# GEOLOGY, MINERALOGY, AND GENESIS OF SELECTED FIRECLAYS FROM LATAH COUNTY, IDAHO

### *by*

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#### ABSTRACT

Fireclay deposits occur in Latah County, Idaho, as residual weathered products, and as lacustrine sediments comprising part of the Miocene Latah formation. The residual deposits were developed upon granitic (granodioritic, gneissic) masses by surface weathering. The lacustrine fireclays were derived dominantly from weathered residuum and to a minor extent from volcanic ash.

Mineral proportions in the residual clay are typically as follows: kaolin minerals, *65* percent ; quartz, **20** percent ; K-bearing micas, **12** percent; and montmorillonitechlorite mixed-layer clay, trace.

The sedimentary fireclay deposits range widely in clay content, from some that are almost wholly kaolin to others containing as little clay as the residual material, or alternatively, to those meeting minimal requirements of fireclay. As the content of kaolin decreases in the deposits, there is a corresponding increase in content of quartz, K-bearing micas, and in the less abundant components orthoclase, mixed-layer illitemontmorillonite, and mixed-layer chlorite-montmorillonite.

In both the transported and residual clay bodies the kaolin minerals are, in order of decreasing abundance, halloysite, endellite, and fireclay mineral.

The lake deposits also contain seams of poorly crystallized kaolin that is inferred to have been derived from volcanic ash because (1) it contains minor quantities of tridymite. sanidine, and volcanic glass, and **(2)** it contains notably more endellite and allophane (amorphous and relatively soluble in NaOH) than is present in the other kaolin deposits. Endellite seemingly has developed in two separate geologic environments: as an alteration product of granodiorite gneiss by surface weathering and as an alteration product of volcanic ash deposited and altered in a fresh-water lake. It is postulated that endellite is a relatively common product of weathering.

### INTRODUCTION

In Latah County, Idaho, occur deposits of transported and residual weathered clays, and bodies of rock from which clays were weathered (Tullis, 1944; Scheid, 1950). Certain portions of these argillaceous materials have been tested in search for aluminum ore and have been used commercially as fire clay. Field studies of the fireclay were made in 1957, and laboratory studies done in 1958 and 1959.

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# GEOGRAPHY AND GEOLOGIC SETTING OF THE CLAYS FROM LATAH COUNTY, IDAHO

Latah County is in the west-central part of the panhandle of Idaho (Fig. **1)**  and comprises an area of approximately **1085** square miles. It is partly within the Walla Walla Plateau of the Columbia Plateau Province, which is underlain by Columbia River basalt, and pertly within the Coeur d'Alene Mountains of the Northern Rocky Mountain Province, made up, in general, of metamorphosed Belt sediments and batholithic intrusives.



FIGURE 1.-Geologic map of Latah County, Idaho.

The oldest rocks of the region are the metamorphosed Precambrian Belt sediments which comprise quartzites, schists, gneisses, and minor amounts of calcareous rocks. These rocks probably once covered Latah County but now crop out principally in the eastern and northern parts of the county (Fig. **1).** 

The next younger rocks in Latah County are Permian (?) volcanics (Scheid, **1960)** end occur just north of Deary and in two small outcrops near **Bovill.** 

These older rocks were intruded by large granitic masses probably during either late Jurassic or early Cretaceous time. Most workers in the region tentatively assign a Cretaceous **(2)** age to the intrusive rocks (Scheid, 1950) and consider them as a part of, though separated from, the larger Idaho batholith. The largest intrusive mass in Latah County trends northeastsouthwest through the Thatuna Hills and Paradise Ridge.

The intrusive rocks, except for the hornblende syenite in the northern part of the county, include important amounts of granite but are chiefly granodiorite. The granodiorite is typically light gray, medium grained and granular, and is composed chiefly of potash and soda-lime feldspars, quartz, muscovite, biotite, and hornblende.



**FIGURE** 2.-Diagrammatic cross section showing relationship of clays.

During Miocene time weathering and erosion exposed the Thatuna batholith and associated rocks and produced mature topography having several thousand feet of relief. Subsequently during Miocene time the Columbia River basalts, which originated in the west, were extruded upon the erosion surface as a series of great flows. They flowed up drainage systems and formed freshwater lakes by damming the surface streams. The fresh-water lakes became local basins of sedimentation in which the Latah formation was deposited.

Thus, the Latah formation is a series of lacustrine and stream deposits interbedded with Columbia River basalt flows (Fig. **2)** and is exposed over an irregular front along the eastern margin of the lava area. Scattered outcrops of the Latah formation occur over an area approximately 175 miles long and 75 miles wide that extends in a north-south direction from near Coeur d'Alene, Idaho, to just east of Whitebird, Idaho, and in an east-west direction from Asotin Canyon, Washington, to the headwaters of Orofino Creek in Idaho.

The Latah sediments are composed of interbedded clay, sand, and gravel derived from the granitoid and metamorphic rocks of the surrounding mountains. These sediments are rich in floral remains, and diatomaceous tuffs are locally present (Knowlton, **1926).** The Latah sand and gravel beds are generally gray to yellow and consist mostly of granite and quartz fragments, kaolin (the term kaolin is used in this report to refer to the kaolin group of clay minerals, and is not used as a specific mineral name) and, locally, feldspar and muscovite. Bands of iron-oxide-cemented sand and gravel are common.

