CLAY MINERAL FORMATION IN MUD POTS, YELLOWSTONE PARK, WYOMING

by

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ABSTRAOT

KAOLINITIC, montmorillonitic, illitic, and mixed.layer clay minerals are found in mud springs and mud pots of Yellowstone Park. A sequence of alteration is proposed as Phase I, alteration of bedrock and sediments by hot spring waters to produce three·layer clay minerals (including mixed layer species) and kaolinite-group minerals; Phase II, further alteration to produce a mud composed predominantly of kaolinite and some form of silica.

INTRODUCTION

General Statement

ARGILLIC alteration is a common phenomenon associated with many hydrothermal deposits. Although the surface alteration environment in Yellowstone National Park may not duplicate a deeper environment exactly, this area is one place where clay mineral alteration can be studied extensively in a natural high-acid hydrothermal environment. A long-range study of mineral association in mud springs in the Park and laboratory studies of material collected in the Park certainly should lead to a better understanding of mineral genesis and equilibrium in the low-pH-Iow-temperature hydrothermal environment.

Acknowledgments

The National Park Service permitted the author to collect material for study in the summers of 1960 and 1961, and Park Rangers provided historical data about mud pot activity not available from the literature and made valuable suggestions about routes to several of the more inaccessible sampling locations. Dr. H. H. Murray, Georgia Kaolin Company, provided electron micrographs of the clay size material used in the study.

Previous Geologic Studies in Yellowstone Park

Early geologic investigations in Yellowstone Park area are reported by Hayden (1872; 1873; 1883), Hague, Weed, and Iddings (1896), and Hague

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et al. (1899), and in the monographic work of Allen and Day (1935). More recent reports by Dorf (1960), Boyd (1961), and Brown (1961) have furnished paleobotanic, petrologic, and stratigraphic data. Fenner (1934; 1936) investigated hydrothermal alteration of rhyolite, and many authors have included Yellowstone Park material in more general studies. For example, White (1955, pp. 108-9), in a report of thermal springs and epithermal ore deposits, restudied the bore-hole material described by Fenner (1936). The interested reader is referred to these papers and the references therein.

FIELD AND LABORATORY PROCEDURE

Field Collecting

The areas sampled were chosen primarily on the basis of descriptions given by Allen and Day (1935) and on advice from Yellowstone Park personnel. The descriptions of the collecting sites are given in the appendix. The mud was removed from springs in a 1000-ml stainless steel beaker attached to a 15-ft jointed bamboo pole. An attempt was made to obtain the samples of mud at about a foot below the surface of the spring. Rapid insertion of the beaker to about a foot below the surface and "swishing" the beaker in a circular pattern at this depth probably collected material from this depth predominantly. Thirty-six mud springs, paint pots, and mud volcanoes were sampled and twenty-seven samples contained enough clay minerals to be included in this report. The samples were stored in sealed polyethylene containers.

Temperature Measurements

The temperature of the mud was determined by a conventional laboratory mercury thermometer. At most sample locations it was possible to hang the thermometer in the spring for 3 min at a foot below the surface, and the temperature was read immediately after removing the thermometer. The temperature of the mud just after its removal from the spring was also determined. At no sample location was the reading of the temperature of mud in the spring and in the beaker different by more than 2°C. At a few locations, the temperature of the mud in the spring could not be safely determined, and thus the temperature of the mud in the beaker was the only reading made.

pH Measurement

pH measurements were made with a Beckman Model G Meter by using large electrodes and at a temperature range between 25° and 30°C. Many factors influence the relation of the pH determinations made and the actual pH of the mud in the natural sites. Natural gases begin to escape from the mud in the sampling container as soon as the sample is removed from the mud pot; ideally the electrodes should be placed in the mud pot but safety factors and lack of suitable hardware prevented this operation. The amount and character of the fluids in the mud may affect the pH, and the viscosity of the mud may vary during the year. During wet intervals the mud slurry may be thin and during the dry intervals the mud slurry may be very stiff. The pH readings reported here are gross and are included only to indicate the data obtained by the methods described.

Laboratory Preparation

General.-The polyethylene containers were opened, a split was removed, and the vessels were resealed. The splits were filtered, and the water and solids were analyzed separately. The solids were fractionated at the 2-micron size by sedimentation in water.

 $X-ray$. Standard X-ray procedure using General Electric XRD-5 instrumentation (CuK α radiation) was followed. Powder analyses of the coarse and fine fractions of each sample were made, and part of the less-than-2 micron fraction was prepared as oriented aggregates on glass slides for study of untreated, glycolated, heated (200°C, 400°C, and 450°C), and potassiumand magnesium-saturated material. The quantitative estimation of clay mineral abundance in the less than 2-micron size was made by the general methods described by Schulz (1953) and Shover (1964). A part of each sample (as collected) was sealed in polyethylene containers; the clay mineral composition of these materials was studied in the fall of 1964 to determine what, if any, change might occur over a 3-year period.

