semi-plastic clays	Main minerals – kaolinite, hydromicas; some siderite, pyrite, potassium feldspar
Organic matter		All clays contain organic matter; plant remnants occur in toasted clays
Structure	Toasted clay	Typified by aggregates of variously oriented particles; ooides of a 0·01–0·1 mm size occur
	Plastic and semi-plastic clays	Uniform pelite mass
Content of free alumina	Toasted clay	Up to 6–8 per cent free Al_2O_3 (in so-called "kremnyovkas", hard kaolinitic flint-like refractory clays) as very small diaspore segregations
	Plastic or semi-plastic clays	Not observed
Refractoriness	Toasted clay	1650–1770°C, The "kremnyovkas" are the most refractory (1750–1770°C)
	Plastic or semi-plastic clays	1580–1690°C
Sources of material		Upper Devonian sand-clay rocks; finely dispersed particles of kaolinite, micas and other silicates were transported into the basins.

elsewhere in the USSR, usually in the Lower Carboniferous. Thus, in the Pripyat depression of Byelorusia (Mayevskaya *et al.*, 1965) layers of toasted clays (0·2–1·0 m) occur among deposits of a "kaolinitic stratum" of the Lower Carboniferous, which corresponds to the Bobrikov horizon. These intercalations, the number of which may reach 20, are separated by semi-toasted clays, plastic kaolinitic clays, argillites, aleurolites, sandstones and sands. Toasted clays are associated with coals or are interbeded with them. Small siderite and dolomite segregations, carbonized plant residues (frequently pyritized), and gibbsite as well as detritic particles of quartz, feldspar and muscovite occur in the toasted clay beds. Bauxites comprising kaolinite, hydromicas, gibbsite and hydrous ferric oxides occur (Dmitriev, 1968).

Some characteristics of the Borovichy toasted clay and those of a typical flint clay from Farnberg, Missouri, studied by the author are given in Table 2.

According to Goncharov (1962), the bulk density of the toasted clay from Borovichy varies from 1·996 to 1·454, the specific gravity – about 2·586 and the porosity – from 40·72 to 24·96 per cent.

Note the rather high porosity of the toasted clays and the open character of almost all the pores; however, despite this, the clays do not soften even upon extended submersion in water. The amount of organic matter in toasted clays is very small. The loss on ignition approximates the theoretical water content of kaolinite. The elevated dehydroxylation temperatures demonstrate the high degree of structural perfection of the kaolinite in the investigated toasted clays; this agrees with B. B. Zvyagin's data on the structural characteristics of kaolinite.

A Borovichy sample, in which the kaolinite particles are practically indiscernable, produces only a weak effect under the polarizing microscope. Electron microscopically, suspensions of the toasted and flint clays exhibit pseudohexagonal particles

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Table 2. Some characteristics of Borovichy toasted clay and flint clay from Farnberg, Missouri

Characteristic	Borovichy Toasted Clay	Farnberg Flint Clay
Bulk density, g/cc	1·701	2·177
Porosity, %	34·63	16·78
Open porosity, %	98	97
Loss on ignition, %	14·06	13·33
C(org.), %	0·10	0·11
CO_2	none	none
Spec. gravity	2·602	2·616
Temperature of endotherm peak	605–610°C	610°C
Structural characteristics of the kaolinite	Triclinic kaolinite with monoclinic unit cell	Triclinic kaolinite with triclinic-monoclinic unit cell

(0·1–0·8 mm) and parallel intergrowths thereof (Fig. 1); the latter are preserved even after a 5-min treatment with ultrasound which indicates extremely firm bonding of the particles. Replicae obtained from fracture surfaces (Fig. 2) show that the toasted and flint clays consist of differently oriented tightly contiguous kaolinite formations. During the initial crystallization period these formations were growing as monocrystals, but later, owing to splitting, yielded a large number of individual platelets, the inter-arrangement of which in varying degree is nearly parallel. Therefore, kaolinitic formations simultaneously represent monocrystals and blocks of more or less parallel laminae. This explains why it is so difficult to obtain electron-microscopic preparations of toasted and flint clays consisting only of separate kaolinite particles. The splitting of the kaolinite monocrystals into blocks of platelets may be considered as due to certain changes in the conditions of crystallization over the extended period of formation.