The clay beds of the Latah formation are mostly light tan or gray but some are streaked with yellow or red, and thin, white, uniform seams of clay are common. They contain, in addition to kaolin, variable quantities of quartz sand and muscovite flakes. Almost pure kaolin clay lenses in them constitute commercial clay deposits. In Latah County these lenses are concentrated in a belt paralleling the contact between the granitic masses and the basalt between Moscow and Bovill, Idaho.

After the Columbia River basalts were erupted, weathering and erosion produced valleys up to 160 ft deep in the upper flows. Minor local volcanic activity then took place and lava moved small distances down the hillsides and valleys both north and south of the Thatuna Hills.

Overlying all formations already mentioned, and blanketing the entire area except for the higher hills of older rocks, is the Palouse formation of Pleistocene age. This formation is unconsolidated, massive to thick-bedded, brown to reddish-brown silt, and characteristically maintains vertical faces for many years in road cuts and stream banks. It generally has been considered to be wind deposited, but Scheid (1945, p. 16) suggests that, although most of the silt may have been wind-borne, deposition took place for the most part in a lake or in a series of small lakes.

The geologic units previously described, except the Palouse formation, are shown diagrammatically in Fig. 2, which illustrates the types that were sampled for this study. The Benson Clay deposit in the  $NW\frac{1}{2} NW\frac{1}{4}$ , sec. 33, T. 40 **N.,** R. **3** W., B.M., approximately 4 miles northeast of Troy, Idaho, was sampled as being representative of the granitic residual clays. It is described generally as being residual clay from granite, but in some places a gneissic structure is displayed. The original granitic knob has been altered here to depths of at least 100 ft, as has been shown by drilling. Moreover, the altered material has been protected from erosion by a basalt cap which ranges in thickness from 1 to 20 ft.

Unaltered rock is not exposed in the Benson deposit, but a relatively unaltered counterpart of the deposit was collected from the nearest exposure, a creek bed approximately one-half mile southwest of the Benson Pit, where the basalt cap has been eroded and relatively fresh gneissic rock is exposed.

Three samples of clay from the Latah formation were obtained from the exposed face in the fire clay pit of the **A.** P. Green Company one-half mile north of Helmer, Idaho **(NEi,** *NW\*,* sec. 16, T. 40 **N.,** R. 1 W., B.M.) The three samples represent extremes in color, grain size, mineralogy, and texture of clay exposed by mining operations. The lowermost 15 ft exposed and sampled is a loose, white, sandy, micaceous clay (sample SC-2). Overlying this sandy clay is **8-12** ft of extremely fine-grained, brown, plastic clay (sample SG1) which contains thin continuous seams of white clay (sample

AD-1). All clay samples were collected and stored in air-tight containers to preserve the hydration state of endellite and therefore its characteristic mineralogic properties.

### DETAILED DESCRIPTION OF SAMPLES

The samples cited in preceding paragraphs are described below in order of their genesis: first, the fresh parent material; second, the residual clay, and last, the clays from the Latah formation. Percentages of the various minerals estimated from thin-section studies are visual approximations.

### Microscopic Descriptions

*Fresh parent rock*.-The parent rock is a light- to moderate-gray inequigranular granodiorite gneiss composed of anhedral quartz grains, lightcolored feldspar, muscovite, and biotite. Segregation of biotite into layers containing only small amounts of quartz and feldspar imparts gneissic structure to the rock. Most of the grains are embayed and penetrated by adjoining minerals. Feldspar approximates 70 percent of the rock. Oligoclase  $(Ab_{75}An_{25})$ , which constitutes 75 percent of the feldspar, occurs in large anhedral, randomly oriented, slightly sericitized grains that locally show growth and alteration zoning. Many large, fresh, optically continuous grains contain small inclusions of altered feldspar, perhaps of an earlier generation, and irregular growths of quartz. Orthoclase (25 percent of the feldspar) occurs as anhedral grains of variable size penetrating irregularly into, and lying between, other minerals of the rock. Trace amounts of microcline are present.

Spatial relationships between the feldspar grains are complex. Contacts are extremely irregular; there is evidence of a great deal of reaction between oligoclase and microcline, and some feldspar occurs as inclusions in other feldspar grains. Seemingly several generations of each kind of feldspar are present within a single thin section.

Quartz (25 percent of the rock) occurs as grains ranging from a fraction of a millimeter to **5** mm in longest diameter. They are strongly sutured, irregularly shaped, interlocking, generally elongate, and show subparallel orientation and undulatory extinction. A few grains contain small zircon crystals and much acicular rutile. More than one generation of quartz is indicated by occasional myrmekitic growths of quartz where microcline is in contact with plagioclase, and by small irregular patches of quartz in the feldspar grains.

Biotite (25 percent) occurs in medium-sized grains, and in distinct bands from which thin stringers extend along grain boundaries and along fractures and cleavage planes.

Muscovite **(3** percent) occurs as large scattered flakes and as small shredded grains in association with biotite with which it was probably formed contemporaneously.

