

ARGILLIZATION BY DESCENDING ACID AT STEAMBOAT SPRINGS, NEVADA*

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(Received 12 February 1973)

Abstract—Steamboat Springs, Nevada, an area of present-day hot springs, clearly illustrates the genetic dependence of some kaolin deposits on hot-spring activity. Andesite, granodiorite and arkosic sediments are locally altered at the land surface to siliceous residues consisting of primary quartz and anatase, plus opal from primary silicates. These siliceous residues commonly exhibit the textural and structural features of their unaltered equivalents. Beneath the siliceous residues, kaolin and alunite replace primary silicates and fill open spaces, forming a blanketlike deposit. Beneath the kaolin-alunite zone, montmorillonite, commonly accompanied by pyrite, replaces the primary silicates. On the ground surface, the same alteration mineral zones can be traced outward from the siliceous residue; however, hematite rather than pyrite accompanies montmorillonite.

Chemical analysis indicates that sulfuric acid is the active altering agent. The acid forms from hydrogen sulfide that exsolves from deep thermal water, rises above the water table and is oxidized by sulfur-oxidizing bacteria living near the ground surface. This acid dissolves in precipitation or condensed water vapor and percolates downward destroying most of the primary minerals producing a siliceous residue. Coincidence of the water table with the downward transition from siliceous residue to kaolin-alunite signifies decreasing hydrogen metasomatism because of dilution of descending acid by ground water.

In hot-spring areas, beds of siliceous sinter deposited at the surface by hypogene thermal water look, superficially, like areas of surficial acid alteration. Features diagnostic of a surficial alteration are the relict rock structures of a siliceous residue and a kaolin-alunite zone immediately beneath.

INTRODUCTION

Hot spring areas comprise a unique geologic environment between sedimentary and deep hydrothermal conditions and grade into both, thus providing natural laboratories where relationships between these environments can be examined. At Steamboat Springs, Nevada, studies of the deep thermal waters and their reactions with the rocks, spurred by the discovery of precious metals deposited by these waters, have clarified the relation of the hydrothermal ore-deposit environment to hot springs. We now describe the rock-water reactions close to and at the ground surface to permit comparison with those in ordinary weathering environments.

Many investigators have studied the general geology of the Steamboat Springs thermal area. The most recent study (White *et al.*, 1964) should be consulted for large scale maps and details of geology that are summarized here. The area, which lies about 10 miles south of Rena, Nevada, is underlain by basement rocks consisting of a Late Cretaceous granodioritic pluton intruded into metasedimentary and metavolcanic

rocks of probable early Mesozoic age (Fig. 1). Tertiary and Quaternary volcanic and sedimentary rocks lie on an erosion surface that bevels the basement rocks. Deep thermal water has flowed to the surface along fractures for at least 100,000 yr and possibly 1,000,000 yr. Deposition of siliceous sinter on the land surface and alteration of the surrounding rocks have been the principal geologic manifestations of thermal activity.

It is now well established that thermal water rising to the surface in hot springs is almost entirely meteoric water that has circulated to great depths (Craig, 1963; White, 1968, pp. C13-C15). During its deep transit, meteoric water is heated by contact with hot rocks adjacent to a magma chamber as well as, perhaps, by vapors emanating from the magma (Fig. 2).

The density of deep thermal water, which is lower than the colder meteoric water descending on the borders of the geothermal system, provides gravitational energy to drive the thermal water up along permeable zones (usually fractures) to discharge at the surface as hot springs or geysers. A geothermal system is a large convecting hydrologic system. In some systems most of the thermal water is discharged from the area after a single convection cycle to be replaced by new meteoric water, but others discharge only a small

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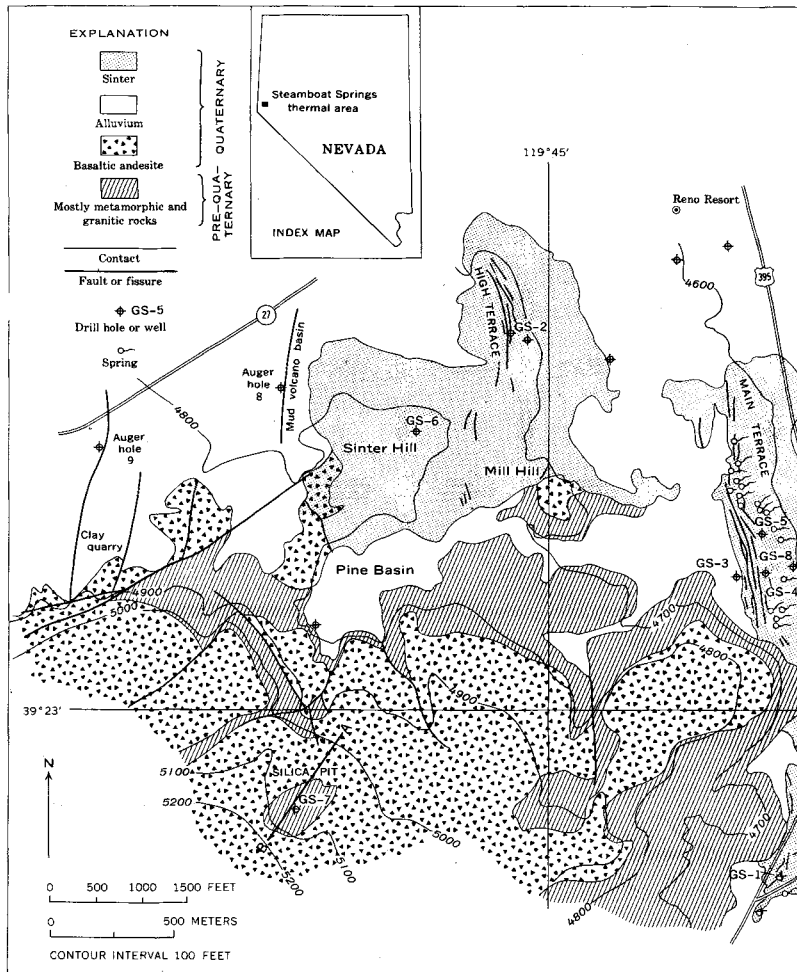


Fig. 1. Generalized geologic map of Steamboat Springs thermal area, Washoe County, Nev. (Modified from plate 1, White *et al.*, 1964).

part of their water during each cycle (White, 1968, pp. C8-C13).

During the flow of water through the rocks, and especially after the water becomes heated, chemical reactions take place between the water and surrounding rocks. The thermal water becomes a mildly acid fluid containing carbon dioxide, hydrogen sulfide, sodium chloride, and other substances in part extracted from the rocks (Ellis and Mahon, 1964; 1967) and, probably, in part contributed by fluid from the magma. Destruction of some minerals and formation of others by reaction of the rock with the rising thermal water is termed 'hypogene alteration'.