The voluminous literature on the study of flint clay deposits and the associated refractory clays has recently been analyzed by Keller (1968).

Using personal observations and some less well known results of Soviet investigators, the author summarizes below the existing data on the toasted-type refractory clays.

(1) There exists a special sedimentary formation of refractory clays including toasted clay (flint clay). For this formation, the author has proposed the name "toasted complex". In its complete development, this complex includes toasted clays of kaolinitic and diaspore-kaolinitic composition, semi-toasted clays, semi-plastic and plastic clays. The concept "toasted complex" is equivalent to the concept "flint clay facies" suggested by Keller (1968), but the first conforms more to the Soviet geological terminology.

(2) The association of refractory clays of the toasted complex with coal-bearing strata reflects two conditions favoring their formation:

(a) The influx of a large amount of finely dispersed particles into basins; (b) the presence of organic acids, the action of which caused chemical regrouping in the detrital material and the formation of kaolinite.

The acidic environment was not favorable for the formation of montmorillonite, but the slow course of silicate synthesis and crystallization favored kaolinite formation (halloysite is formed when the synthesis reaction is rapid). The decomposition of silicates, including muscovite by organic acids has been confirmed recently (Ershova, 1968).

(3) The formation of toasted clay complexes occurred under continental humid and warm conditions in shallow basins containing rich vegetation (lakes, swamps) located not far from the sea on peneplanatized areas of the Earth's crust (Ries, 1927; Keller *et al.*, 1954; Vikulova, 1957; Keller, 1968). The underlying rocks of many deposits are limestones or dolomites, which have been subjected to karstic processes. The parent material for the formation of toasted refractory clays was finely dispersed detritic silicate particles transported from dryland. Their decomposition and subsequent formation of clay minerals was facilitated by the small size of the particles and the action of dissolved organic acids.

(4) Some authors believe that the parent material for the toasted clays originated during laterite weathering. The formation of the parent toasted clay material in Southern France is associated with lateritic weathering of insoluble limestone residues (Halm, 1952). According to Loughnan (1962) some volcanogenic rocks in Australia have been subjected to lateritic weathering; it is assumed that alumina hydrates, formed during lateritic weathering underwent resilication in basins, where refractory clays were being formed. However, the assumption that the toasted clays originate during lateritic weathering is based only on the existence of such clays containing alumina hydrates, but this is not confirmed by geological observations. Moreover, all the clays of the toasted complex of a particular deposit were formed from the same parent material; alumina hydrates are absent in the semi-toasted and plastic clays in which the parent material has been least altered, but are present in the clays formed through more intensive alteration of the parent material. This may be explained as follows:

The detritic material transported from dry land was in an environment where it was subject to extended and energetic interaction with organic acids. Thus, the detrital kaolinite was preserved without essential change while the micas were gradually decomposing with formation of a solution of aluminum and silicon. A significant amount of the compounds of these elements reacted forming kaolinite. However, not all the dissolved aluminum could react to form kaolinite. This may be considered as due to the absence of reactive soluble silicon compounds.

As is known, the rate of silicic acid condensation with the formation of three-dimensional polysiloxane, $(SiO_2)n$, or hydropolysiloxane $(SiO_2)n(H_2O)m$, depends on pH of the solution: in acid solution (according to some investigators, at pH 3·2) this process is slow, but at pH 6 is almost instantaneous. Therefore, in weak acid solutions, such as in swamps and lakes, where the toasted clay material was deposited, the interaction between the aluminum and silicon compounds could be incomplete and this would favor the formation of colloidal free alumina and silica. The hydrophilic silica, forms a rather stable hydrosol even at high electrolyte concentrations, in contrast, the aluminum hydroxide forms a hydrophobic hydrosol which is very unstable even at low electrolyte concentrations. This stability difference between the colloidal silica and alumina can be considered as a possible cause of their depositing independently as free alumina and silica.