Chemical.-Chemical analyses of water and solids were made by using conventional wet chemical techniques described by Hillebrand *et al. (1953)* and Shapiro and Brannock (1956). The spectrographic data were obtained by optical emission techniques developed in the Geochemistry Section of the Indiana State Geological Survey.

Petrographic.-A petrographic microscope was used to study grains from the coarse fraction. Thorough alteration of feldspars, mafic minerals, and amorphous material interfered with detailed examination; quartz and cristobalite grains were not so altered.

Electron microscope.—Electron micrographs of the clay fraction from each sample were provided by H. H. Murray, Georgia Kaolin Company. Magnification of the photographs studied is 17,000 and 34,000 times actual size.

ANALYTICAL RESULTS

Temperature and pH Data

The temperature and pH data obtained in July 1961 are given in Table l. Temperature readings made by Park Rangers at West Thumb in June and July 1960 and 1961 are given in Table 2, and these data are considered as reliable as the author's data. In the summer of 1961 the author made temperature measurements with the rangers on three separate occasions, and a variation in temperature of less than 1°C was noted. For details concerning location and other data of collecting areas consult the Appendix.

TABLE 1.-TEMPERATURE AND PH DATA OF SAMPLES COLLECTED IN JULY 1961

Chemical Data

Chemical analyses by conventional wet-chemical methods were made from the solids from every sample used in this study, and the results of these analyses of selected samples are given in Table 3; spectrographic data are given in Table 4. The data presented in Table 3 were determined on a dried (at 110^oC) basis and $H_2O(-)$ was not included in the summations and calculations. The totals listed were derived by excluding from the L.O.I. value the amount of volatile components (S, H_2SO_4, CO_2) determined. The remainder of the L.O.I. value was assumed to be water of crystallization and other volatiles not determined, and this remainder was used in the summation.

Mineral Data

Nonclay minerals.-Both quartz and cristobalite are present in many samples, and one or the other is abundant in all samples included in this study. Generally, the feldspars have been altered very thoroughly, and they

Date	$7-9-60$	$7 - 16 - 60$	$7-23-60$	$7 - 30 - 60$	$8 - 6 - 60$
Temperature $(^{\circ}C)$	93	93	93	93	93
Date	$8 - 13 - 60$	$8-20-60$	8-27-60	$6-24-61$	7-1-61
Temperature (°C)	92	93	92	86	92

TABLE 2.-TEMPERATURE MEASUREMENTS MADE BY PARK RANGERS OF THE MAIN MUD POT AT THUMB

produce poor X-ray data. X-amorphous material, predominantly rhyolite, is rare to moderately abundant, and various other minerals are present in varying amounts in most samples. For example, one sample studied but not included in this report gave diffraction data which indicated that rutile and cristobalite were the only crystalline phases in the sample. The inability to identify certainly the X-amorphous and thoroughly altered non-clay mineral is unfortunate indeed. The chemical data from the entire samples are compatible generally with the bulk mineral composition. The abundance of K_2O in some samples, particularly in the Mud Volcano area, is not understood. For example, the K_2O abundance in the solids of Mud Geyser would be more easily explained if illite and/or mixed-layered material were present in the clay-size fraction. X-ray data from the bulk sample of Mud Geyser do not indicate clearly presence ofK-bearing minerals and very careful petrographic study of the material does not permit certain identification of K-bearing constituents like K-feldspar, zeolites, glass, or amorphous material.

Montmorillonite group.-Minerals of the montmorillonite group dominate the clay suite in several samples (Table 5) and are most abundant in the springs and mud pots of the Mud Volcano area. The detailed nature of the montmorillonite species is not well known, but X-ray data for 060 indicate a dioctahedral coordination for all clay minerals studied (except possibly two samples from the Turbid Lake area), and chemical data from bulk samples suggest that the montmorillonite is typical fluffy masses of small crystals. No recognized difference was seen in the montmorillonite in samples collected in 1961 and the same sample stored as collected and studied in 1964. It is important to note here that general clay mineral-acid solubility data indicate that montmorillonitic clays should be altered in H_2SO_4 , but the acid in the stored samples is not concentrated enough to have caused recognizable changes from 1961 to 1964.

