

HALLOYSITE FORMED IN A CALCAREOUS HOT SPRING ENVIRONMENT

by

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ABSTRACT

An unusual halloysite deposit occurs on the west side of the Lake Mountains in Utah County, Utah. A field and laboratory study was made of this Fox deposit to determine the paragenesis of the clay minerals, especially halloysite. Successive lenses of unaltered tuff, partially altered tuff, clay and travertine beds, indicate that the clays have resulted from alteration of siliceous volcanic tuffs in a Tertiary (?) calcareous hot spring environment. Clay minerals identified were montmorillonite, kaolinite, halloysite·4H₂O (endellite) and halloysite·2H₂O. Montmorillonite, which developed in a zone of less intensive silica leaching farthest from the hot spring vents, is the predominant clay mineral. Irregularly distributed pockets of halloysite and kaolinite developed nearest the hot spring vents in a high-calcium environment. In the clay, or associated with it, are calcite as travertine, quartz as rounded carbonate-corroded grains, feldspar, tridymite, biotite and glass.

Experiments that approximate the chemical environment prevalent in the halloysite alteration zone were conducted on phase relations in part of the system lime–alumina–silica–water. Results suggest the formation of halloysite·4H₂O in this kinetic system from intermediate calcium aluminate or calcium silicate hydrates with halloysite-type structures, or both.

INTRODUCTION

The objective of this study was to determine the genesis of a Utah halloysite deposit which is unusual in several respects. The porous texture of the clay, modified by varicolored diffusion banding and by bedding, is unusual; also its close association with travertine seems anomalous.

The Fox clay deposit, property of the C. D. Fox family since 1889, is located in sections 20 and 29, T. 7S., R. 1 W., S.L.B.M., about 40 miles southwest of Salt Lake City in the foothills of the Lake Mountains (Fig. 1).

Rock units exposed in the immediate area of the deposit include Paleozoic rocks of the Lake Mountains proper, which are folded into a broad syncline with an axis that trends northwest and intersects the range at an angle. The structure is described by Bullock (1951); he considers the clay and associated travertine to be Tertiary (?) in age and a part of the Salt Lake formation. Approximately 400 ft of the formation is exposed in the vicinity of the deposit. The clay ranges in occurrence from coatings on travertine to 15 ft

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beds. Lake sediments, alluvium, and a basalt flow are included by Bullock in the Quaternary system.

The sedimentary rocks of the Salt Lake formation overlie one another conformably. Dips of the travertine-clay contacts indicate that the present topographic highs were originally basinlike areas between the then-active hot springs (Fig. 2).

Although halloysite is the principal clay mineral in the main pit, it is of no value as catalytic material owing to included iron and manganese oxides.

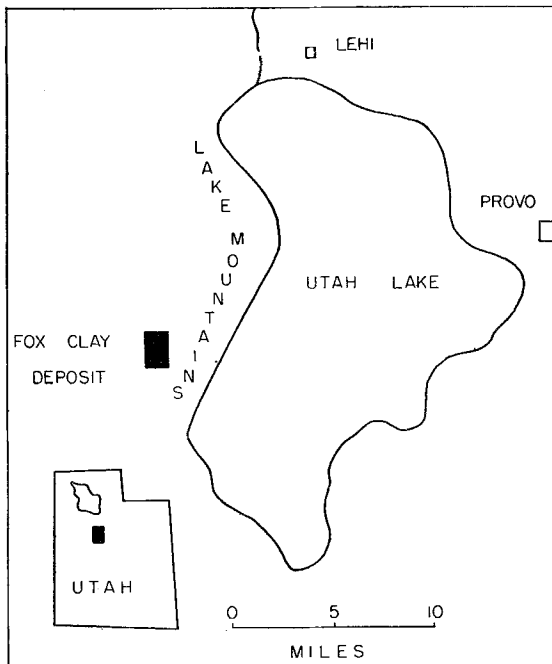


FIGURE 1.—Index map showing location of Fox clay deposit, Utah County, Utah.