Epidote occurs in trace amounts associated with biotite and muscovite, and along fractures and cleavage planes of other minerals.

The rock resembles the granodiorite gneiss that crops out in the Orofino, Idaho, region, approximately 30 airline miles southeast of Troy **(C.** H. Johnson, personal communication). Tullis and Laney (1933) refer **to** the parent material of the clays near Troy, Idaho, as being metamorphic rocks. Johnson (1947) concluded that the granodiorite gneiss in the Orofho region has a sedimentary heritage. The close similarity in mineral composition, granularity, texture, and habit of minerals between the granodiorite gneiss of the Orofino region and that described above suggests a similar origin for the two rocks. It is assumed, therefore, that the granodiorite gneiss, the fresh parent rock of the Benson residual clay, was derived from pre-existing sediments and, thus, may be termed a metasedimentary rock.

*Benson residual clay.*—The Benson residual clay has the texture of granite. It is a soft, white to cream colored, poorly indurated, crumbly material. All the feldspar and dark minerals of the granodiorite have been altered to clay; only quartz and muscovite remain.

Quartz (10-15 percent) occurs in composite grains that are extremely sutured, irregular but generally elongate and in parallel alignment, and range from about  $5 \mu$  to 5 mm in longest diameter. The major difference between these composite quartz grains and those occurring in the granodiorite gneiss is partial to complete replacement of these grains by kaolin. Isolated quartz grains are enclosed in a clay matrix and may have been included in feldspar.

Muscovite **(2** percent) occurs in altered large scattered grains and in small stringers and shreds. In some flakes there is an outward gradation of mica into clay material, probably kaolin.

Sericitic mineral (8-10 percent) occurs as tiny shreds scattered throughout the section, but is also concentrated in irregularly shaped patches. The sericite may be an alteration product of large feldspar grains although feldspar no longer persists.

Kaolin (75 percent), which was identified by x-ray analysis, occurs as **a** very fine-grained matrix, as large vermicular crystals, and in all intermediate gradations. Kaolin apparently has formed through alteration of feldspars, biotite, and muscovite, and replaces quartz.

The modes of occurrence of quartz and muscovite in this sample, and the relative amounts of kaolin and sericite, leave little doubt that the kaolin deposit was formed through alteration of a rock very similar to the granodiorite gneiss exposed southwest of the Benson pit, and therefore it is assumed that granodiorite gneiss is the parent material. Although parent mineralogy can not generally be determined from the residual clay itself, the alteration products of specific minerals were determined by Tullis and Laney (1933) from partially altered samples. They stated that the biotite altered to kaolinite and in so doing formed the largest clay crystals in the rock. The crystals range from microscopic size up to **14** mm in length and have vermicular habit. Feldspar, on the other hand, altered to sericitic and optically isotropic

material. Tullis and Laney reported that kaolinite formed from both the sericitic material and the isotropic substance, and that the isotropic substance may be the mineral halloysite. Only rarely was muscovite observed to bc changed completely to kaolinite although it graded outward into sericitic material. Quartz also was reported to be replaced by kaolinitic material.

*Xanzple* SC-2.-Sample SC-2, which represents the white sandy micaceous clay, **is** noncompact and contains abundant mica flakes and fine-grained quartz in addition to the clay. It crumbles easily and slakes readily in water.

In thin section this sample is observed to be a poorly bedded, poorly sorted sandy fireclay. Quartz (40 percent) occurs as extremely angular grains that range in size from submicroscopic to  $0.2 \text{ mm}$  in diameter. Some grains show undulatory extinction, others are rutilated, and a few are extremely brecciated. Practically all quartz grains are embedded in clay matrix.

Muscovite flakes, which amount to about **7** percent of the rock, measure as much as 1 mm in diameter, but most measure less than 0.5 mm in diameter. They are oriented parallel to the indistinct bedding of the rock, and show different degrees of alteration; some flakes are almost completely altered, whereas others are nearly unaltered.

Grains of orthoclase *(5* percent), whose maximum diameter is approximately 0.2 mm, range from very fresh to extremely altered, and the most altered grains may lie adjacent to the freshest grains.

Kaolin (45 percent) has two modes of occurrence. About half of the kaolin is pseudomorphic after rounded feldspar grains; ita birefringence varies normally from one composite grain to another in accord with differences in grain size of the kaolin. The other half of the kaolin occurs as fine-grained matrix that is optically isotropic to weakly birefringent.

Trace amounts of zircon, and ilmenite that is partly altered to leucoxene, are embedded in the clay matrix.

The mineralogy of this sample indicates a source rock very similar to the granodiorite gneiss, and extreme variations in degree of alteration of adjacent feldspar grains indicate little postdepositional alteration. The round composite kaolin grains, pseudomorphic after feldspar, suggest slight rounding during very short transport.

*Xample SC*-1.—This sample of brown plastic clay is soft, gray to very light brown and contains very little silt. It breaks into blocky fragments having subconchoidal surfaces and slakes very slowly in water.