Illite group.-Minerals of the illite group are identified clearly only in three samples (Table 5). The variety of the illite species is not known; X -ray data indicate a polymorphic form between 1 M and 1 Md and probably dioctahedral coordination. The electron micrographs show that the illite is in the form of thin laths averaging about 1 micron in length and having a length: width ratio of about 3: 1. Crystal outlines are somewhat irregular. The abundance

LOI = loss on ignition, (1050°C) ; N.D. = none detected. Analyses by M. E. Coller.

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TABLE 3.-CHEMICAL ANALYSES OF MUD FROM YELLOWSTONE PARK TABLE 3.-CHEMICAL ANALYSES OF MUD FROM YELLOWSTONE PARK

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TABLE 4.-SPEOTROGRAPHIC DATA OF MUD FROM YELLOWSTONE PARK

TABLE 4. -SPECTROGRAPHIC DATA OF MUD FROM YELLOWSTONE PARK

TABLE 5.-QUANTITATIVE ESTIMATION OF CLAY MINERAL ABUNDANCE AS PARTS IN 10 OF TOTAL CLAY MINERAL COMPOSITION

M, montmorillonite group; I, illite group; K, kaolinite group; Mx, mixed layer group. The numbers listed under "Clay Abundance" indicate to thc nearest 10% the amount of < 2 micron-size material in the entire sample estimated by hydrometer readings.

of illite in the Turbid Lake samples decreased about 0.5 parts in 10 of the clay mineral suite from 1961 to 1964, and there was a comparable increase in mixed-layer clays. A decrease in illite abundance was not seen in Thumb 5 in this same time.

Kaolinite group.-Minerals of the kaolinite group are found in every sample (Table 5). The crystallinity index, as defined by Hinckley (1963), of the kaolinite in the ten samples containing kaolinite as the only clay mineral ranges between 0.85 and 1.1; this indicates a moderate to high degree of crystal perfection. The kaolinite crystals have sharp hexagonal boundaries and range in size from about 0.25 microns to about 2 microns. In Fountain Paint Pot 1 and 2, a weak peak at 3.43 Å between peaks at 3.57 Å and 3.37 Å indicates that dickite or nacrite may be present in small amounts.

A few crystals showing the typical tubular morphology of halloysite appear

in electron micrographs of Mud Volcano samples, but the abundance is so low that halloysite X -ray characteristics are masked. Diffraction characteristics for halloysite are somewhat evident in material from the Black Dragon and Black Pit, but the tubular morphology cannot be seen on electron micrographs of these materials. Kaolinite, montmorillonite, and mixed-layer crystals are identified easily in the electron micrographs, and the certain presence of halloysite cannot be demonstrated at this time. The potassium acetate treatment described by Wada (1961) and modified by Miller and Keller (1963) did not produce conclusive results; the data indicated that a modest amount of halloysite-kaolinite intergrade may be present. No difference was seen in the kaolinite group of minerals between the study in 1961 and 1964.

Mixed-layer group.—Random mixed-layered clay minerals are present in lesser amounts in a number of samples (Table 5). In every sample, one of the interlayer species is expanded with glycol treatment and rendered nonexpandable after K^+ saturation; also, the mixed-layer material collapsed to 10 A after heat treatment. These data indicate that the interlayering probably involves illite and montmorillonite. The electron micrographs of samples containing mixed-layer show thin, thoroughly corroded, lath-shaped crystals typical of the illite described above. The abundance of random mixed-layered minerals increased very modestly (less than 1 part in 10 of the total clay mineral composition) between 1961 and 1964. In one sample, Sylvan Springs 2, a mixed-layer mineral with a strong tendency toward regular interlayering is present. A shoulder at about 24.5 Å $(3.6^{\circ} 2\theta,$ copper radiation) appears from an oriented aggregate; the 002 peak is masked by the 001 peak of montmorillonite. The high-spacing shoulder moves to about 27.7 Å $(3.3^{\circ} 2\theta,$ copper radiation) upon glycolation, and at 13.6\AA an 002 peak is very evident. After glycolation a broad, moderately intense peak appears between 10.3 A and 8.9\AA , the 003 of the "regular" interlayer and 0.02 of glycolated montmorillonite. The peak for 005 of the regular interlayer is clearly distinct from the 003 of glycolated montmorillonite. After heating to 450° C the montmorillonite and the mixed-layer mineral are 10 A. Even though the data are poor the tendency toward regular interlayering is clear, and the intergrades are illite-like and montmorillonite-like. The "regular" mixed-layer mineral remained unchanged when the material was studied in 1964.