Halloysite also renders impractical the use of the clay in refractories because of its high unidirectional shrinkage. Expensive prefiring and regrinding would be necessary before the clay could be used as a refractory material. Selective mining also would be necessary to avoid a high montmorillonite content.

Interbedded clay and travertine crop out over an area of about one square mile. Allsman (1941) estimated clay reserves of the Fox deposit to be 3,000,000 tons.

Crawford and Buranek (1948) reported total production to 1948 of clay from the Fox deposit to be about 30,000 tons. The clay was used chiefly in the manufacture of brick, ceramic pipe and paper.

PREVIOUS THEORIES OF GENESIS

Several references to the mineralogy of the Fox clay are found in the literature. Allsman (1941) reported that the Fox clay beds were composed of kaolin intermixed with fine quartz grains. The iron-stained condition of the clay bed as exposed in the main pit was described. Chemical analyses of the clay from the main pit also were given.

Crawford and Buranek (1948) refer to the Fox Clay as consisting essentially of halloysite intermixed with finely divided quartz grains. They considered

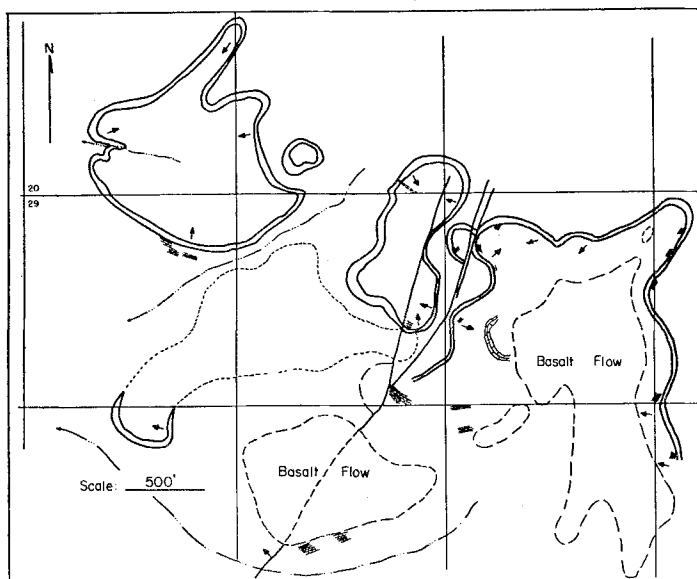


FIGURE 2.—Map of outcrop of main clay bed in Fox deposit. Dips were taken on the travertine-clay contacts. Limestone symbol shows travertine outcrops.

the Fox clay deposit to have resulted from the alteration of pyroclastics by calcium bicarbonate-charged ground waters. They pointed out that the deposit lies in an old drainage channel from the nearby Lake Mountains, and that travertine overlies much of the deposit. They believed that bicarbonate-charged ground waters could have effectively leached varying amounts of silica from the volcanic ash, and left a material relatively rich in kaolin, halloysite, and similar claylike silicates, and some free quartz.

Stringham and Sharp (1950) first pointed out the water-laid character of the quartz sand lenses within the exposed clay beds. They reported the Fox clay as occurring between two sedimentary limestone beds and lensing out within the area that they studied. They stated that since the clay contains clastic quartz grains, and as no evidence of volcanic ash was observed, the Fox clay deposit must be sedimentary in origin. The original material,

according to Stringham and Sharp, weathered to halloysite·4H₂O (endellite), was transported along with some quartz to its present site, with dehydration to halloysite·2H₂O occurring during transportation.

Bullock (1951) regarded the Fox clay as a hydrothermally altered tuff bed of the Salt Lake formation. He recognized that the pyroclastics were water-laid and that the travertine was deposited from the same thermal waters, and he reported that halloysite·4H₂O was present in certain horizons in the clay deposit.