Hypogene alteration

Mineralogical studies of drill cores from Steamboat Springs (Sigvaldason and White, 1961, 1962; Schoen

and White, 1965, 1967) provide an understanding of the hypogene alteration that is necessary in order to evaluate the overlying surficial alteration. In summary, the alteration of rocks by thermal water flowing along fractures produces zones of distinct mineral assemblages enveloping these hydraulic conduits. The alteration mineral assemblages vary somewhat depending upon the primary minerals in the rock. In the alteration zone farthest from the thermal-water conduit (zone of least alteration), hornblende alters to montmorillonite or mixed-layer illite-montmorillonite, and iron-rich chlorite; biotite alters pseudomorphically to chlorite; calcic plagioclase alters to montmorillonite or mixed-layer illite-montmorillonite and, at depths greater than 200 ft, to calcite and albite; primary K-feldspar and quartz generally are unaltered. The most intense alteration occurs adjacent to thermal water

conduits where all primary and secondary minerals except quartz are replaced by illite (with less than 10 per cent interlayered montmorillonite), quartz and pyrite. The genesis of these alteration minerals depends principally upon hydrogen metasomatism of the rocks by thermal water (Hemley and Jones, 1964).

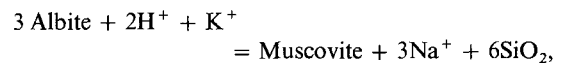
Hydrogen metasomatism consists of an attack on the rock minerals by small, mobile hydrogen ions that take the place of cations such as iron, magnesium, calcium, sodium, potassium, aluminium and silicon. The new minerals formed increase the analytical-water content of a rock because of the increased number of hydrogen ions present.

Hydrothermal K-feldspar and celadonite dominate the alteration mineralogy of the upper 300 ft of the hot spring system in some places at Steamboat Springs (Schoen and White, 1967). This assemblage indicates a process of dominantly potassium metasomatism rather than hydrogen metasomatism. Loss of CO_2 by boiling of the thermal water as pressure decreases near the ground surface, and the consequent pH rise, causes an increase in the potassium ion/hydrogen ion ratio, which results in K-feldspathization (Brown and Ellis, 1970, pp. 123–125).

Potassium metasomatism consists of a replacement of cations in susceptible minerals by potassium ions. The large size of the potassium ion limits its replaceability to ions of similar size or charge; hence, the calcium and sodium in plagioclase are most readily removed during potassium metasomatism. In addition, potassium-deficient minerals such as illite or illite-

montmorillonite may be reconstituted. New, potassium-rich phases, such as celadonite, may form from the small amounts of iron, aluminum and silicon in solution and in altering mafic phases. The water content of potassium-metasomatized rocks is usually much less than that of rocks subjected to hydrogen metasomatism.

At Steamboat Springs the two hypogene metasomatisms discussed above are not entirely exclusive of one another even though the shallow potassium metasomatism took place at a relatively higher pH (low hydrogen-ion activity). Much of the deep, hydrogen-metasomatized rock exhibits a small increase in K_2O as well as a large increase in H_2O with respect to unaltered rock (Sigvaldason and White, 1962), a process illustrated by the reaction:



in which both potassium and hydrogen are incorporated into muscovite. K-feldspathization is not recognized in the deeper levels in contrast to 'sericitization.'

Surficial alteration

Unaltered surface rocks and an absence of deposits of white siliceous sinter characterize many parts of the Steamboat Springs area. Presumably, the deep fractures that localize upward flow of thermal water and vapor are either not present or are too impermeable in

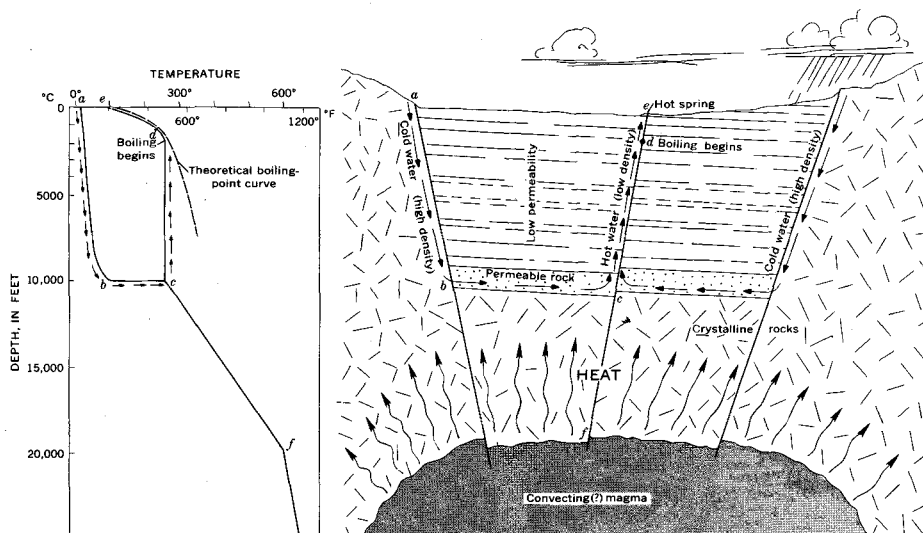
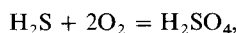


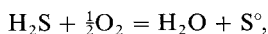
Fig. 2. Simple, high-temperature hot-spring system with deeply circulating meteoric water assumed to be heated entirely by conduction. Graph shows temperatures and depths that are reasonable for one flow path (from White, 1968).

such areas. In other areas at Steamboat Springs, however, although no thermal water discharges at the surface, glaring white rocks crop out. Careful examination shows that these rocks consist of bleached, siliceous residues of normally dark rocks and that they are not deposited beds of siliceous sinter.

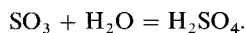
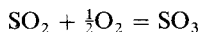
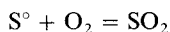
These areas of surficial alteration occur only where the thermal water table is below the land surface. The uniquely aggressive alteration of the rock extends downward only to or slightly below the water table. This means that the altering agent is not hypogene thermal water but rather must be associated more indirectly with the thermal water. Studies at Steamboat Springs and elsewhere prove that the altering agent is strong sulfuric acid, but no sulfur trioxide, or even sulfur dioxide, occurs in the thermal waters. We conclude that the sulfuric acid forms from hydrogen sulfide, dissolved under pressure at depth, that exsolves from the thermal water as pressure decreases upward and rises to the surface into an oxidizing environment. The overall reaction is:



but it may proceed by intermediate reactions such as:



for native sulfur occurs frequently in surficial deposits. Subsequent oxidation reactions may be:



As Ehrlich and Schoen (1967) pointed out, although H_2S oxidizes rapidly to sulfur, further oxidation requires high temperatures, exotic noble-metal catalysts, or both. Studies of soil bacteria in hot-spring areas of surficial alteration show the presence of members of the genus *Thiobacillus* (Kaplan, 1956; Ivanov and Karavaiko, 1967; Zavarzin *et al.*, 1967; Schoen and Ehrlich, 1968; Ivanov *et al.*, 1968) that catalyze the oxidation of H_2S and S° to H_2SO_4 in their life processes. The rate of acid production by these microorganisms appears to be sufficient to account for all of the acid found in these areas (Schoen, 1969).

Thiobacilli produce either SO_3 , which dissolves in water from condensed vapor, rain and snowmelt, or more likely produce H_2SO_4 directly. The H_2SO_4 , diluted by condensing water vapor and other moisture, percolates downward and laterally outward from its site of formation at and near the ground surface, reacting with unstable minerals in the unsaturated zone. At and immediately below the water table, neutralization of the sulfuric acid terminates the aggressive rock alter-

ation found above. The surficial alteration is effected by a descending rather than rising fluid.

In this paper we will describe the detailed mineralogic and chemical changes that occurred in areas of surficial alteration at Steamboat Springs, Nevada. From these data, zones of alteration can be delineated and compared with similar zones recognized in hydrothermal and weathering environments. Finally, we will consider some economic implications.

