

## FLINT CLAY BY HYDROTHERMAL ALTERATION OF SEDIMENTARY ROCK IN MEXICO

ROBERT F. HANSON\* and W. D. KELLER‡

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**Abstract**—This paper documents the first report of flint clay in Mexico, located at Estola, Guerrero, 199 km south of Mexico City, on Mexico Highway 95. It is the first report (known to the writers) of flint clay formed by hydrothermal alteration. It describes the *in-situ* alteration of a calcareous, silty shale to flint clay (well-ordered kaolinite).

The changes during alteration are mineralogical, chemical, and structural. Calcite, comprising about one-third of the shale, quartz and probably some feldspar comprising a scant third, and a mixture of greenish-yellow (limonitic) clay minerals are dissolved or altered ultimately to white kaolinite (monomineralic). Calcium carbonate, free and combined silica, and iron compounds are dissolved, while simultaneously the alumina is relatively enriched. The fissility, inequigranularity, and cementitious fabric of shale are changed to the massively homogeneous, finegrained, interlocking fabric that is typical of flint clay.

The sequence of changes, which overlap, are; (1) dissolution of carbonate minerals, (2) mobility of iron, replacement of quartz and feldspar by kaolinite; and (3) intensive "digestion" of rock substance to homogeneous, essentially monomineralic, kaolinite flint clay. Alunite, and secondary vein-calcite or gypsum may accompany the flint clay.

This occurrence lends support to the concept that flint clay is formed from presumably only sedimentary parent rock.

### INTRODUCTION

REFRACTORY clay deposits of hydrothermal origin in Mexico have been reported heretofore exclusively from the alteration of "primary-mineral" rocks, such as those in volcanic flows, pyroclastic bodies, or schist (Keller and Hanson, 1969). Recently discovered flint clay developed by hydrothermal alteration of sedimentary rock, a calcareous, silty shale containing about one-third calcium carbonate, adds another genetic variety and correspondingly new geochemical reactions to those previously studied.

### FIELD OCCURRENCE

The clay deposit occurs at the small settlement of Estola, Guerrero, just outside the south limits of Tonalapa, at kilometer-post 199 on Mexico Highway No. 95 leading toward Acapulco from Mexico City. It has been exposed in part in a stream bluff 10 m high, cut at the outside of a meander. Back from the cliff, hydrothermally altered, iron-oxide-rich surficial clay extends some 100 meters in

N-S direction, and about 30-50 meters E-W. The thickness of the clay beneath is indeterminate from surface exposures.

The country rock of the nearby region is the Cretaceous Morelos Formation composed of calcareous shale and medium-bedded muddy siltstones. Strong deformation occurred in the region before the flint-clay alteration took place, and post-clay faulting likewise has been observed with the deposit. This locality is part of the N-S regional structural grain of this part of Guerrero. The shale layers exposed at the margins of the flint-clay deposit range in attitude from nearly horizontal to strongly dipping, and are jumbled in what appears to be a highly disturbed and brecciated fault zone in the north part of the deposit.

### LITHOLOGY OF THE SHALE

The fresh shale, sample No. 1, collected near the south margin of the clay deposit, is light yellowish to greenish gray, matching the color group "21-c-d-e" of the Goldman-Merwin sedimentary-rock color chart, or 5Y-7/2 7/6 8/4 of the NRC Rock-Color Chart. Proximate grain analyses of three shale samples, collected within the area of clay deposits were made by dissolving them in 6N HCl, washing out the excess acid, and then separating them by

\*Refractarios A. P. Green, S. A., Mexico, D. F., and †University of Missouri-Columbia‡

‡Present address: University of South Florida, Tampa, Florida 33620.

sedimentation into coarse silt, and fine silt and clay fractions. The two clastic fractions were weighed, and the acid soluble amount determined by difference. Most of the acid-soluble material is calcite, but gypsum, which is sporadically present, and minor clay and iron oxide also would be dissolved. Analyses are expressed in wt. %.