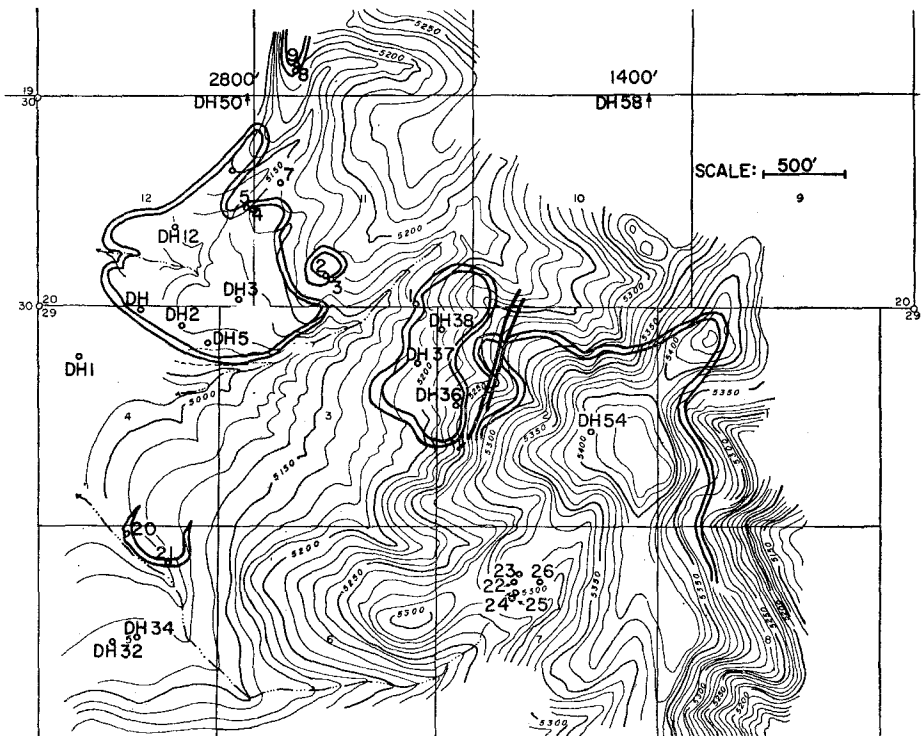


FIGURE 3.—Sample locations and drill holes in the Fox deposit. Samples 10 through 19 were taken on clays that crop out as far as 2000 ft north of the area shown in this map. Contour interval = 10 ft.

METHODS OF INVESTIGATION

Surface samples of the clay and travertine were taken, and core samples were furnished as indicated in Fig. 3. In addition to analysis of the moist samples, the clay samples were solvated in ethylene glycol vapor to characterize montmorillonite at 17 Å, and analyzed by x-ray diffraction. Electron micrographs were made of certain clay samples to help distinguish between

halloysite and kaolinite. Grain mounts were made of the plus 200-mesh fraction of each clay sample and were examined optically. Thin sections of selected clay samples, and of the travertine directly overlying them, also were examined.

RESULTS

x-Ray diffraction analysis shows that the predominant clay mineral of this deposit is montmorillonite with relatively small pockets of mixed halloysite and kaolinite. Figure 4 is an electron micrograph of an halloysite-kaolinite-montmorillonite mixture from drill hole 12. Note the lathlike morphology of the well-crystallized montmorillonite. The halloysite shows the typical tubular morphology, and the kaolinite, hexagonal plates.

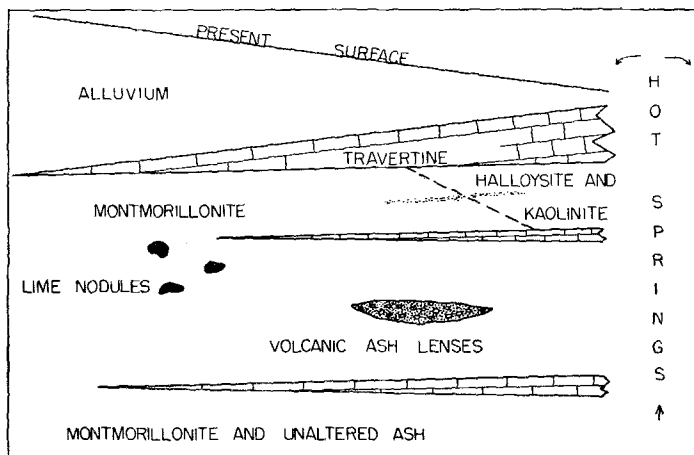


FIGURE 5.—Diagrammatic cross section of the Fox deposit, showing spatial distribution of clay minerals and other lithologic units, and their relation to the hot springs.