Definitions

Because our usage of certain mineralogic and geologic terms may not correspond to the usage of others, we define here those most likely to be misinterpreted, together with pertinent criteria.

Clays. The altered rocks frequently contain the clay minerals montmorillonite and kaolinite. Montmorillonite exhibits an X-ray basal spacing at approximately 12 Å in air-dried samples saturated with sodium or potassium and approximately 14 Å in air-dried samples saturated with calcium or magnesium. Both of these varieties of montmorillonite exhibit a 17 Å basal spacing after 12 hr exposure to the vapors of ethylene glycol at 60°C. Kaolinite exhibits an X-ray basal spacing at approximately 7 Å that does not expand when exposed to ethylene glycol unless pretreated with potassium acetate. Heating kaolinite to 550°C for 1 hr destroys its X-ray crystallinity.

We found that kaolinite associated with surficial alteration can be readily subdivided qualitatively on the basis of X-ray crystallinity, which is an indication of structural ordering. X-ray diffractograms of well ordered kaolinite resolve the 11 $\bar{1}$ and 1 $\bar{1}\bar{1}$ doublet at 4.18 and 4.13 Å respectively. This usage of 'well ordered' agrees with Brindley's criteria (1961, p. 62). Moderately ordered kaolinite does not resolve this doublet but does show a few of the stronger (*hkl*) peaks. Poorly ordered kaolinite produces X-ray diffractograms with only a few broad peaks, similar to Fig. 3 of Molloy and Kerr (1961). Our well ordered kaolinite corresponds to type *A* kaolinite of Brindley *et al.* (1963); our moderately ordered to their types *B* and *C*; and our poorly ordered kaolinite to their type *D*.

Brindley *et al.* (1963) found that their type *C* and *D* kaolinites possessed tubular morphology and classed them as so-called 'halloysite'. [In accordance with Deer *et al.* (1962, p. 194) we use the term 'metahalloysite' for the dehydrated form of halloysite with a 7 Å X-ray periodicity.] Although we did not examine the morphology of our clay samples by electron microscopy, we did treat several samples containing abundant poorly ordered kaolinite with potassium acetate according to the technique modified by Miller and Keller (1963). The results show that some of our poorly

ordered kaolinites are pure metahalloysite, some are pure, poorly ordered kaolinite and some are mixtures of both phases. Because of the low sensitivity of the potassium acetate test, we did not treat every poorly ordered kaolinite sample but only those containing abundant kaolín. For the purposes of this study we simply recognize that our poorly ordered kaolinites may be either of the end-member types mentioned or a mixture of the two.

Feldspars. Typical plutonic and volcanic plagioclase exhibits its $20\bar{1}$ X-ray peak at about 4.04 \AA whereas plutonic potash feldspars and relatively pure volcanic and hydrothermal potash feldspars exhibit their $\bar{2}01$ peak at about 4.23 \AA . In one of the volcanic rocks at Steamboat Springs, known informally as the Steamboat basaltic andesite, in addition to normal volcanic plagioclase, two other feldspars occur with X-ray properties intermediate between plagioclases and potash feldspars. The more abundant possesses an X-ray peak at about 4.10 \AA . We believe this reflection to be the $20\bar{1}$ of the plagioclase structure displaced from its usual position at 4.04 \AA by a high potassium content. The normative composition of the Steamboat basaltic andesite includes Or—15 per cent, Ab—34 per cent, An—23 per cent. As no potash feldspar can be identified in thin sections as a distinct mineral, we infer solid solution of potassium in the plagioclase structure of this mineral. We use the term ‘anorthoclase’ to describe this mineral in accordance with use of the word on card 9-478 of the ASTM powder diffraction file describing similar X-ray and compositional characteristics. The mineral potash-oligoclase (Macdonald, 1942) may be similar.

The second unusual feldspar in the Steamboat basaltic andesite occurs in only trace amounts and exhibits an X-ray peak at about 4.17 \AA . We believe this to be the $\bar{2}01$ peak of a potash feldspar displaced from the usual 4.23 \AA spacing by solid solution of sodium and calcium. We refer to this material as ‘sanidine’ in accordance with use of the word on card 13-456, ASTM powder diffraction file describing similar X-ray and compositional characteristics.

Areas of surficial alteration. In the past, areas of surficial alteration associated with hot spring activity have been referred to as a class by many different terms. Our previous reports on Steamboat Springs use the expression ‘acid-altered areas’ (Schoen and Ehrlich, 1968) or simply ‘bleached rocks’ and ‘areas of near-surface acid bleaching’ (White *et al.*, 1964). Allen and Day (1935) used the terms ‘sulfate areas’ and ‘acid tracts’ in their description of similar areas in Yellowstone Park. Some Japanese scientists use the word ‘hell’ for these areas (Murozumi *et al.*, 1966) and in Italy the word ‘manifestazione’ has been used (Stefani,

oral communication, 1968). The word ‘solfatara’ is applied by volcanologists to fumaroles near and above the boiling temperature of water that contain some sulfurous gases (Rittmann, 1962, p. 7). And the term ‘solfatara field’ (Rittmann, 1962, p. 10) more properly describes a group of sulfurous fumaroles and the intervening ground altered by sulfuric acid. The common association of vulcanism with most solfatara fields has not hindered use of the term for phenomena not closely connected with past or present volcanic activity.

Feeble sulfurous fumaroles occur at Steamboat Springs associated with fissures on the active spring terraces, but most of the areas of surficial alteration are nearly at atmospheric temperatures. In a few places a little gas is evolving at relatively low temperatures (generally less than 60°C). The term ‘acid-altered area’ therefore, appears best for Steamboat Springs as it implies dominantly past, rather than present, activity.

DETAILS OF SURFICIAL ALTERATION

Surficial alteration at Steamboat Springs affects all of the rock-types in the thermal area. Even fairly pure deposits of siliceous sinter on the Main Terrace seem to be attacked along fractures by sulfuric acid (White *et al.*, 1964, p. B53 and Figs. 24 and 25). The following descriptions of individual acid-altered areas reveal the mineralogical and chemical similarities and differences in the alteration of basaltic andesite, granodiorite and arkosic sediments.

Silica pit

In the southwest corner of the Steamboat Springs thermal area lies a patch of intensely bleached rocks (Fig. 1). Within this patch is an excavated pit about 100 ft dia. and 30 ft deep. A trench about 500 ft long provides access to the pit from the northeast. Originally opened in a futile search for economic deposits of cinnabar and later operated briefly in the early 1930’s as a source of silica for glass, the pit and trench provide excellent exposures of varying intensities of surficial alteration in the horizontal dimension. Although active alteration appears to have ceased, wisps of vapor can be seen on cold, humid days within the pit where a temperature of 82°C was measured in a small fissure.

Mineralogy. Figure 3, a geologic cross-section in the vicinity of the silica pit, shows the approximate position of the floor of the pit and trench as well as locations of samples. Most of the samples studied come from the Steamboat basaltic andesite. Table 1 lists the mineralogy of these samples.