DISCUSSION

General

The superficial material in the areas sampled generally is either one or some combination of the following: stream, glacial, glaciofluvial, glaciolacustrine, and hot spring deposits. These Quaternary deposits are composed of fragments from various rhyolite flows, tuffs, and plugs, and in the Turbid Lake and Sedge Creek area, andesite fragments may be found sparingly in rhyolitic detritus. There is very little possibility of discovering what rock

types are crossed by the complicated plumbing that feeds mud springs and paint pots, nor is it possible to determine how much mud is derived from the immediate surficial material and how much mud is transported from some distance by the plumbing system.

Fenner (1936) and White (1955) pointed out in studying material obtained from boreholes in Yellowstone Park that kaolinite is present in the nearsurface, acid alteration zone and that montmorillonitic clay is present in the deep alteration zone. Commonly the mud pots have little or no discharge as surface water, and it is questionable whether much, if any, solid material is being transported to the surface from the deeper alteration zones.

The uncertainty in attempting to determine the actual source of minerals in the mud may invalidate many aspects of conclusions reached in this and similar studies. At the present time, the author feels that the predominantly rhyolitic character of the bedrock and sediments in the area studied makes it possible to assume that alteration of this rock type is producing most of the mud studied.

Sequence of Formation of Olay Minerals in Mud Pots

It may be premature to detail a sequence of alteration and mud pot development, but several general conclusions can be made from this study. Water, mud, and suitable plumbing are required to form mud springs, mud pots, and mud volcanoes. The factors influencing these prerequisites govern the formation of the type of feature (such as mud spring or mud pot) and its future development. Plumbing modifications may increase or decrease the water supply, and eliminating the water supply may decrease drastically further alteration in the rocks of the surface zone above the water table. An ideal sequence may be outlined as follows:

Phase I.-The initial stage begins with the alteration of the surficial bedrock and sediments by hot spring waters. The alteration products are crystalline and amorphous material and various ions in solution; three-layer clay minerals and kaolinite-group minerals are formed from pre-existing silicates and might be precipitated directly from solution. If material is transported to the surface from deeper alteration zones, these materials will undergo the same kind of changes occurring to the surficial material.

The two pots in the Turbid Lake area appear to be in the early stage of Phase I development. The Black Dragon, Black Pit, Mud Volcano, and mud pots in the Mud Volcano area are in an intermediate stage of development in Phase 1. Sample Thumb 5 clearly is in an early to intermediate stage in Phase 1. Sylvan Spring 1, 2, 3, and 7, Sulfur Caldron, Mud Geyser, Thumb 3, and Sedge Creek pots fall into the late stage of Phase I.

Careful study of all the descriptions available from very early reports to the present and discussions with Park personnel indicate that many of the above listed areas are considered to be the youngest, that is, most recent, mud pot areas of the Park. In 1960 the Chief Park Naturalist, Mr. Robert

N. McIntyre, recommended that I include the Sylvan Springs area in the study because strong mud pot activity began there after the 1959 earthquake occurred in the Park region. The park rangers at West Thumb indicated in 1961 that the two samples, Thumb 3 and 5, are from "new" mud springs formed after the 1959 earthquake. The Black Dragon and Black Pit in the Mud Volcano area formed during the winter of 1947-8 according to McIntyre.

Phase II.—Decreasing water circulation, perhaps produced by plugging the plumbing with alteration products, prevents the upward transportation of material from below the surface zone and further alteration is restricted to the material at the surface and in contact with the hot spring waters. The kaolinite group of clay minerals continue to form in the surface zone from three-layer clay minerals, feldspars, zeolites, and other silicates as Na and K decrease in abundance. Eventually the mud is composed predominantly of kaolinite, some form of silica, and modest amounts of sulfate and other minerals.

Artist Paint Pots, Fountain Paint Pots, Thumb Paint Pots 1, 2, and 4, and Sylvan Springs 8 represent development of Phase II. Allen and Day (1935) provide detailed descriptions and photographs of the pots at Thumb, Fountain, and Artist, and the early reports of Hayden (1872) and Hague *et al.* (1899) provide descriptions that indicate that these pots were well developed at the time of the earlier studies in the Park. The present activity of the Artist Paint Pots is so reduced at present that the identity of these pots would be difficult to make from the earlier descriptions. McIntyre indicated that the activity in this area is nearly dead. The water in the pots appears to be primarily surface run off and the higher pH data support this idea.

CONCLUSIONS

The clay mineral composition of the mud pots studied has been formcd by continual alteration by hot acid waters. The surficial bedrock and unconsolidated materials, and any material transported to the surface from subsurface zones, are altered to form three-layer clay minerals and kaolinitegroup minerals. Kaolinite is the only clay mineral present in the mud pots believed to represent the most advanced stage of alteration. If this hypothesis is correct, the mud pots described as being in Phase I of clay mineral development will eventually contain kaolinite as the only clay mineral present in the muds.