All the halloysite examined, including all moist surface samples, was found to be halloysite·2H₂O with the one exception of the bottom sample (30 ft depth) of core 36 which contained halloysite·4H₂O. The other 19 cores either contained no halloysite·4H₂O when taken, or had dehydrated to halloysite·2H₂O owing to improper sealing of the glass jars. As a consequence, the depth above which surface dehydration occurred could not be determined. These cores were seemingly a random selection from various drill holes, but they show that the clay is not a single continuous bed throughout the deposit.

A diagrammatic section across the deposit (Fig. 5), as inferred from the cores, shows alternating lenses and beds of clay and travertine, relatively unaltered volcanic tuff, clay with calcite nodules and stringers, and lenses of rounded to angular sand grains consisting predominantly of quartz. Tridymite was identified in the relatively unaltered tuff.

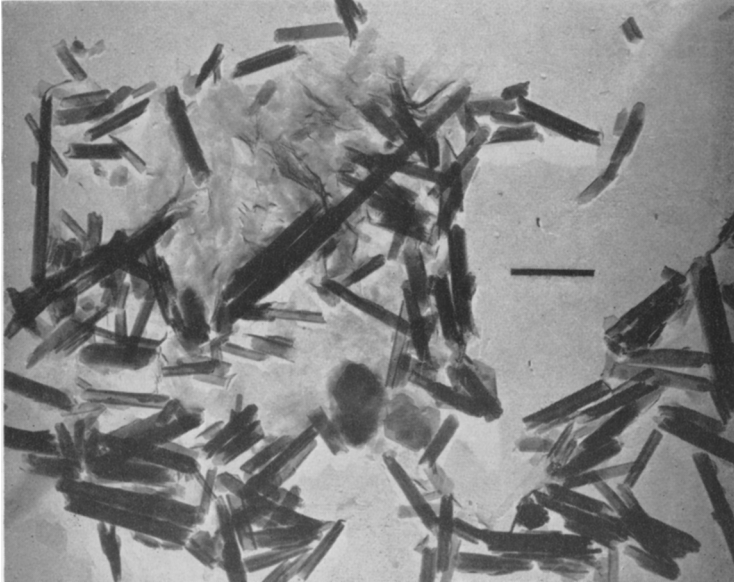


FIGURE 4.—Electron micrograph by J. J. Comer of a halloysite-kaolinite-montmorillonite mixture from drill hole 12. Note lathlike habit of the well-crystallized montmorillonite. The black line is 1 micron.

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FIGURE 6.—Photomicrograph of travertine immediately overlying clay from the Fox deposit. Glass, potash and calcic feldspars, and quartz fragments are found in the travertine. Note the peripheral carbonate corrosion of certain grains. Cross nicols. The black fragments are glass.

A thin section of travertine immediately overlying clay (Fig. 6) showed that the rapidly deposited travertine partially preserved the original volcanic tuff. The tuff included in the travertine is predominantly glass, with quartz and calcic feldspars. Note the peripheral carbonate replacement of some of the grains. The mineralogy of this preserved tuff is the same as that of the relatively unaltered volcanic tuff found in the cores.

The plus 200-mesh fractions, comprising 5–20 percent of the whole sample, are composed chiefly of angular to well-rounded quartz grains that range from 0.1 to 0.5 mm in major dimension. An occasional euhedral plagioclase fragment also was noted.

DISCUSSION

Figure 5 shows diagrammatically the spatial relationships of the clay minerals and associated lithologic units. A close relationship between Tertiary hot spring activity and the alteration of the tuff to clay minerals was noted. The same hot spring waters were responsible for a partial sorting of the parent tuff, along with some carbonate corrosion of the quartz, to give the residual clay its bedded character.

To form the halloysite–kaolinite mixture, which has a 2 : 1 silica to alumina ratio compared to about a 4 : 1 ratio for the montmorillonite, more silica and alkalis were removed from the siliceous pyroclastics. A basic chemical environment facilitates the removal and transportation of silica; hence, a higher pH condition most probably prevailed where the halloysite and kaolinite are situated.