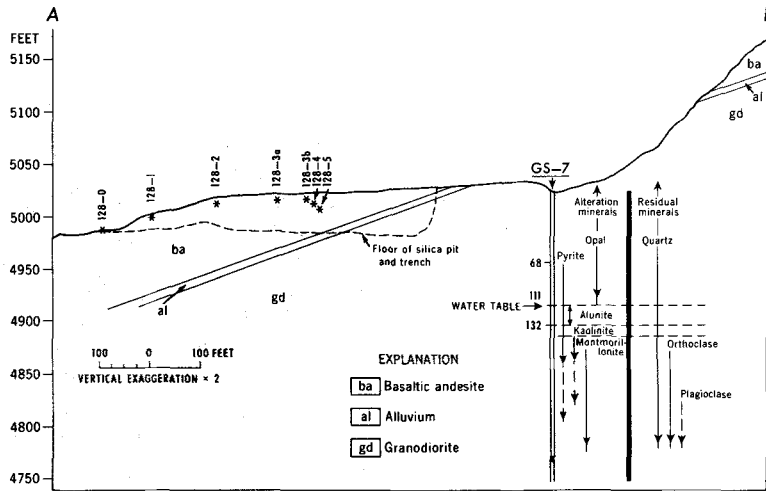


Fig. 3. Geologic cross-section of silica pit showing locations of samples and mineralogy of core from drill-hole GS-7.

Because samples 128-4 and 128-5 are open-space fillings, they cannot be directly compared to surficially altered basaltic andesite. These fillings consist of minerals precipitated from solutions that leached the interiors of blocks of basaltic andesite or descended from leached rocks at higher levels. Open-space fillings help characterize the fluids that traversed the rock fractures, and awareness of their existence adds a measure of caution to interpretations of chemical gains and losses of the altered rocks.

The mineralogy of samples 128-0-128-3b gives a clear indication of progressive alteration of basaltic andesite as the center of alteration is approached. Mineralogical study of 14 additional samples taken from the trench between 128-0 and 128-2 showed, however, that this simple model of alteration does not describe the detailed complexities. Thin section and X-

ray study of these 14 samples showed that, superposed on the general pattern of diminishing alteration horizontally outward from an area completely converted to opal, was a smaller-scale but similar alteration that decreased in intensity away from individual fractures. In rock with closely spaced fractures, susceptible phases such as plagioclase were completely removed, whereas the interiors of large, solid blocks nearby remained relatively fresh.

The 14 additional samples also exhibited some finer details of the progressive alteration illustrated by the 128 series. Montmorillonite provides the first mineralogical indication of alteration, probably forming from fine-grained and glassy mafic constituents in the groundmass. At about the same time much of the ferrous iron in the rock oxidizes to ferric oxide and hydroxide, as indicated by deep red stains in the vicinity of

Table 1. Mineralogy of basaltic andesite at the silica pit (Fig. 3), Steamboat Springs, Nevada

| Sample | Feet south of entrance to silica pit | Mineralogy* |
|--------|--------------------------------------|--|
| 128-0 | 0 | Fresh: Pc, Ol, Anorth, San, ilmenite, tr. pyroxene and quartz |
| 128-1 | 105 | Moderately altered: Kp, M, Anorth, San, ilmenite, tr. Ol |
| 128-2 | 220 | Strongly altered: Kw, Ana, tr. α -Crist and ilmenite |
| 128-3a | 340 | Completely altered: opal, tr. α -Crist and Ana |
| 128-3b | 400 | Completely altered: opal, α -Crist, Ana, tr. β -Crist |
| 128-4 | 405 | Vein filling: β -Crist, tr. opal and Ana |
| 128-5 | 425 | Vein filling: alunite |

* Kw and Kp, well and poorly ordered kaolinite; M, montmorillonite; Crist, cristobalite; Pc, plagioclase; Ol, olivine; Anorth, anorthoclase; San, sanidine; Ana, anatase; tr., trace.

olivine phenocrysts and mottling of color on a larger scale. Further alteration causes the destruction of polysynthetic twinning in plagioclase phenocrysts and replacement of the lamellae by kaolinite. This change coincides with the alteration of montmorillonite to kaolinite. Anorthoclase rims on plagioclase phenocrysts persist even after all polysynthetic twinning of the interior is destroyed. The shapes of most plagioclase phenocrysts persist until the outlining rim of anorthoclase alters to kaolinite. At about the same stage of alteration where all montmorillonite alters to kaolinite, many of the tiny black ilmenite inclusions in the groundmass alter to creamy white blebs of anatase. The final stage of alteration of basaltic andesite destroys even the kaolinite and yields only opal, some of which may crystallize to cristobalite and residual anatase.

In addition to surface samples at the silica pit, a hole drilled by the U.S. Geological Survey close by provides a view of the alteration mineralogy with depth. Drill hole GS-7 was collared in completely altered granodiorite about 250 ft southwest of the silica pit (Fig. 1). Sigvaldason and White (1962) described the mineralogy of drill core to a depth of 385 ft and provided chemical analyses and temperature data. Only the upper part of the hole, that was subjected to surficial alteration, is considered here.

Figure 3 depicts the mineralogy of selected pieces of drill core from GS-7. The upper 111 ft comprise approximately equal amounts of opal (β -cristobalite to about 50 ft and amorphous below) and residual quartz. Below the water table at 111 ft, alunite becomes abun-

dant. From 111 to 114 ft amorphous opal fills all interstices producing a very dense rock. The sample at 120 ft is nearly pure alunite with residual quartz and a little pyrite. Well ordered kaolinite then increases as alunite diminishes below 120 ft. Below 132 ft alunite is gone and the mineral assemblage consists of 14 Å montmorillonite, diminishing kaolinite (which persists to about 250 ft) illite, residual quartz, orthoclase and plagioclase as well as sporadic biotite. Pyrite, generally concentrated in small fractures, makes up about 3 per cent of the rock from a depth of 68 down to 170 ft and less than 1 per cent of the rock below this depth. Below 133 ft the effect of hypogene alteration, as marked by montmorillonite and illite, supersedes that of surficial alteration.

The most striking fact about the mineralogy of GS-7 drillhole is the coincidence of the water table with the downward change from an opaline residue of intensely altered granodiorite to alunitized and then argillized granodiorite. We believe that saturated rocks below the water table neutralize descending sulfuric acid and cause the observed rapid changes in alteration mineralogy at the water table.

Although we have observed similar sequences of alteration minerals in other drill holes at Steamboat Springs (Sigvaldason and White, 1961, 1962; Schoen and White, 1965, 1967) and in acid-altered areas elsewhere, none of these show such striking changes in mineralogy at and immediately below the water table. The reason for this may be related to recent fluctuations in water levels as well as rate of lateral flow of ground water. At GS-7, discharge of ground water is