There is also a basis for the assumption that the formation of complex, slightly soluble organic aluminum compounds play some role in the separation of silicon and aluminum liberated during weathering of silicates. The experimental data showed that the aluminum fulvates precipitate readily at pH 4·5–4·8 particularly at high content of dissolved organic matter and at low aluminum concentration (Sokolova, 1968).

It should be emphasized that the high contents of free silica in toasted clays are usually explained as due to the presence of clastic quartz grains, although no substantiation is given for this assumption. It is quite possible that the quartz in toasted clays, occurring as fine particles at least in part is authigenic. There is no doubt about the authigenic origin of the chalcedony in some of the toasted clays from New South Wales (Australia) (Loughnan, 1962) and of the free silica in the toasted clays of Southern France (Halm, 1958).

Thus, the predominant role in the formation of the toasted clay complex must be attributed not to the character of the parent material, but to the conditions of its alteration in the sedimentary basins.

(5) The structural characteristics of toasted clays (flint clays) are indicative of their precipitation as gelatinous clumps. Irregular aggregates appear during their crystallization. Their differing orientation and interpenetration account for their lack of laminarity, their lithoidal appearance, increased hardness and absence of plasticity in water.

It is obvious that in the later stages of formation of toasted clays, especially at the stage of epigenesis, the recrystallization of kaolinite could occur with the formation of larger crystals. In certain places, free alumina is redeposited with formation of alumina-enriched toasted clays or the formation of bauxites.

Toasted clays are a very striking example of the influence of formation conditions on the properties of mineral aggregates.

(6) The precipitation of smaller clumps or individual particles, possibly because of slower decomposition of detrital material has apparently played an important role in the formation of plastic toasted clays. The presence of intact mica in such clays may be regarded as supporting the assumption of slow detrital decomposition and the delayed appearance of aluminum and silicon in solutions.

(7) Clays formed in the swamps of Holland (Hudig *et al.*, 1964) are Recent Sediment analogues of the toasted complex (flint clay facies); they range in age from 5000 to 7000 yr. X-ray and electron-microscopic study of these clays showed that they contain a swelling illite-like mineral, a mixed-layered micaceous mineral, kaolinite (up to 25 per cent), chlorite, potassium feldspar, 10–20% quartz, up to 15% boehmite. The presence of boehmite in swamp sediments genetically unrelated to laterites supports the concept presented in this paper concerning the formation of free alumina in toasted clays as a consequence of silica polymerization.

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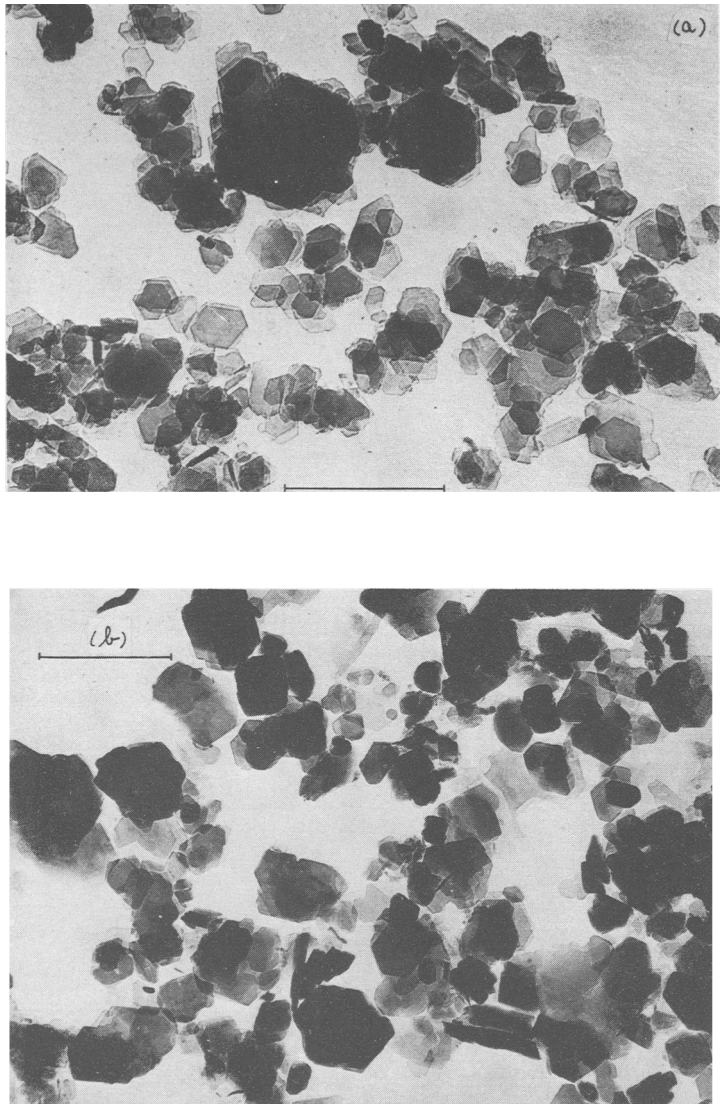