According to White (1955), the pH of travertine-depositing thermal waters ranges from 6 to 7.5 at the spring vents, and as the water flows down the discharge apron, the pH rises owing to loss of CO_2 to the atmosphere. Thus, the bicarbonate is converted to carbonate, following the equilibrium reaction $\text{Ca}(\text{HCO}_3)_2 \rightleftharpoons \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$; the carbonate then combines with available calcium and precipitates as travertine. After the precipitation of CaCO_3 , the hot waters return to near-neutral in pH, as the solubility of CaCO_3 in low- CO_2 hot water is practically nil. The highest pH of the spring water is attained after a substantial amount of the CO_2 in solution is lost and before too much of the calcium has been removed from solution as CaCO_3 . Such a condition would prevail in a limited area immediately surrounding the hot spring vent. Halloysite and kaolinite are localized in this zone.

Three conditions should be considered in proposing a possible mechanism for the formation of halloysite in this deposit: (1) halloysite has not been synthesized in the equilibrium system alumina–silica–water (Roy and Osborn, 1954); (2) halloysite is observed in this deposit and others to form in a lime environment; and (3) a kinetic, rather than an equilibrium, process resulted in the formation of the Fox clay. Other halloysite deposits also are formed in kinetic systems, requiring the addition or removal, or both, of components other than those which compose halloysite. The Dragon deposit, a hydro-

thermal replacement of limestone, and the North Carolina residual deposits, formed by weathering of feldspar, are well known examples.

Experiments to determine the mechanism involved in halloysite formation were conducted in the laboratory in the system lime–alumina–acid–water at 80°C, conditions that approximate the environment of the halloysite zone. Calcium aluminate hydrates were found to be unstable phases in the above system. A phase of the composition $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{hydrate}$ was produced at a pH of 8–10 that had the halloysite· $4\text{H}_2\text{O}$ type structure; i.e., a layered lattice with a basal spacing of about 10 Å that collapses on dehydration. A kaolinite type phase was produced at higher pH.

The formation of a halloysite-type structure also was accomplished with lithium, another cation that can enter octahedral coordination, to give a compound $\text{Li}_2\text{O}\cdot 9\text{Al}_2\text{O}_3\cdot\text{hydrate}$. A paper briefly describing the experimental results has been presented elsewhere (Sand and Ames, 1956).

Calcium silicate hydrates also should be considered as possible intermediate phases, Grudemo (1955) has observed a kaolinite analogue as an intermediate unstable phase, or minor constituent in the preparation of tobermorite (CSHI and CSIII). Grudemo (1952) also has reported the claylike morphology of CSH(B) and C_2SH_2 . Taylor and Howison (1956) have described the relationships between the structures of clay minerals and tobermorite.

The formation of intermediate calcium aluminate or calcium silicate hydrates, or both, with halloysite-type structures is considered by the authors as a possible mechanism for the formation of halloysite· $4\text{H}_2\text{O}$. Because the calcium aluminate hydrates are unstable when exposed to atmospheric conditions, they could be present during the kinetic alteration process only as intermediate “boundary phases” between the volcanic glass and halloysite· $4\text{H}_2\text{O}$. It is believed by Taylor (personal communication) that both the calcium and aluminum are in octahedral coordination in the compound $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot n\text{H}_2\text{O}$; a detailed structural analysis by his group is in progress. Considering that the aluminum is in octahedral coordination, the introduction of silicon in tetrahedral coordination and subsequent removal of calcium could yield a halloysite, with the calcium aluminate hydrate functioning as an intermediate host structure. Much experimental work remains to be done, however, before the possible role of calcium aluminate and calcium silicate hydrates in halloysite genesis can be fully evaluated.

To summarize the genesis of the Fox deposit: a series of tuffs were deposited in Tertiary hot springs, which locally sorted the tuffs, and eventually altered them predominantly to montmorillonite, with pockets of halloysite and kaolinite developed near the hot spring vents. The field observations and laboratory experiments indicate that halloysite is a product of a non-equilibrium process involving more components than those making up its composition.

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