In thin section, sample SC-1 is extremely fine grained and most of the individual grains are not resolved at  $450 \times$ , but do show a high degree of preferred optical orientation. It is composed mainly of weakly refringent kaolin minerals (identification confirmed by x-ray diffraction) but contains also scattered small flakes of muscovite and sparse quartz grains.

The muscovite flakes appear fresh and are scattered at random throughout the thin section but show a high degree of parallel orientation. They range from about  $2\mu$  to as large as 0.1 mm maximum diameter in a few flakes.

Quartz grains, on the other hand, which are also scattered at random throughout the section, do not exceed **0.05** mm in diameter. The content of quartz and muscovite was estimated at one percent each, but if present as submicroscopic components may exceed greatly this figure.

The high degree of orientation and relative freshness of the muscovite flakes, and the extremely high proportion of clay, indicate a sedimentary origin with relatively little postdepositional alteration for this material. Sedimentary processes have served to separate effectively the clay from the non-clay mineral components of the altered granitic source rock.

*Sample AD-*1.--Sample AD-1, which is from a seam of soft white clay, has a moderately speckled appearance owing to inclusions of brown silt-size particles. This material breaks into blocky fragments having subconchoidal surfaces. It slakes very readily in water and crumbles into a very he-grained white powder when dried.

In thin section the sample is moderately well-bedded fire clay containing elongate "patches " of weakly birefringent and vermicular kaolin in an otherwise isotropic groundmass. Bedding results from parallel orientation of the weakly birefringent patches.

The patches of vermicular kaolin, although generally elongate, do not exhibit sharp boundaries, are irregular in outline, and the individual vermicular crystals penetrate into the isotropic groundmass. Isolated vermicular crystals are sparse (less than one percent). The patches approximate *26* percent of the section.

The isotropic material, which makes up about **70** percent of the thin sections, is composed of amorphous material and extremely fine-grained kaolin. In addition to the patches of vermicular kaolin, small amounts of quartz, tridymite, sanidine, volcanic glass (?), and a few large isolated " worms " of kaolin are in the isotropic material.

Quartz, which occurs as grains on the order of **.05** to 0.1 mm in diameter, amounts to about one percent of the rock. Sparse tridymite and sanidine occur as grains approximately the same size as those of quartz. **A** few, light brown, isotropic, conchoidally fractured grains are assumed to be volcanic glass.

The predominant isotropic material, the grains of tridymite, sanidine, and volcanic glass, and the irregularly shaped patches of birefringent kaolin serve to distinguish sample **AD-1** from others, and make it sufficiently different from other samples that a different origin is proposed. The presence of tridymite, sanidine, and glass fragments in the rock indicates a volcanic source. Inasmuch as these mineral grains appear to " float " in an isotropic matrix and the clay occurs as thin, white, uniformly thick seams interbedded with lake sediments, it seems likely to be altered from volcanic ash deposited in a lake that normally received sediments derived from granitic terrain. Alteration of the ash (probably fine grained) has resulted in formation of the isotropic substance from which the vermicular kaolin is believed to have " grown."

### ANALYSES OF SAMPLES

In addition to the identification of minerals and estimation of their abundance in thin sections of the samples, detailed particle size, mineralogical, and chemical analyses were made of the samples, as follows.

### *Size Analyses*

Size distribution analyses were made of clay samples by wet-sieving through a 325-mesh screen, and using the Andreason pipette for the < *325*  mesh material; they are presented in Table 1. Size fractionation was found to be useful mainly in study of the distribution of specific minerals.

#### *Mineralogical Analyses*

The clay samples were sealed in the field after collection to prevent drying and crystal dehydration. x-Ray diffraction data were obtained in duplicate from samples run in a water-saturated state, after ignition at 550°C, and after solvating the field-wet material with ethylene glycol.

The term kaolinite was applied to the well-crystallized variety of kaolin that gave sharp, well-defined first and second order basal reflections at about 7.15A and 3.578 respectively, and three other prominent groups of lines as follows: those from  $4.46\text{\AA}$  (020) to  $3.57\text{\AA}$  (002); triplets having spacings 2.55Å, 2.52Å, and 2.49Å; and triplets at 2.37Å, 2.33Å, and 2.28Å. Fireclay mineral was reported if there was the slightest indication of substitution of 110 and 111 reflections and moderate to low intensity " doublets," or two broad bands, for the typical kaolinite "triplets." Halloysite  $(2H<sub>2</sub>O)$  was recorded for those patterns showing no 110 or 111 reflections, i.e., a smooth curve between 02 and 002, a broad 001 reflection at about 7.2-7.4A that did not expand on glycolation, and a single broad band like that produced from a 2-dimensional hk diffraction grating in place of the typical kaolinite "triplets." Mixtures of halloysite and fireclay mineral were determined by the presence of two weak bands superposed on the halloysite diffraction band (35-  $39^{\circ}$  2 $\theta$ ), and a narrower 001 reflection than for typical halloysite.

Endellite was identified by an 001 reflection at 10A which shifted to approximately 11 $\AA$  upon glycolation, and which collapsed to roughly 7.25 $\AA$ upon heating. The peaks at  $11 \text{\AA}$  and  $7.25 \text{\AA}$  were sharper and more intense than the 10Å reflection.