Fig. 1. Intergrowths of kaolinite particles in suspensions: (a) toasted clay from Borovichy; (b) flint clay from Missouri.

[*Facing page* 4]

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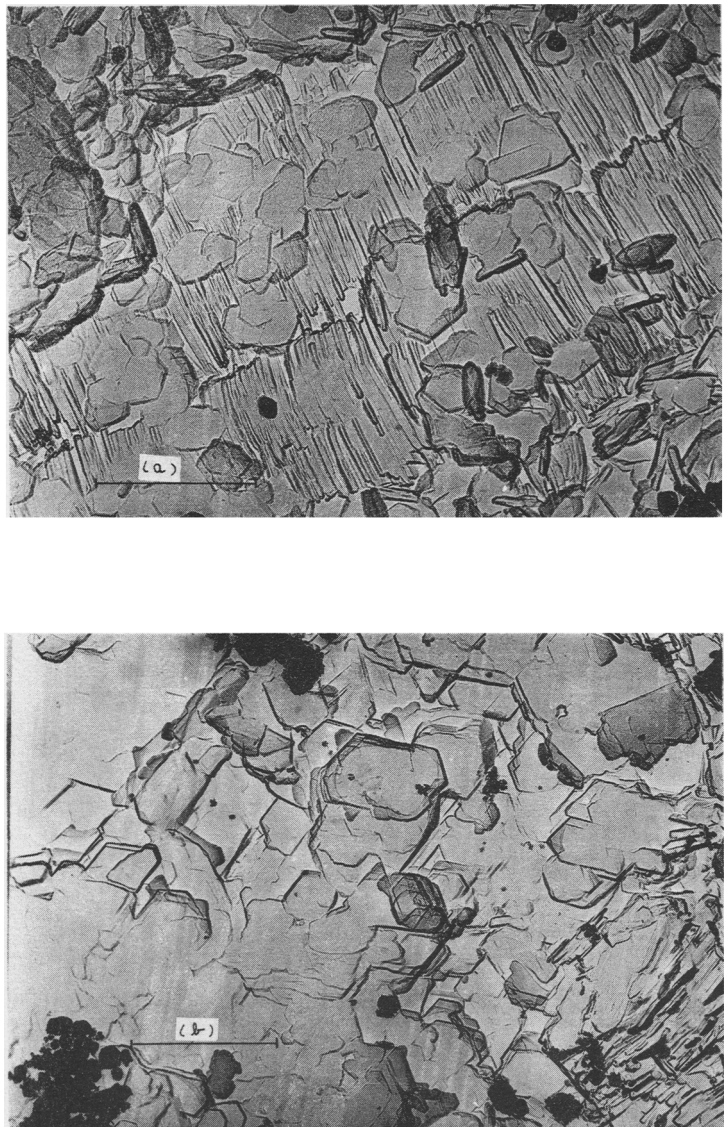

Fig. 2. Structure (replicae from fracture surfaces) of toasted clay from Borovichy (a) and flint clay from Missouri (b).