Table 2. Chemical analyses of rocks from the silica pit, Steamboat Springs, Nevada

| | 128-0 | 128-1 | 128-2 | 128-3b | 128-4 | 128-5 | 7-120 |
|--------------------------------|-------|-------|--------|--------|----------|-----------|----------------------|
| SiO ₂ | 54.38 | 50.09 | 52.27 | 92.42 | 94.7 | 7.0 | 21.8 |
| Al ₂ O ₃ | 17.83 | 20.77 | 27.87 | 0.53 | 0.00 | 34.5 | 29.0 |
| Fe ₂ O ₃ | 2.57 | 8.40 | 2.59 | 0.07 | 0.02 | 0.02 | — |
| FeO | 4.97 | 1.11 | 0.06 | — | — | — | — |
| MgO | 4.12 | 1.05 | 0.50 | 0.00 | 0.35 | 0.00 | 0.00 |
| CaO | 6.58 | 0.82 | 0.04 | 0.00 | 0.11 | 1.0 | 0.12 |
| Na ₂ O | 4.03 | 2.05 | 0.03 | 0.01 | 0.09 | 2.7 | 0.31 |
| K ₂ O | 2.50 | 2.41 | 0.07 | 0.01 | 0.08 | 5.7 | 7.9 |
| H ₂ O ⁻ | 0.12 | 3.78 | 2.88 | 0.97 | — | — | — |
| H ₂ O ⁺ | 0.16 | 6.50 | 10.84 | 1.94 | — | — | 11.4 |
| TiO ₂ | 1.89 | 2.44 | 2.52 | 4.13 | 0.75 | 0.28 | 0.26 |
| P ₂ O ₅ | 0.57 | 0.32 | 0.17 | — | 0.00 | 1.1 | 0.42 |
| SO ₃ | 0.01 | 0.09 | 0.46 | — | Ign. 2.5 | Ign. 47.4 | 27.7 |
| S | 0.01 | — | — | — | — | — | FeS ₂ 1.6 |
| CO ₂ | 0.01 | 0.00 | 0.00 | 0.00 | — | — | 0.18 |
| MnO | 0.11 | 0.06 | 0.01 | — | 0.01 | 0.04 | 0.01 |
| Total | 99.86 | 99.89 | 100.31 | 100.08 | 98.6 | 99.7 | 100.7 |
| Bulk sp. | | | | | | | |
| gravity | 2.59 | 1.52 | 1.10 | 0.90 | — | — | 2.36 |
| Powder sp. | | | | | | | |
| gravity | 2.80 | 2.52 | 2.44 | 2.18 | 2.09 | 2.62 | 2.79 |

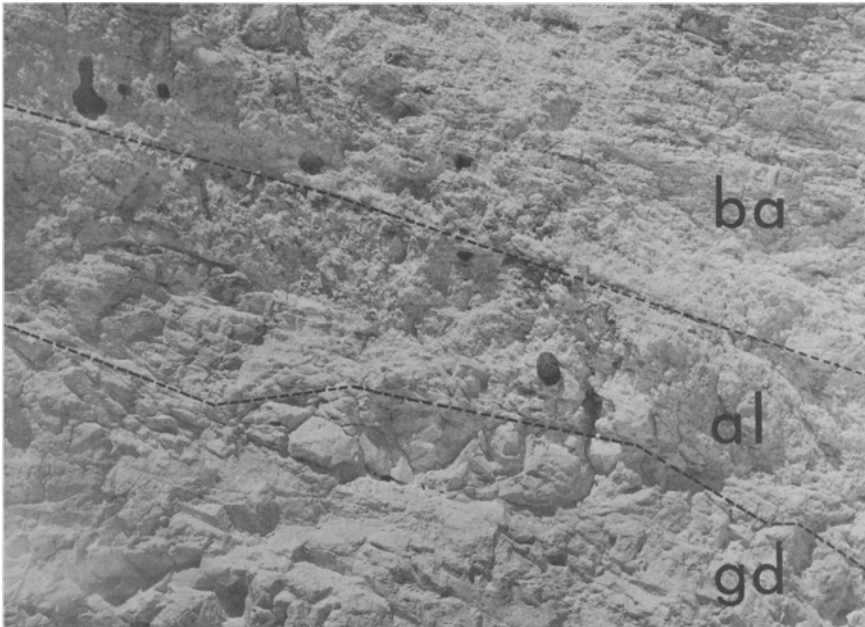


Fig. 4. Intensively altered granodiorite (gd), alluvium (al) and basaltic andesite (ba) in the silica pit showing preservation of joints and bedding planes. Hat indicates scale.

presumably so low that descending sulfuric acid is not immediately flushed out but rather effects some control of alteration mineralogy as much as 22 ft below the water table.

Chemistry. Whole-rock chemical analyses of the samples of basaltic andesite from the silica pit (Table 2) reflect the change of mineralogy with progressive alteration. In addition to mineralogy and chemical



Fig. 5. Joint spacing in nearly fresh basaltic andesite at northeast entrance to silica pit (knife about 5 in. long).



Fig. 6. Joint spacing in moderately altered basaltic andesite at silica pit.

composition, surficial alteration produces great changes in the porosity of a rock. Calculated porosities, based on the difference between powder specific gravity and bulk specific gravity of each sample in Table 2, range from 7.5 per cent in fresh Steamboat basaltic andesite up to 58.7 per cent in completely altered sample 128-3b. The individual chemical analyses presented in Table 2 cannot be directly compared

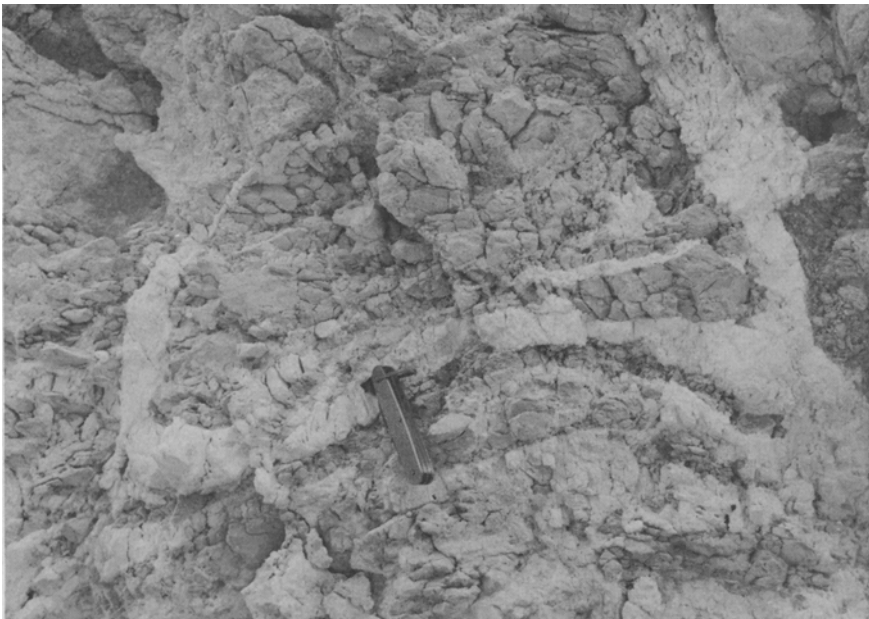


Fig. 7. Joint spacing in intensively altered basaltic andesite at silica pit. White veinlets consist of nearly pure opal fillings low in TiO_2 . Cream-colored, relict basaltic andesite, high in TiO_2 , photographs as light gray.

Table 3. Composition in mg per cubic centimeter of rocks from the silica pit, Steamboat Springs, Nevada

| | 128-0 Fresh andesite | 128-1 Altered andesite | 128-2 More altered andesite | 128-3b Most altered andesite |
|--------------------------------|----------------------------|------------------------------|-----------------------------------|------------------------------------|
| SiO ₂ | 1408 | 761 | 575 | 832 |
| Al ₂ O ₃ | 462 | 316 | 307 | 5 |
| Fe ₂ O ₃ | 67 | 128 | 28 | 1 |
| FeO | 129 | 17 | 1 | — |
| MgO | 107 | 16 | 6 | 0 |
| CaO | 170 | 12 | 0 | 0 |
| Na ₂ O | 104 | 31 | 0 | 0 |
| K ₂ O | 65 | 37 | 1 | 0 |
| TiO ₂ | 49 | 37 | 28 | 37 |
| P ₂ O ₅ | 15 | 5 | 2 | — |
| H ₂ O ⁻ | 3 | 57 | 32 | 9 |
| H ₂ O ⁺ | 4 | 99 | 119 | 17 |
| SO ₃ | 0 | 1 | 5 | — |
| MnO | 3 | 1 | 0 | — |
| BaO | 4 | 2 | 0 | — |
| Total | 2590 mg cm ⁻³ | 1520 mg cm ⁻³ | 1104 mg cm ⁻³ | 901 mg cm ⁻³ |

to determine gains and losses of constituents during alteration until they are first corrected for porosity changes. Implicit in these corrections is the assumption that the volume of rock has remained constant during alteration. Although constancy of volume is generally assumed in alteration studies out of necessity, rarely is any evidence given to substantiate the assumption.