The presence of a small amount of endellite (possibly interlayered with a larger proportion of halloysite) was assumed if the 001 reflection of halloysite tailed off appreciably toward the low-angle side.

Illite was distinguished on diffractograms by its  $10\text{\AA}$  peak (usually low, broad and somewhat skewed toward lower angles) which showed no change upon glycolation. The  $10\text{\AA}$  peak was sharpened slightly by heat treatment of the clay. A low, broad peak otherwise typical of illite 001 which was further characterized by a rather sharp apex at 10A was taken as indicative of a mixture of illite and muscovite.

Montmorillonite was distinguished on diffractograms by 001 peaks at 18-19A, 17A, and 10A from water-saturated, glycolated, and heat-treated samples respectively.

The ratio of endellite to halloysite was determined quantitatively by differential thermal analysis using the method proposed by Sand and Bates (1953). Accurate quantitative estimates of mineral content from x-ray diffractograms of these clay samples are not offered because (1) 001 peaks of kaolinite and halloysite coincide, (2) the degree of crystallinity is different in the two minerals, **(3)** the intensities of the 001 reflections from equal masses of halloysite and endellite are not equal, and (4) the degree of crystallinity varies among these minerals. Quantitative estimates were made using the petrographical microscope after qualitative identifications were made by x-ray diffraction.

Mineralogical analyses of selected size fractions of the clay samples are presented in Table 1. These data are close to, but not in complete agreement with, mineral estimates from the thin sections. The thin section estimates are more representative of the average of the rock sampled, whereas the data in Table 1 represent fractionated spot samples.

The Benson residual clay contains much material larger than 325 mesh **(67**  percent by weight) of which approximately 50 percent is in composite kaolin grains containing the minerals halloysite, endellite, and fireclay mineral. Quartz and muscovite compose the remaining part of this fraction. Quartz, which constitutes 35 percent of the coarse fraction, decreases in amount with decreasing particle size and was not detected in the  $\langle \cdot \rangle$  *p* fraction. Muscovite, composing 8-12 percent of the coarse fraction, also decreases in content with decreasing particle size but illite, although not present in the coarsest fraction, shows a corresponding increase. The kaolin minerals are more abundant in the finer fractions, except for the  $\langle 1 \mu \rangle$  fraction in which illite and montmorillonite-chlorite constitute a large percentage.

The content of kaolin in sample SC-2, the white sandy micaceous clay, ranges from about 10 or 15 percent in the > 325-mesh fraction to almost 100 percent of the  $\langle 1 \mu \text{ fraction}$ . The more poorly crystallized and more highly hydrated forms are concentrated in fractions containing small size particles.

Quartz is abundant (70 percent) in the coarse fraction, but does not occur in the  $\langle 1 \mu \text{ fraction}$ ; the small amount of muscovite in the coarse fraction gives way to a small amount of illite in the fine fraction. Orthoclase makes up about 10 percent of the >325-mesh fraction but was not identified in any material less than ten microns in equivalent diameter. **A** rich heavy mineral suite occurs in the coarse fraction.

Sample SC-1, the brown plastic clay, is composed predominantly of extremely fine-grained kaolin which occurs as aggregates in the different fractions. Halloysite and minor quantities of fireclay mineral and endellite are present in most size fractions, but fireclay mineral was not detected in the  $\langle 1 \mu \text{ fraction.}$  As in the residual clay, the more poorly crystallized and hydrated forms of kaolin are more abundant in the finer fractions.

		TABLE 1. DISTRIBUTION OF MINERALS IN SELECTED SIZE RANGES OF CLAY SAMPLES, LISTED IN ORDER OF ABUNDANCE					
Benson Residual Clay		Sample SC-2		Sample SC <sub>1</sub>		Sample AD-1	
Percent of Fraction	Sample Percent đ	Percent of Fraction	$S\text{ample}$ Percent ಕ	Percent of Praction	Sample Percent ď	Percent of Fraction	Percent Sample ಕ
>325-Mesh Fraction	66.82	>325-Mesh Fraction	66.25	>325 Mesh Fraction	0.72	>325 Mesh Fraction	3.65
$<$ 43 $\mu$ - > 20 $\mu$ Fraction 26.11 35 $8 - 12$ SO, $75 - 80$ Fireclay Min. Fireclay Min. Halloysite Muscovite Halloysite Muscovite Endellite Endellite Quartz		$\langle 43 \mu - \rangle 20 \mu$ Fraction 65 $\frac{1}{2}$ œ $10 - 15$ $_{\text{trace}}$ Ъ, S Fireclay Min. tourmaline Heavy Min. sillimanite Orthoclase staurolite Halloysite Halloysite Muscovite Endellite ilmenite Endellite anatase apatite Quartz zircon Juartz rutile	5.57	$<$ 43 $\mu$ $>$ 20 $\mu$ Fraction 10 10 L. trace $\boldsymbol{\mathcal{L}}$ ĩ. trace g Fireclay Min. Fireclay Min. Halloysite Halloysite Muscovite <b>Tridymite</b> Muscovite Cordierite Endellite Endellite Quartz Quartz	2.30	$<$ 43 $\mu$ - $>$ 20 $\mu$ Fraction 95 trace 95 trace trace $_{\text{trace}}$ m Fireclay Min. Heavy Min. Heavy Min. Halloysite Halloysite Tridymite Tridymite Endellite ilmenite Endellite ilmenite Sanidine Quartz Quartz zircon zircon rutile rutile	4.52
$rac{8}{5}$ Quartz		$\infty$ າດ Orthoclase Muscovite		$<\!\!10\,\mu->\!\!7\,\mu$ Fraction	4.04	$<$ 10 $\mu$ – $>$ 7 $\mu$ Fraction	4.96