Proximate analysis of shales

Shale	No. 1	No. 7	No. 13
Acid soluble	33	33	30
Coarse Silt	40	21	25
Fine silt-clay	27	46	45

In thin sections of shale No. 1, the carbonate minerals are seen to be in clay to silt-size crystals, Fig. 1. The 211 X-ray diffraction peak of the calcite shows essentially no shift, indicating very little Mg in solid solution. Quartz particles range in size from essentially clay up to 0.12 mm in cross-section—the 0.05 mm diameter size is common; they are typically sub-angular and moderate in sphericity and some of them consist of interlocking aggregates. Much of the quartz is strongly undulatory, as if it may have been derived from metamorphic rocks. Judging from the 2 per cent of  $K_2O$  in the analysis of the shale, analysis No. 1, it is expected that some of the clouded fragmental particles showing undulatory extinction may be K-feldspar. On the other hand, K-feldspar was not abundantly present in refractive-index, oil-immersion mounts studied under the microscope. K-mica, or illite, may account for most of the  $K_2O$ .

The clay-mineral portion of the shale appears to be uniformly and finely distributed throughout the rock, producing mainly a clouded or dusted appearance in thin section. Where the shale was acid-treated in the laboratory, the clay was dispersed in the suspension and settled out as yellowish clay-to silt-size flocs. X-ray diffractograms indicate that kaolinite makes up two-thirds to three-fourths of the clay fraction, the remainder being chlorite and illite (mixed-layered toward the larger d-spacing side) in approximately equal proportions.

#### THE HYDROTHERMAL ALTERATION

At margins of the Estola clay deposit, alteration or transition zones between apparently unchanged shale to flint clay may range in width from 2–4 m, as observed in the present (July, 1970) exposures of the deposit. The changes effected during alteration, although not occurring separately, may be discussed conveniently as structural, mineralogical, and chemical.

The most obvious visual change is structural. The fissile, inequigranular, cementitious, yellowish gray-green shale becomes, at maximum alteration, a massive, homogeneous, very fine-grained, slightly off white clay that fractures conchoidally. Intermediate between these end members, the fissility becomes progressively less sharp on the outcrop (resembling deteriorating resolution and poor focus under a microscope) grading into massive clay layers separated by fewer, newly developed partings. The color, in going from shale to flint clay changes from yellowish gray-green, through reddening or deepening brown, thence to dark to purplish red or dark gray, and ultimately to off-white. Iron oxide rich rock commonly outlines the margins of the clay body—a typical relationship in other Mexican hydrothermal refractory clay deposits. Indeed, mobilization of iron by dissolution, and redeposition of part of it as an oxide is an almost universal early-stage reaction during hydrothermal formation of kaolin deposits in Mexico (Keller and Hanson, 1969).

Mineral changes accompanying the loss of fissility from the shale are dissolution of calcite, selective enrichment of quartz, and increased abundance of disseminated red iron oxide, Fig. 2. Chlorite is not indicated in the X-ray diffractogram of No. 2 and may have been removed with calcite, but illite and especially kaolinite are more abundant than in sample No. 1. Although red iron-oxide is vastly more abundant in sample No. 2 than in No. 1, total iron is shown by the analyses (Nos. 1 and 2, in Table 1) to be lower in 2 than in No. 1. This relationship probably means that iron occurs mainly

Table 1. Analyses of shale and clay at Estola

	1*	2†	3‡	4§
SiO <sub>2</sub>	42.07	65.40	66.89	45.94
Al <sub>2</sub> O <sub>3</sub>	14.23	18.57	20.66	37.83
Fe <sub>2</sub> O <sub>3</sub>	7.35	3.23	0.49	0.10
TiO <sub>2</sub>	0.17	0.31	0.35	0.06
MgO	3.38	0.41	0.17	none
CaO	13.50	0.46	0.22	0.07
Na <sub>2</sub> O	0.34	0.51	0.48	0.51
K <sub>2</sub> O	2.29	2.83	1.95	0.08
P <sub>2</sub> O <sub>5</sub>	0.21	0.33	0.22	0.16
SO <sub>4</sub>	0.06	0.21	0.83	0.12
CO <sub>4</sub>	9.95			
H <sub>2</sub> O <sup>+</sup>	6.45	7.70	7.65	15.12
	100.00	99.96	99.91	99.99

\*Fresh shale.