At the silica pit, the slight topographic depression that coincides with the altered area leads one to suspect some collapse of the rocks. Close examination of the altered rocks shows, however, that all the joints and beddingplane contacts of the unaltered rocks are preserved without measurable distortion (Fig. 4). The topographic depression of the silica pit, and many other acid-altered areas, is probably due to relatively rapid leaching of silica nearest the surface by downward percolation through the porous altered rock.

In addition to increased porosities affecting rates of leaching, an increase in the frequency of joints in the silica pit may also be important. Figures 5-7 show increasingly closer spacing of joints in the more altered parts of the basaltic andesite. This may be a surface expression of more highly fractured rocks that lie at depth and localize the upward flow of thermal fluids.

Realizing that some small volume change might not markedly affect the rock structures, we conclude that surficial alteration at the silica pit has been essentially at constant volume. Table 3, derived from the chemical analyses and specific gravities of Table 2, presents gains and losses of the constituent oxides during alteration at the silica pit.

Great losses took place in altering relatively fresh andesite like sample 128-0, to rock like sample 128-1 that is altered beyond montmorillonite to predominantly kaolinite. CaO has been reduced to 7 per cent and MgO to 15 per cent of the original value. (We presume that a sample from the montmorillonite-rich zone would not show such a large depletion of magnesium.) Na₂O and P₂O₅ were reduced to 30 and 33 per cent respectively of the fresh andesite value. SiO₂ was reduced to 54 per cent, Al₂O₃ to 68 per cent, and TiO₂ to 76 per cent of the original. Total iron in sample 128-1 is 70 per cent of the amount in sample 128-0. This relatively small loss was effected by oxidation of the ferrous iron to the relatively immobile ferric state. Additions to sample 128-0 during alteration consist of protons (measured as H₂O⁺) and sulfur (probably as sulfate).

Sample 128-2, a more altered rock than 128-1, shows further losses of the same elements as 128-1, but iron is almost gone. This indicates strong acid leaching by solutions low enough in pH for Fe³⁺ to be soluble. Aluminum and titanium show little additional reduction and clearly constitute the relatively immobile elements through this stage of surficial alteration. Protons and sulfur continue to increase.

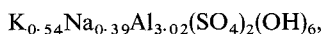
Finally in sample 128-3b, consisting of amorphous opaline residue with newly crystallized cristobalite and residual anatase, almost everything in the original rock except SiO₂ and TiO₂ has been removed, the porous framework being maintained by a boxwork of silica precipitated from the reacting liquid. The increase in silica over sample 128-2 indicates the extent of this

precipitation of silica. Constancy of titanium, even at this advanced stage of alteration, indicates that titanium is generally a better standard to use than aluminum when calculating relative gains and losses in hydrogen metasomatism reactions, if bulk specific gravities are unavailable. In sample 128-3b, low values of H_2O^+ and SO_3 indicate that extreme acidity rendered all solid phases, except SiO_2 and TiO_2 , soluble. No solids showing exchange of original rock compounds by protons and sulfur were preserved.

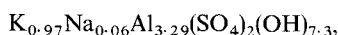
Tables of gains and losses that take porosity into account, like Table 3, are not common in the geologic literature dealing with rock alteration. Instead one usually finds raw chemical analysis data, without specific gravities, that imply deceptively large increases in silica, alumina, and titania with progressive alteration. A notable exception by Lovering (1957) presents examples of acid alteration from Valley of Ten Thousand Smokes in Alaska, Solfatara in Italy and Lassen Peak in California. The gains and losses during alteration at each of these areas show trends similar to those in Table 3 for Steamboat Springs.

The refractory response of titanium to hydrogen metasomatism can be used, where relict textures are absent, to help decide whether deposits of alteration minerals represent pre-existing rocks or open-space fillings. If the TiO_2 value shows an increase over that in the fresh rock, commensurate with the measured decrease in specific gravity, the rock contains little or no open-space filling. Conversely, if the TiO_2 value is lower than the fresh rock or almost nil, the deposit probably represents an open-space filling. Application of this principle to a known veinlet from the silica pit (sample 128-5, $\text{TiO}_2 = 0.28$ per cent vs 1.89 per cent in the fresh rock) and a known veinlet from the clay quarry (sample 381-1, $\text{TiO}_2 = 0.19$ per cent vs 1.89 per cent in the fresh rock) shows that both are open-space fillings.

Sample 128-5 from the silica pit consists almost entirely of alunite, and the analysis in Table 2 can readily be recalculated to derive a structural formula for the alunite. By excluding SiO_2 , Fe_2O_3 , CaO , TiO_2 , P_2O_5 and MnO , recalculating to 100 per cent, and assuming ignition loss to consist solely of H_2O^+ and SO_3 from the alunite we obtain:



where the anion formula is shown idealized because of the lack of separate analyses. Another almost pure alunite sample comes from a depth of 120 ft in GS-7 drill hole (7-120, Table 2). Exclusion of SiO_2 , FeS_2 , CaO , TiO_2 , P_2O_5 , MnO , and CO_2 and recalculation to 100 per cent yields:



assuming the SO_3 value yields the idealized two sulfate molecules. Excess aluminum and hydroxyl may be present as a trace of kaolinite. Though neither of these analyses possesses much accuracy, both show an interesting relationship in the variation of sodium substitution for potassium. We will consider the possible significance of this variation in the section on Geochemistry of Argillization.

Clay quarry

An acid-altered area known as the clay quarry lies in the northwest corner of the Steamboat Springs thermal area (Fig. 1). Small amounts of kaolin clay from this quarry have been used in the manufacture of ceramics in nearby Reno. The quarry lies on the north slope of a hill consisting, near the surface, of Steamboat basaltic andesite. In plan view the acid-altered area is roughly circular, about 200 ft in dia. and is surrounded by a halo of reddish iron-stained rocks that, in turn, is enclosed by unaltered, light-gray andesite (Fig. 8).

Mineralogy. Seven rock samples from within the quarry displayed a varied mineralogy that showed the following general trends. Samples from close to the center, where ground warm to the touch still exists, contained well ordered kaolinite with alunite or else were completely opalized. Near the edge of bleaching, moderately ordered kaolinite and alunite occur. And a short distance away, in the red iron-stained fringe, moderately ordered kaolinite with somewhat broader peaks, alunite and a trace of montmorillonite occur. In addition, we have the impression that the altered andesite quarried from near the surface consisted largely of commercially valuable kaolinite, but that the kaolinite content decreased downward into the older alluvium.