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 $\sim 10^{-1}$ 

Quartz and muscovite each make up about *5* percent of all fractions except the  $\langle 1 \mu \text{ material}$ . In this fraction no muscovite could be identified, but a small proportion of illite-montmorillonite was found. Trace amounts of cordierite and tridymite occur in the coarse fraction.

Sample AD-1, the white, predominantly isotropic material, is composed chiefly of endellite and halloysite, although large, vermicular crystals, which were expected to be well-crystallized kaolinite, was also noted. It was somewhat surprising, therefore, to find that x-ray diffraction patterns of the sample showed fireclay mineral and not well-crystallized kaolinite. In order to determine whether diffraction maxima from well-crystallized kaolinite were masked by more poorly crystallized material, or whether the larger crystals failed to give a good kaolinite pattern, large clay crystals were hand picked for further study.



**FIGURE 3.**—X-Ray<sup>T</sup>diffraction patterns of hand-picked vermicular crystals of fireclay mineral (A) and well-crystallized kaolinite from Murfreesboro, Arkansas (B).

The hand-picked crystals (Plate **l),** up to **1** mm in diameter, are curved, semitransparent to white grains which possess perfect cleavage on the basal plane (001). Their (001) face is opaque to translucent and has a pearly luster. Comparison of their diffraction pattern, Fig. **3,** with that of well-crystallized kaolinite (Murfreesboro, Arkansas) shows these hand-picked crystals to be a poorly ordered kaolinite. Only one peak that does not coincide with reflections given by Brindley and Robinson (1947) for fireclay mineral shows on the diffractogram. This peak, which represents a spacing of about **2.30&**  is weak and broad. TWO weak reflections of fireclay mineral at 1.977A and 1.541 Å are absent however. The hand-picked crystals, though well formed morphologically, were determined, therefore, to be megascopically large crystals of fireclay mineral. The non-kaolin minerals in this sample (AD-1) are quartz, tridymite, sanidine, ilmenite, rutile, and zircon, all of which are present in minor quantities and are restricted to the coarser fractions.



PLATE 1.-Hand-picked kaolin crystals (fireclay mineral). 28  $\times$ 

 $[facing \ page \ 56$ 

## *Chemical Analyses*

Total chemical analyses made from the granodiorite gneiss, Benson residual clay, and samples SC-2, SC-1, and AD-1 are presented in Table 2

	Granodiorite Gneiss	Benson Residual Clay	Sample $SC-2$	Sample SC-1	Sample $AD-1$
Moisture at					
$105^{\circ}$ C	0.01	0.76	0.52	2.25	2.18
Additional					
L.O.I.	0.91	6.30	6.14	12.20	12.03
SiO <sub>2</sub>	72.15	66.79	68.60	44.58	44.93
Al <sub>2</sub> O <sub>3</sub>	17.11	22.44	20.25	37.42	38.10
FeO	0.50	0.07	0.02	0.06	0.02
Fe <sub>2</sub> O <sub>3</sub>	0.69	1.10	0.77	0.95	0.67
TiO <sub>2</sub>	0.24	0.35	0.91	1.16	1.09
MnO <sub>2</sub>	0.005	0.004	0.009	0.005	0.01
CaO	1.75	0.83	0.24	0.24	0.23
MgO	0.39	0.40	0.38	0.71	0.45
$P_2O_5$	0.02	0.02	0.02	0.02	0.02
Na <sub>2</sub> O	4.02	0.04	0.10	0.12	0.13
$\rm K_2O$	2.11	0.84	1.95	0.18	0.06
SO <sub>3</sub>	0.01	0.01	0.02	0.03	0.02
Undetermined	0.08	0.04	0.07	0.08	0.06

TABLE 2.-CHEMICAL ANALYSES OF THE SAMPLES

TABLE 3.-RESULTS OF CHEMCAL ANALYSES RECALCULATED TO RELATIVE NUMBER OF CATIONS

	Granodiorite Gneiss	Benson Residual Clay	Sample $SC-2$	Sample $SC-1$	Sample $AD-1$
$H$ at 105°C	0.07	3.38	2.65	8.41	8.23
Additional H	6.03	31.50	31.31	45.60	45.41
Si	63.64	44.46	46.58	22.39	22.57
Al	17.79	17.61	16.21	21.95	22.57
$Fe2+$	0.37	0.04	0.01	0.02	0.01
$Fe3+$	0.46	0.54	0.39	0.36	0.25
Ti	0.16	0.18	0.47	0.43	0.41
Mn	0.003	0.002	0.004	0.002	0.003
Cа	1.65	0.59	0.18	0.13	0.12
Mg	0.51	0.40	0.38	0.53	0.34
P	0.02	0.01	0.01	0.01	0.01
Na	6.87	0.05	0.13	0.12	0.13
ĸ	2.37	0.71	1.69	0.11	0.04
s	0.005	0.004	0.008	0.01	0.006
Total	99.95	99.90	100.02	100.07	100.10

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as weight percent of the oxides. The oxides have been recalculated (Table 3) to show the ratio of the number of cations, and are discussed on this basis in the section on changes during argillation and sedimentation.