†Altered shale at stage where calcite has been removed.

‡Semi-plastic clay.

§High-quality flint clay.

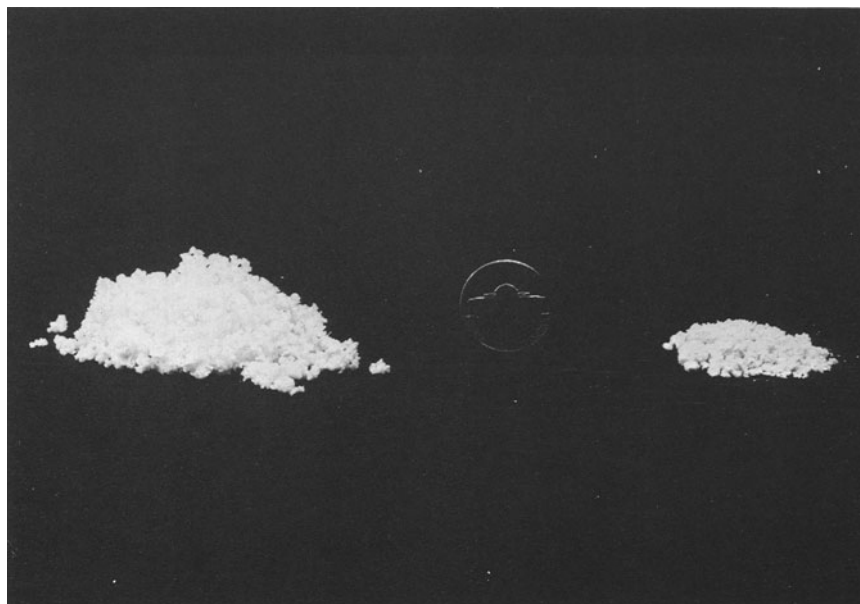


Fig. 1. Photograph of 0.1 g samples of  $-2\mu$  Volclay (left) and Otay (right) montmorillonites after spray-freezing and freeze-drying.

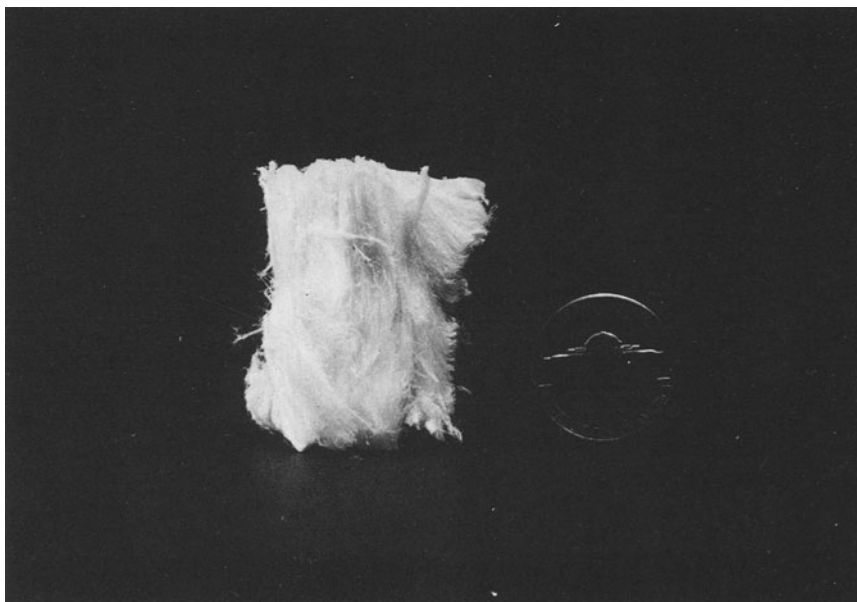


Fig. 2. Photograph of fibrous Volclay montmorillonite aerogel obtained from a 1 wt.% clay suspension