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Résumé—Le terme "flint clay" utilisé aux U.S.A. et dans de nombreux autres pays correspond très approximativement au terme "toasted bread (sukhar) clay". Aux U.S.A. et en U.R.S.S. les occurences typiques de "toasted bread" sont confinées à des dépôts du carbonifère inférieur. Par leurs propriétés et occurence, les argiles "toasted" du dépôt de Borovichy (province de Novgorod) et qui ont été étudiées attentivement, sont très similaires aux argiles "flint du Missouri, mais diffèrent surtout par le fait qu'elles ont une gravité spécifique de masse inférieure et une porosité plus élevée que les argiles du Missouri. Les variété présentant un excès d'alumine libre (diaspore, boehmite) peuvent être observées à la fois dans les argiles "toasted" et flint. L'auteur suggère le terme "toasted complex" (Sukharnii komleks) qui correspond au terme du W. D. Keller "flint clay facies". Les argiles du "toasted complex" sont des sédiments d'anciens lacs et marécages qui contenaient une végétation riche. Leur matériau de source était finement des particules de silicate dispersées et déplacées des terres sèches. La structure et les propriétés des argiles "toasted" sont expliquées par la précipitation de kaolinite sous forme de touffes colloïdales dans lesquelles la cristallisation est survenue avec une formation d'imbrication de cristaux serrés et des ségrégations orientées différemment.

Kurzreferat—Der in Amerika und verschiedenen anderen Ländern gebrauchte Ausdruck "Flintton" entspricht ziemlich genau dem Ausdruck "Toastbrot (Sukhar) Ton". Sowohl in den USA als auch in den USSR sind die typischen vorkommen "getoasteter Tone" auf Ablagerungen des Unterkarbons beschränkt. In ihren Eigenschaften und Vorkommen sind die weitgehend untersuchten getoasteten Tone des Borivichy Lagers (Nowgorod Provinz) den Flinttonen aus Missouri äusserst ähnlich, wobei der einzige nennenswerte Unterschied darin besteht, dass sie ein geringeres Raumgewicht und höhere Porosität aufweisen als die Flinttone aus Missouri. Abarten mit einem Überschuss an freier Tonerde (Diaspor, Boehmit) finden sich unter den "getoasteten" sowie unter den Flint Tonen. Der Autor schlägt den Ausdruck "Toast Komplex" (Sukharnii kompleks) vor, der dem von W. D. Keller verwendeten Ausdruck "Flint Ton Fazies" entspricht. Die Tone des "Toast Komplexes" sind Ablagerungen aus uralten Sümpfen und Seen, die reiche Vegetation enthalten. Ihr Quellenmaterial waren fein verteilte, vom Festland zugeführte Silikatteilchen. Das Gefüge und die Eigenschaften getoasteter Tone werden durch die Ausfällgung von Kaolinit als kolloidale Klumpen, in welchen Kristallisation stattfand, unter Bildung intimer Verwachsungen und verschiedenartig ausgerichteter Abscheidungen, erklärt.

Резюме—Понятию flint clay, которое употребляется в США и ряде других стран, в советской литературе соответствует понятие "сухарная глина" или "сухарь". Как и в США, в СССР типичные месторождения "сухарных глин" приурочены к отложениям нижнего карбона. Наиболее детально изученные сухарные глины Боровичского месторождения (Новгородская область) по свойствам и условиям залегания не отличаются от flint clays штата Миссури. Среди "сухарных глин", как и среди flint clays, наблюдаются разности с повышенным содержанием свободного глинозема (диаспор, бёмит). Автором предложено понятие "сухарный комплекс", которое близко к понятию "flint clay facies" В.Д. Келлера. Глины "сухарного комплекса" представляют осадки болот и озер с обильной растительностью. Исходным материалом для их образования послужили тонкодисперсные частицы силикатов, снесенные с суши. Особенности строения и свойства сухарных глин объясняются осаждением каолинита в виде коллоидальных сгустков, в которых происходила кристаллизация с образованием плотно сросшихся и различно ориентированных кристаллитов и их блоков.