The content of allophane in clay samples was determined quantitatively by the dissolution method of Hashimoto and Jackson (1960). These data are presented in Table 4 and will be discussed in the following section.

	Percentage of 100 mg Sample <b>Dissolved</b>	Mg taken in sol. from $100 \text{ mg}$ Sample		$SiO_2$ : $Al_2O_3$
		SiO <sub>2</sub>	$\rm Al_2O_3$	
Benson residual clay	4.40	3.40	1.0	5.7:1
Sample SC-2	3.70	2.00	1.7	2:1
Sample SC-1	5.75	2.85	2.9	1.7:1
Sample AD-1	17.25	6.65	10.6	1.1:1

TABLE 4.-ALLOPHANE CONTENT OF CLAY SAMPLES

# CHANGES DURING ARGILLATION AND SEDIMENTATION, WITH INFERENCES ON ENVIRONMENT

The mineral, chemical, and physical changes by which the parent rocks and products were transformed to fire clay deposits may be inferred by comparing their chemical compositions from fresh to argillized material.

From Table 3 it is seen that hydrogen amounts to 6.03 percent, by number, of the cations in the granodiorite gneiss, but increases to 31.5 percent in the residual clay, and increases to more than 45 percent in samples SC-1 and AD-1. The increase of hydrogen ions constitutes one of the greatest relative changes in ionic composition during alteration. The hydrogen content of sample SC-2 is practically the same as that in the residual clay.

Silicon decreased by about one-third during alteration of the parent material (63.64 percent in granodiorite gneiss) to residual clay (44.46 percent), and in sample SC-2; it decreased by another one-third (to slightly more than 22 percent) in samples SC-1 and AD-1.

The relative number of aluminum ions did not change during alteration of the parent granodiorite gneiss to residual clay. This indicates the immobility of the aluminum ions at the pH of the altering system. In addition, there is little difference in aluminum content between all five samples, although there is a slight increase in samples SC-1 and AD-1.

Ferrous iron, although only 0.37 percent in the parent rock, is almost nonexistent in the clay samples. Ferric iron, however, decreased only slightly during alteration and transportation, from 0.46 percent in the parent rock to 0.54 percent in the residual clay and 0.39 and 0.36 percent in the sedimentary clays.

Calcium, sodium, and potassium (1.65,6.87, and 2.37 percent, respectively, in the parent rock) decreased markedly during alteration. Magnesium, which amounts to only 0.51 percent of the parent rock, varies little from sample to sample.

The obvious mineralogical changes that occurred during weathering were : loss of feldspars, biotite, and epidote, and partial loss of quartz and muscovite, accompanied by the formation chiefly of kaolin and also some illite and montmorillonite-chlorite (Table 5).

Original	Product
biotite	$\rightarrow$ kaolin
$\operatorname{feldspar}$ $<$	>sericitic minerals (mont.-chlorite?)—→kaolin $\rightarrow$ isotropic material $\rightarrow$
muscovite-	sparse 'kaolin
quartz $-\$	$\rightarrow$ partially replaced by kaolin minerals

TABLE 5.-MINERALOGICAL CHANGES DITRING WEATHERING

The most pronounced chemical changes occurring during the alteration of the granodicrite gneiss to the Benson residual clay were hydrogenation, desilication, oxidation of ferrous iron, and loss of Ca, Na and K ions. The large increase in abundance of hydrogen ions during alteration of the parent granodiorite gneiss would have been favored by availability of hydrogen ions in the weathering environment. In the processes of rock hydration and hydrolysis of alkali feldspars, hydrogen ions are introduced into the silicate structure replacing  $Na^+$  and  $K^+$ . A constant source of  $H^+$  is required if the reaction is to proceed; hence percolating acid solutions would have been most favorable to the hydrolysis reaction.

The abrasion pH determined for the residual clay was 7.2 and, according to Correns (1949, p. 210), alumina is relatively insoluble between  $pH 4$  and 10. It is noted that the aluminum content is the same in the fresh and the altered sample (Table 3). According to work by Krauskopf (1956) silica is also relatively insoluble in pure water at a pH of 7.2 and increases little in solubility until a pH of 9 is reached. However, feldspars have abrasion pH values as high as 9 (Stevens and Carron, 1948) and considerable silica may therefore go into solution at the interfaces of hydrolyzing feldspar and water. Krauskopf points out that polymerization of silica in dilute solutions is slow and may require months or years to form sols. Hence, silica may have been removed from the system in otherwise neutral, or slightly acid, solutions made basic at the interfaces between mineral grains and water by the hydrolysis reaction.