A second suite of seven samples, taken from the near-vertical side of a bulldozer trench located on the west edge of the acid-altered area (indicated by arrow on Fig. 8), provides a detailed study of the alteration mineralogy. The samples come from the bleached rock and up across the iron-stained rock into surface soil containing plant roots. Designated by the letters *a-g* on Fig. 9, their X-ray mineralogy is tabulated in Table 4.

Chemistry. Table 5 contains chemical analyses of two samples of altered basaltic andesite taken from near the center of the clay quarry. Both consist dominantly of well ordered kaolinite, but 381-1 contains more alunite than 381-3, and 381-3 contains a little α -cristobalite. Field evidence (narrow, sharply bounded, pure white zone and lack of relict rock textures) indicates that sample 381-1 consists of open-spacing filling. The low value of TiO_2 (0.19 per cent) coupled with the low bulk specific gravity corroborate



Fig. 8. Clay quarry, Steamboat Springs, Nevada. Arrow indicates approximate location shown in Fig. 9.

this conclusion. Field evidence for sample 381-3 is less clear, but the relatively low TiO_2 and low bulk specific gravity support an origin by open-space filling for most of the sample.

Table 6 contains analyses for total iron in samples a-g of the 320 series, together with the calculated iron content of a cubic centimeter of each sample compared to fresh rock. The enrichment of iron in sample *b* and



Fig. 9. Sample locations for 320 series, west edge of clay quarry.

Table 4. Mineralogy of altered basaltic andesite at the clay quarry (Fig. 9)

| Sample | Inches above red-white contact | Color | Mineralogy* |
|--------|--------------------------------|--------------|--|
| 320-g | 48§ | Dark gray | Kp, M, †‡ |
| -f | 36 | Light gray | Kp, M, †‡ |
| -e | 24 | Med. gray | Kp, † |
| -d | 12 | Brownish-red | Kp, tr. alunite and hematite, † |
| -c | 10 | Light red | Km-p, alunite, tr. α -Crist |
| -b | 1 | Red | Km, hematite, tr. α -Crist |
| -a | -8 | White | Km, alunite, α -Crist, tr. opal |

* Km and Kp, moderately and poorly ordered kaolinite; M, montmorillonite; Crist, cristobalite; tr., trace.

† Also contains detrital quartz, plagioclase, K-spar, or mica.

‡ Contains roots.

§ Sample *g* is only 1-1/2 ft below land surface.

also in sample d, both of which contain detectable hematite, is evident. Far more striking is the effect of the increased porosity of sample b in reducing a large analytical weight percentage of iron to a relatively small enrichment.

Areas of granodiorite

Surficial alteration of granodiorite exists in many discrete areas in the zone of outcropping granodiorite across the central part of the Steamboat Springs thermal area. The only surficially altered granodiorite outside of this band is at the silica pit and has already been described. In spite of the numerous exposures of altered granodiorite, no clear progression of alteration minerals with distance from center of alteration was observed. Suites of samples taken at Pine Basin, Mill Hill and south of the Main Terrace (Fig. 1) do, however, show some regularity.

Montmorillonite (14 Å) is the most abundant alteration product where alteration conditions were mild

(inferred by the presence in the sample of all original orthoclase, some plagioclase, and sometimes even biotite). As these primary minerals decrease in abundance, kaolinite (moderately to poorly ordered) becomes increasingly abundant and montmorillonite decreases. Alunite is often abundant where kaolinite is abundant, but only traces of alunite occur with abundant montmorillonite.

A suite of four samples taken from the south side of Mill Hill range in appearance from soft and white through hard and gray to very hard and red over a horizontal distance of 40 ft from east to west, but, surprisingly, the mineralogy of these samples is virtually identical. They consist of moderately to poorly ordered kaolinite, alunite, residual quartz and a trace of residual orthoclase. No montmorillonite is present. Apparently, the gross differences of the hand specimens reflect complexities of staining and cementation that occurred contemporaneous with or after the alteration.

Areas of arkosic sediments

An acid-altered area developed as a depression known as the Mud Volcano Basin, at the northern edge of the Steamboat Springs thermal area (Fig. 1). This basin formed during a prehistoric hydrothermal eruption of water and mud (White *et al.*, 1964, p. B-43; White, 1955a). Auger hole 8, 14 ft deep, sampled extensively bleached Holocene alluvium near the southern end of the basin. Residual detrital minerals in this hole consist of quartz throughout and a small amount of potassium feldspar and illite in the uppermost sample at 2 ft in depth. Alteration minerals consist of well ordered kaolinite, alunite, α -cristobalite, and in the deepest samples, a little pyrite. The temperature at a depth of 3 ft was 70.6°C. The hole did not reach the water table.

Table 5. Chemical analyses of rocks from the clay quarry, Steamboat Springs, Nevada

| | 381-1 | 381-3 |
|--|-------|-------|
| SiO ₂ | 29.6 | 45.8 |
| Al ₂ O ₃ | 38.0 | 37.6 |
| Total Fe as Fe ₂ O ₃ | 0.32 | 0.38 |
| MgO | 0.00 | 0.22 |
| CaO | 0.74 | 0.60 |
| Na ₂ O | 0.60 | 0.24 |
| K ₂ O | 2.8 | 0.11 |
| TiO ₂ | 0.19 | 1.1 |
| P ₂ O ₅ | 1.6 | 0.32 |
| MnO | 0.13 | 0.08 |
| Ign. loss | 26.9 | 14.8 |
| Total | 101 | 101 |
| Bulk S.G. | 1.60 | 1.20 |
| Powder S.G. | 2.58 | 2.52 |

Table 6. Iron analyses and compositions in mg per cm³ of rocks from the clay quarry, Steamboat Springs, Nevada.

| Sample | Total Fe as Fe ₂ O ₃ (%) | Bulk S.G. | mg Fe/cm ³ rock |
|----------------------------|--|-----------|----------------------------|
| 128-0b (fresh andesite) | 8.3 | 2.59 | 215 |
| 320-a | 1.9 | 0.86 | 16 |
| 320-b | 26.5 | 1.02 | 270 |
| 320-c | 11.9 | 1.05 | 125 |
| 320-d | 12.7 | 1.76 | 224 |
| 320-e | 10.5 | 1.41 | 148 |
| 320-f | 8.8 | 1.27 | 112 |
| 320-g | 13.3 | 1.51 | 201 |

Auger hole 9, collared in Holocene alluvium at the extreme northwest corner of the Steamboat Springs thermal area (Fig. 1), lies in a slight circular depression at the base of an inconspicuous fault scarp at least a thousand feet from any notable thermal feature. The hole bottomed at 13.8 ft with a temperature of 34.1°C, without reaching the water table. Residual detrital minerals in auger hole 9 consist of plagioclase, quartz and a trace of illite. The predominant alteration mineral is 14 Å montmorillonite that increases in amount with depth. A small, fairly constant amount of poorly ordered kaolinite and a trace of alunite are present.

The alteration mineralogy in auger hole 9, in light of its regional setting, might be explained as simply weathering; however, the increase in montmorillonite with depth contrasts with an expected greater weathering intensity at the land surface. Some control of the alteration reaction increases with depth. The bottom-hole temperature, though low, represents a thermal gradient more than two hundred times the world average. Evidently in the past, and perhaps even now, water vapor, hydrogen sulfide and carbon dioxide separated from the underlying water table (probably about 70 ft deep) and produced surficial alteration.