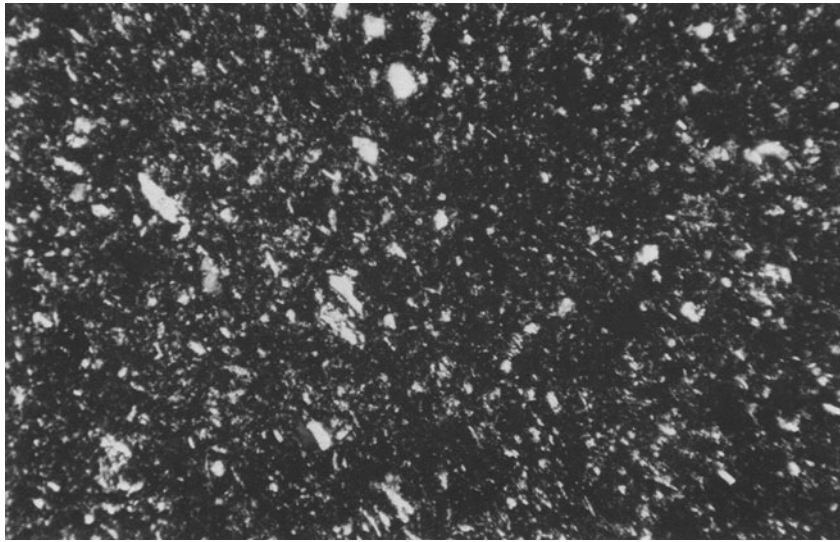


Fig. 3. Photomicrograph of thin section of semi-plastic clay, crossed polars. Dark background is mainly kaolinite. Light areas are quartz, and flakes of illite in sub-parallel orientation along the diagonal of the picture. Same scale as other photos.

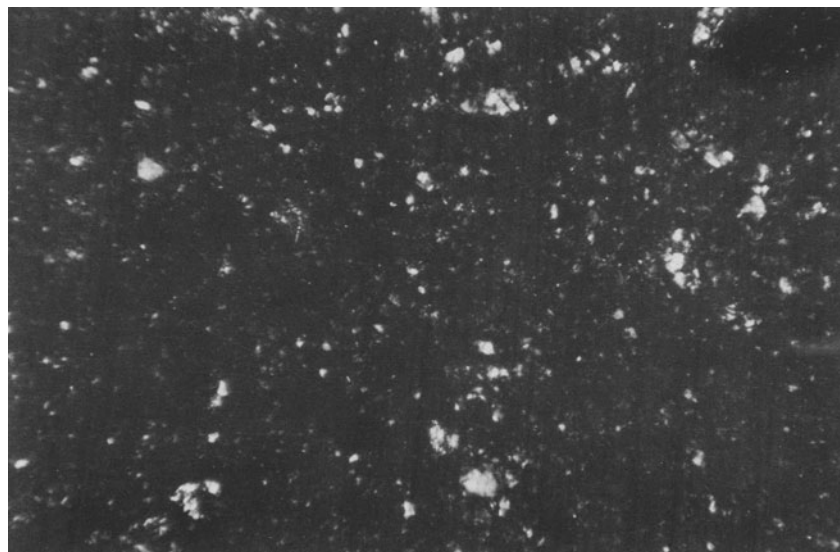


Fig. 4. Photomicrograph of thin section of reddish-tinted, siliceous flint clay, sample No. 4, crossed polars. The bright spots are quartz-silt grains representing possible relic grains and secondarily deposited silica. Same scale as other photos.

in No. 1 as chlorite and some pyrite which were dissolved and partially removed: the remainder was oxidized to the pigmenting oxide.

Dissolution of calcite and chlorite, and an increase in kaolinite are likewise reflected in the changes in chemical analyses. Analysis No. 2 shows strong decreases in Ca, CO<sub>2</sub>, Mg, Fe, and increases in Si and Al, over analysis No. 1. Much of the increase in the latter two is mostly by selective enrichment due to the removal of the calcite and chlorite. Some may result, however, from kaolinite deposited in No. 2.

Comparisons between these specimens cannot be strictly quantitative, although they are of the right order of magnitude, because it is uncertain that the sequential samples are exact stratigraphic counterparts of one another. Although they were collected not more than 3 meters distant from each other, the shales and mudstones have undergone movement and possible flowage, and the loss of fissility during alteration makes exact correlative tracing impossible. When the volume loss is as much as one-third, the changes are likely to be extensive, but not easily traced in detail.