The relative abundance of the common elements described above accords with that given by Keller (1956, 1957, 1958) for alteration in a humid temperate environment. Thus it is inferred that the Benson residual clay developed in a humid temperate climate.

The formation of endellite in the zone of weathering places an added restriction on the environment of formation of the Benson residual clay. Because endellite is dehydrated irreversibly to halloysite, its presence implies that the zone of weathering was, at all times, saturated with water and did not dry out seasonally. Additional support is given to this interpretation of climate by fossil flora included in sediments which were accumulating in local basins concurrently with the formation of the Benson residual clay. More than 150 fossil species reported from it by Berry (1928,1934) were interpreted as indicative of a temperate humid climate with well-distributed rainfall.

Sample SC-2 (the white arenaceous and micaceous clay) and the Benson residual clay are insignificantly different in their cationic compositions although they show minor mineralogical differences. The greater abundance of and lesser amount of kaolin in coarse fractions of sample SC-2 than in the residual clay probably was brought about by the physical processes of erosion, transportation, and deposition. Orthoclase and the trace amounts of heavy minerals in sample SC-2, although not identified in the residual clay, may have been derived from incompletely weathered granodiorite.

Although both the detrital brown plastic clay (sample SC-1) and the residual clay contain qualitatively the same kaolin minerals (halloysite, endellite, and fireclay mineral), they differ in that (1) quartz and muscovite are sparse in the plastic brown clay, but abundant in the residual clay, (2) kaolin minerals are more abundant in the plastic brown clay, and (3) cordierite and tremolite, which are present in the plastic brown clay, seemingly are absent in the residual clay. SC-1 contains more hydrogen and less silicon, calcium, and potassium than does the residual clay. Sample SC-1 and the residual clay contrast rather markedly in physical properties: more than 66 percent of the residual clay is composed of particles which are greater than 43  $\mu$  (325-mesh) in diameter and only 1.35 percent are less than 1  $\mu$  in diameter, whereas  $55$  percent of sample  $SC-1$  is composed of particles less than  $1 \mu$  in diameter and only 0.72 percent is particles greater than  $43 \mu$ .

The differences between SC-1 and the residual clay probably arose during sedimentation. In SC-1 the fineness of grain, the well-oriented kaolins, and the small, well-oriented muscovite flakes, indicate that this material is the fine fraction winnowed from a source rock similar to the residual clav. The relative decrease in amount of silicon and the corresponding increase in hydrogen and aluminum in SC-1 are a result of increase in the clay content and decrease in quartz content of the source material as it underwent winnowing. The presence of extremely small quantities of tridymite and cordierite may mean some volcanic activity during the time of accumulation of this clay.

Sample AD-1 is anomalous because of its mineral composition. About 70 percent of the sample is microscopically isotropic material from which crystals of kaolinite-like vermicular fireclay mineral have grown. Allophane constitutes approximately **17** percent of the sample, and its (allophane)  $\text{SiO}_2: \text{Al}_2\text{O}_3$  ratio is very low (Table 4). The remaining portion of the kaolin minerals in sample AD-1 is a mixture of endellite and halloysite in an approximate ratio of 55 : 45. Endellite is concentrated in the fine fraction. Sample AD-1, although mineralogically different from SC-1, has a similar cationic composition. This similarity is inferred to be due to similarity in chemical environments (ions present) during formation (not necessarily place of deposition) of the two types.

The grains of non-clay minerals, tridymite and sanidine, and fragments of volcanic glass, which " float " in the extremely fine-grained, isotropic matrix of sample AD-I, as well as occurrence of this clay in thin, white, uniform seams, attest to a volcanic origin for the clay. Because the thin, uniform seams of this type clay are interbedded with the sedimentary clay it is inferred that volcanic ash fell in a lake normally receiving sediments from a granitic terrain. Inasmuch as the sedimentary clays which contain the thin seams of ash-derived clay show little, if any, evidence of postdepositional alteration, the ash must have altered to allophane and kaolin minerals prior to burial.

### SUMMARY

Fire clay deposits in the Latah formation of Idaho are composed of kaolin minerals which were formed in several ways: some were formed as residual minerals during the weathering of feldspathic rocks; some were secondarily transported and deposited in fresh water lakes; and minor amounts originated from hydrolysis of volcanic ash in fresh water lakes. It is interpreted that endellite was formed by surface weathering and in fresh water lakes. We conclude that geologic conditions under which endellite can form are not uncommon, and endellite is expected to have formed in more occurrences and in greater abundance than the scanty references to it in geologic literature would indicate. Because endellite is irreversibly dehydrated to halloysite, both under geologic conditions and under conditions of sampling if it is not kept wet, it seems probable that the scantiness of records of endellite is due to lack of protection against dehydration after formation rather than to scantiness in origin. Endellite may well be a very common weathering product.

Association of large vermicular crystals of fireclay mineral with finegrained halloysite, endellite, and allophane not only indicates that the vermicular crystals "grew" from the associated minerals but seems to constitute evidence that the reactions allophane  $\rightarrow$  endellite  $\rightarrow$  halloysite- $\rightarrow$ poorly crystallized kaolinite took place.

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