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APPENDIX: LOCATION AND DESCRIPTION OF SAMPLES

The locations of the mud springs and sample collecting sites are given here; for a much more detailed description of the hot spring areas see Allen and Day (1935). The following listings are not equally complete. Well-known springs clearly marked by park signs or clearly discussed by Allen and Day (1935) are not described. The color of the dry mud is given according to the color chart of the National Research Council (1948).

Artist Paint Pots

- l. First paint pot along path into the area; very light gray (N 8).
- 2. Mud pool with sediment completely flocculated along sides; light brown (5YR 6/4).
- 3. Sample of mud from stream of hot water flowing between 1 and 2; pale reddish brown (lOR 5/4).

Sylvan Springs Area

Sylvan Springs are on the west side of Gibbon Meadows; their location is clearly marked on many maps of the park. Allen and Day's (1935) description of the area is not adequate today; for location of the springs sampled see the sketch map (Fig. 1).

FIG. 1. Sketch of sample locations in Sylvan Springs area.

- 1. Mud springs about 17 ft in diameter; small rim about 1 ft high; light gray (N 7).
- 2. Mud pot in pit about 20 ft in diameter and 14 ft deep; mud is stiff, and eruptions splash over 2 ft high; very light gray (N 8).
- 3. Mud pot in shallow crater about 7 ft wide and 15 ft long ; at east end of pit the stiff mud splashes more than 1 ft high, and a steam vent is in the west end of the pit; medium light gray (N 6).
- 7. Mud spring (may be mud volcano at lower water stage) in crater 7 ft in diameter; rim is 3 ft high; mud is thin and splashes continually to about 3 in.; light greenish gray (5GY 8/1).
- 8. Mud volcano in 5- ft-high cone and crater opening about 4 ft in diameter; base of cone is about 10 ft in diameter; medium stiff mud is erupted violontly to more than 2 ft above crater top; medium dark gray (N 5).

Fountain Paint Pots

- 1. Paint pot, south end of pool; pinkish gray (5YR 8/1).
- 2. Paint pot, north end of pool; grayish orange pink (5YR 7/2).
- 3. Paint pot, west side of pool; light brown (5YR 6/4).

Thumb Paint Pots

- 1. Main pot, west side of pool; pinkish gray (5YR 8/1).
- 2. Main pot, just west of center of pool; pale pink (5RP '8/2).
- 3. Small mud spring enclosed by rim 2 to 6 in. high; mud is thin; spring is 20 ft southsouthwest of pool 35 on map in Thumb Ranger Station; yellowish gray (5Y 8/1).

- 4. Main pot, east side of pool; pale red (lOR 6/2).
- 5. Mud springs; very thin mud; 10 ft northwest of pool 21 on map in Thumb Ranger Station; yellowish gray (5Y 7/2).

Mud Volcano Area

Black Dragon. Sample from east center of mud spring; grayish black (N 2).

Black Pit. Sample from center of mud springs; dark gray (N 3).

Mud Geyser. Sample from west side of mud springs; light olive gray (5Y 6/1).

Mud Volcano. Sample from center of pit just under overhang; medium dark gray (N 4). Sulfur Caldron. Sample from east end of pool; yellowish gray (5Y 8/1).

- Mud Pot 1. Mud pot northeast of Sulfur Caldron in crater about 6 ft high, 30 ft in diameter, and 12 ft deep from crater top to mud level; mud is moderately stiff; light olive gray (5Y 6/1).
- Mud Pot 2. Mud pot east of Sulfur Caldron in a crater similar to mud pot 1 above; yellowish gray (5Y 7/2).

Turbid Lake Area

Turbid Lake is about 2 miles northeast of Steamboat Point.

- 1. Small mud spring on the northeast bank side of Bear Creek about 350 ft from the shore of Turbid Lake; light brownish gray (5YR 6/1).
- 2. Mud pot in small crater about 1 ft high, 10 ft in diameter, and 6 ft deep; moderately stiff mud and moderately violent expulsion, several hundred feet northeast of 1; medium gray (N 5).

Sedge Greek Area

Small area southeast of Steamboat Point on terrace on southeast side of Sedge Creek and 1 to 10 ft above the road leading to the main east entrance of the Park. The area is adjacent to and southeast of an unimproved side road leading to a small gravel pit.

- 1. Small mud spring 500 ft north of Cody Road; gentle bubbling; very thin mud; light olive gray $(5Y 6/1)$.
- 2. Small mud spring at about the level of the Cody Road and along the gravel-pit road; thin mud; light brown (5YR 5/6).