Transitional between the prominent red altered zone and the well-defined flint clay is a zone of the clay possessing semi-plastic to semi-flint properties, No. 3 and Fig. 3. Such occurrence of semi-plastic refractory clay is unique here among Mexican hydrothermal clay deposits. Its close association with true flint clay is potentially important to the industrial ceramist. The position and width of this semi-plastic zone varies from place to place in its enveloping halo about the flint clay for the following reasons. Fundamentally, this semi-plastic clay was developed rather than flint clay where less chemical and mineralogical work was done on the parent shale by the altering solutions. The intensity of alteration was dependent, in turn upon the composition of the shale which varied from bed to bed, and on the capacity of solutions to do work which also was variable. Such a zone of semi-plastic clay, which is a member of the flint-clay facies, may be kilometers wide in sedimentary deposits but here it is telescoped to meters in width.

The Estola semi-plastic clay contains kaolinite, quartz, and minor illite as birefringent flakes in sub-parallel orientation, Fig. 3. Quartz is mostly unaltered, but where alteration is increased to flint clay, quartz is replaced by kaolinite.

The chemical composition of No. 3, shown in Table 1, accords with the mineralogy. The K<sub>2</sub>O resides in illite, and also possibly in alunite which, although not identified in this sample, has been observed elsewhere in the deposit, and is suggested by the SO<sub>4</sub> in the analysis. The over-all trend in the rock alteration has been toward loss of iron and

other fluxing elements, and increase in Al.

The flint clay, the end-product of alteration and highest-quality refractory clay, ranges in color from slightly off-white through light-reddish tinted clay (also first-quality material) to unacceptable iron-oxide-rich, flint-clay lenses interspersed within the best clay. The "purest" white to light-gray clay, sample 4a, shows only well-ordered kaolinite. In thin section it is characteristically featureless, typical of top-quality, fine-grained flint clay. Analysis 4 compares favorably with one of first-quality flint clay; it approaches the ideal kaolinite formula.

A reddish-tinted, slightly siliceous variety of the flint clay, illustrated by Fig. 4, contains 1.69 per cent Fe<sub>2</sub>O<sub>3</sub>, and scattered quartz grains. Part of the quartz obviously represents incompletely replaced relic grains, but some may be tiny particles of secondarily deposited silica. This type of "irony", siliceous surface clay appears to be a counterpart of the silica gossans commonly present over hydrothermal clay deposits in Mexico.

The structural changes produced by the hydrothermal kaolinization of a non-clay parent rock are striking. Argillation produces lithologically and structurally isotropic clay from a parent rock possessing contrastingly strongly developed structural features, such as vesicles or flow-banding in lava, pronounced foliation in schist, or fissility in shale. These structures are completely destroyed by the kaolinization process. As the original rock is transformed into clay it undergoes a "chemical digestion", much as might be carried out in a vat in an industrial operation. The complete structural, mineralogical, and chemical change that a rock undergoes when argillized, is one of the most profound of geologic processes.

#### GEOLOGIC CONDITIONS UNDER WHICH FLINT CLAY FORMS

The genesis of flint clay has long been identified with sedimentary processes, conditions and environment. Identification of flint clay formed hydrothermally, i.e. the Estola occurrence, however yields inferences of the geologic conditions prevailing during its genesis, some of which are similar to, and others different from, those under which sedimentary flint clay is formed. Those conditions in common to the two genetic occurrences may be necessary and sufficient for the genesis of flint clay.

Furthermore, an additional perspective may also be brought in to the view of the problem, that of the flint-like clay, but not true flint clay, which is abundant in most other hydrothermal clay deposits in Mexico. At Coacoyula, (Keller and Hanson, 1969),

only 16 km west of Estola, a flint-like \*clay, was formed by the hydrothermal alteration of igneous rock. It follows that the geological conditions which are critical to the formations of this clay are obviously not the same as those critical to the origin of flint clay. Hence comparison of similarities, and contrast of differences, between the processes of the three types of clay occurrences offer an opportunity to interpret the geologic conditions most likely to be necessary and sufficient to produced flint clay.

\*Both clays fracture to conchoidal, flint-like surfaces, and resist slaking more than do plastic clays, but beyond these superficial similarities they are radically different. The Coacoyula flint-like clay, typical of Mexican high-refractory, hydrothermal clays, lacks the relatively high density that characterizes first-quality flint clay in both unfired and fired lumps. Other distinguishing properties of flint clay are that it matures at high firing temperature to a dense mat of interlocking tiny mullite needles and very viscous glass (particularly at high temperature) and shows high ceramic compatibility with plastic clays at both high and low temperature, yielding a ceramically "monolithic" refractory. This combination of qualities presumably is responsible for flint-clay refractories having high resistance to thermal spalling while still retaining high density (usually an antithetical relationship), high resistance to slag and metal baths, good physical strength, and high-temperature load-bearing strengths.

Although it is difficult to evaluate geologically some of these properties, which are indeed critically real, necessary, and diagnostic, they are expressed convincingly in temperature-hours of useful refractory service. However, a significant single criterion, easily available to geologists, and demanded of good flint clay (assuming PCE, texture, fracture, non-slaking, etc. are acceptable) is that the density of the raw, lump clay after room drying be the order of 2.2 or more (and fired density also relatively high). The lump density of typical Missouri, Kentucky, or Pennsylvania flint clay, for example, ranges from 2.2–2.4. That of Estola flint clay is 2.4–2.45. On the other hand, the density of flint-like clay derived from hydrothermally altered Mexican volcanic rocks is commonly  $1.7 \pm$ , and that of many sedimentary kaolins is from 2 to 1.5.

**Résumé**—Cet article décrit pour la première fois la mise en évidence de "flint-clay" au Mexique, à Estola, Guerrero, à 199 km au sud de Mexico, sur le Mexico Highway 95. A la connaissance des auteurs, c'est la première fois qu'on rapporte l'existence de "flint-clay" formée par altération hydrothermale. L'article décrit l'altération *in situ* d'un calcschiste en "flint-clay" (kaolinite bien ordonnée).

Les changements qui accompagnent l'altération sont d'ordre minéralogique, chimique et structural. La calcite, constituant un tiers du schiste, le quartz et probablement du feldspath en constituant un peu moins d'un tiers, et un mélange de minéraux argileux de couleur verdâtre à jaune (présence de limonite) sont dissous ou altérés finalement en une kaolinite blanche monominéral. Du carbonate de calcium, de la silice libre et combinée et des composés du fer sont dissous, tandis que simultanément l'alumine augmente relativement. La schistosité, l'hétérogénéité granulométrique et la texture de ciment du schiste sont transformées en une texture massivement homogène, à grains fins avec interpénétration, qui est caractéristique du "flint-clay".

The following factors were found (Keller, 1968, 1970) to be common to all occurrences yielding sedimentary flint clay; (1) deposition in a paludal environment, (2) parent material was derived from sedimentary rock or an ancient soil, and (3) a period of chemical digestion and removal of fluxing ions by surface water.

Between the Estola and Coacoyula clays there are no observable genetic differences in clay minerals, clay texture, associated minerals, color, structure, water-table position, geomorphology, geologic age. The one striking difference between the two genetic systems is that the parent rock of the Estola flint clay was sedimentary, whereas, in the flint-like clay deposits the parent rock was igneous.

This is in agreement with the observation (Keller, 1970) that among kaolin-containing claystones of sedimentary rocks, flint clays were shown to have been derived parent material with a sedimentary lineage. The clay deposits customarily referred to as sedimentary "kaolins", on the other hand, are typically formed by first-stage weathering of feldspars or other primary-type silicates.

The observation that flint clay is preceded by a previously weathered sediment or sedimentary rock suggests that pre-conditioning by an episode of weathering is necessary for conversion to flint clay. It is concluded that the hydrothermal clay at Estola owes its distinguishing flint properties to having been derived from parent rock that was sedimentary.

## REFERENCES

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La séquence des transformations qui se chevauchent est la suivante; (1) dissolution des carbonates, (2) mobilisation du fer et remplacement du quartz et du feldspath par la kaolinite, (3) "digestion" intensive de la substance rocheuse en "flint-clay" kaolinitique homogène à caractère monominéral. De l'alunite et des veines de calcite secondaire ou du gypse peuvent accompagner le "flint-clay".

Le fait de rencontrer cette formation tend à confirmer le concept selon lequel le "flint-clay" est probablement formé à partir seulement d'une roche-mère sédimentaire.

**Kurzreferat**— In diesem Artikel wird erstmals über Schiefer-ton in Mexiko berichtet, der in Estola, Guerrero, 199 km südlich von Mexico City am Mexico Highway 95 festgestellt wurde. Es ist der erste Bericht (soweit den Autoren bekannt ist) über die Bildung von Schiefer-ton durch hydrothermische Veränderung. Es wird die Veränderung an Ort und Stelle eines kalkigen Schlamm-schiefers zu Schiefer-ton (wohlgeordneten Kaolinit) beschrieben.

Die Vorgänge während der Veränderung sind mineralogischer, chemischer und struktureller Art. Calcit, der etwa ein Drittel des Schiefers darstellt, Quarz und vermutlich etwas Feldspat, ein knappes Drittel ausmachend, sowie eine Mischung von grünlich-gelben (limonitischen) Tonmineralen werden aufgelöst und schliesslich in weissen Kaolinit (monomineralisch) verändert. Calciumcarbonat, freie und gebundene Kieselsäure, sowie Eisenverbindungen, werden aufgelöst, während gleichzeitig die Tonerde verhältnismässig angereichert wird; Die Spaltbarkeit, Ungleichkörnigkeit und das zementartige Gefüge des Schiefers verwandeln sich in das massiv homogene, feinkörnige, ineinander-greifende Gefüge, das für Schiefer charakteristisch ist.

Die Folge der sich teilweise überschneidenden Veränderungsstufen ist: (1) Auflösung des Carbonatminerals, (2) Beweglichkeit des Eisens, Ersatz von Quarz und Feldspat durch Kaolinit; und (3) intensive "Digestion" von Gesteinsubstanz zu homogenen, im wesentlichen monomineralischen, kaolinitischen Schiefer-ton. Der Schiefer-ton kann von Alunit und sekundärem Gang-Calcit oder Gips begleitet sein.

Dieses Vorkommen bekräftigt die Theorie, dass Schiefer-ton aus vermutlich nur sedimentärem Muttergestein gebildet wird.

**Резюме** — Статья представляет собой первый отчет о флинтклее Мексики (Эстола, Гуэрреро, 199 км южнее Мексико-сити по шоссе 95). Это первое (насколько известно авторам) описание флинткля, образовавшегося при гидротермальном изменении. В статье описывается изменение *in-situ* известковых илистых сланцев с образованием флинткля (хорошо упорядоченного каолинита). Изменения носят минералогический, химический и структурный характер. Кальцит (около одной трети вещества сланцев), кварц, вероятно, некоторое количество полевого шпата (менее одной трети вещества сланцев), смесь зеленоватожелтых (лимонитовых) глинистых минералов растворяются или полностью изменяются до образования белого каолинита (мономинеральные агрегаты). Карбонат кальция, свободный и связанный кремнезем, соединения железа полностью разлагаются; одновременно происходит относительное обогащение глиноземом. Сланцеватость, разномерность и цементационная структура сланцев изменяются до образования массивных однородных, тонкозернистых и переслаивающихся текстур, типичных для флинткля.

Последовательность изменений, частично перекрывающих друг друга: (1) распад карбонатных минералов; (2) миграция железа, замещение кварца и полевого шпата каолинитом; (3) интенсивное «переваривание» материала породы до гомогенного, существенно мономинерального, каолинитового флинткля. Флинтклей могут сопровождать алунит и вторичный жильный кальцит или гипс.

Наблюдения авторов служат доказательством образования флинткля, по-видимому, только за счет осадочной исходной породы.