GEOCHEMISTRY OF ARGILLIZATION

Although this paper is primarily a description of rock alteration close to the land surface in a particular hot spring system, the observations apply to the general phenomenon of hydrolysis or base leaching reactions of rocks. The effect of pH appears to be dominant in hydrolysis reactions, for without sufficient protons available to enter mineral structures and disturb electrically balanced bonding forces, most hydrolysis reactions are extremely slow. After pH, temperature is most important in overcoming kinetic barriers to reaction and in accelerating reaction rates.

Finally, the relative concentrations of ions in solution determines the nature of the solid products of hydrolysis. The complexity of the geochemistry of most natural systems is due to seemingly unpredictable variations in the last variable (relative concentrations of ions). Not only are concentrations constantly changing as minerals form and new minerals come under attack, but the rate at which the aqueous altering agent flows through the rocks tends to be inversely correlated with the absolute concentrations that can build up. Hence, in permeable rocks exposed to a high rainfall, rates of percolation are high, concentrations of ions in pore fluids are low and formation of minerals by chemical precipitation is nearly absent. Conversely, in rocks of low permeability, or where water supply limits the rate of through-flow, concentrations of ions increase and the potential exists for precipitation of minerals.

Mineral zonation

The surficial deposits at Steamboat Springs show clearly a consistent zonation of alteration minerals ranging from opal at the center of alteration outward through kaolinite to montmorillonite and finally to fresh rock. This general pattern of mineral zonation is similar to both hydrothermal alteration (Meyer and Hemley, 1967) and weathering (Jackson *et al.*, 1948). That this is so should not be too surprising for the temperature environment of surficial alteration lies between the hydrothermal and weathering environments. But it is of greater importance to recognize that the similarity of mineral zoning is due to the dependence of all three types of alteration on hydrogen metasomatism. It is the reaction of acid with rock that is primarily responsible for the major alteration minerals in all three environments.

Whether the reacting acid is dominantly sulfuric, as in surficial alteration, or dominantly carbonic, sulfuric, hydrochloric, or even hydrofluoric, as in hydrothermal alteration, or dominantly carbonic or organic, as in weathering, is of lesser importance than the con-

centration of protons available for reaction. For instance, opal is the end-product of alteration of a silicate rock by strong acid, whereas gibbsite and hematite are the end-products if the acid is much weaker. Of course, the anions of acids can exert a control on the alteration reaction through their ability to form complexes with major elements in the rocks. This is especially important in the case of iron.

The fate of iron, once it has been released into solution from a mineral reacting with acid, differs in hydrothermal and weathering environments. During hydrothermal alteration, iron in solution in the rock diffuses down a concentration gradient back toward the vein supplying hot fluid. Much iron in solution probably enters the vein and is carried upward and away, down a pressure gradient. But some of the iron reacts with sulfide ions in the hydrothermal fluid to form pyrite, which is characteristically abundant as a vein-filling as well as in wallrock immediately adjacent to a vein. During weathering, iron released by carbonic acid-bearing rainwater precipitates almost immediately as ferric hydroxide because the pH and Eh of the environment are not low enough to keep appreciable amounts of ferric and ferrous ions in solution. Bright red and orange soils containing amorphous iron hydroxide as well as hematite, goethite and lepidocrocite form in this way. Where rainfall is adequate and seasonally well distributed, abundant vegetative cover develops a layer of organic litter on the ground surface. Rainwater leaching through the organic material becomes capable of chelating iron in organic complexes and removing iron from the soil. This is the fate of iron weathered from rocks in most temperate regions.

Iron released during surficial alteration of rocks in acid-altered areas participates in a geochemical cycle that duplicates parts of the hydrothermal and weathering environments. As iron in solution at the land surface moves horizontally away from the source of sulfuric acid, the pH rises due to reaction with fresh rock, and at a pH of about 4, ferric hydroxide precipitates rapidly. Additional strong acid moving outward will redissolve the ferric hydroxide and carry it farther from the source of acid, but it will always reprecipitate as the pH rises. Conversely, iron in solution that percolates downward through the unsaturated zone, reacts with rising vapors of hydrogen sulfide to form crystals of pyrite, usually restricted to veinlets (Fig. 3). The freshness of the pyrite crystals we see in core samples of the opalized unsaturated zone at Steamboat Springs attests to the relative insolubility of pyrite in sulfuric acid and agrees with the predicted thermodynamic stability of pyrite in acid solution at moderate values of dissolved sulfur (Garrels, 1960, Fig. 6.19).

The physical form of the zonation pattern of alteration minerals depends upon the form taken by the envelope of altering fluid which, in turn, depends on rock permeability. Though we do not have adequate data to construct an accurate three-dimensional model, a reasonable hypothetical model can be proposed. The movement of acid into unaltered rock can be thought of as the movement of a hydrolysis front. Ions released by both congruent and incongruent dissolution of minerals, accumulate in the pore liquid and move in response to concentration, pressure and gravity gradients. When the composition of the pore liquid changes, new alteration minerals may precipitate from some of the ions in solution while other ions continue to move in the pore solution.

In the hydrothermal environment, where rock permeabilities tend to be low except along fractures, zones of alteration minerals envelop each solution conduit. Removal of ions from the system is presumed to be by way of the conduits and not by way of the unaltered rocks.

In the surficial environment at the land surface, however, horizontal permeability may be large and may, in fact, be greater than vertical permeability. Hence, solutions carrying products of hydrolysis can move laterally as well as downward. It is in this way that the halo of red, hematite-rich rocks may develop at the edge of an acid-altered area. And, close to the hematite halo, montmorillonite develops, perhaps partly by precipitation from pore solutions containing silica and alumina, derived from the aggressive alteration of feldspars near the center of alteration, combining with pore solutions containing magnesium, calcium, and iron, derived from the weak alteration of feldspars and other minerals in the immediate vicinity. Montmorillonite also may develop pseudomorphically after feldspars and other primary silicates by incongruent dissolution leaving a leached residue of montmorillonite. Perhaps both modes of mineral formation can operate simultaneously to produce the montmorillonite zone. Farther back from the hydrolysis front toward the center of alteration, kaolin minerals and alunite form a zone in response to the composition of the pore fluids, and, at the center of alteration, silica minerals form.

Lateral drainage. There may be some question of the extent to which acid, formed at the land surface, can drain horizontally outward away from its site of formation. The site from which the 320 series of samples was taken at the clay quarry (Fig. 9) showed altered rock dipping outward beneath fresh rock, away from the center of alteration. An even more distinct example of this occurs at the edge of an acid-altered area in the village of Sasso, Italy, where the contact between

altered and unaltered rock dips at approximately 45° away from the active center of alteration. The question arises whether all the sulfuric acid forms at the surface of an acid-altered area and then drains laterally and vertically downward, altering rock on the margins of the field that is overlain by fresh rock, or whether drainage of acid is dominantly vertical, thus implying that some acid must form at depth to account for the pattern of alteration at the margins.

In a dry soil with isotropic permeability, capillary forces produce a strong lateral component of flow initially (Hillel, 1971, p. 138). But after a short time gravity predominates, and water moves vertically. A lateral chemical potential can develop between acidic and neutral water films on mineral grains, that would promote the ionic diffusion of acid laterally into non-acid ground. The importance of these two modes of lateral acid transport is, however, probably small.

A more realistic model of natural infiltration includes layers of different permeabilities. Water moves dominantly downward in a permeable layer but, on reaching a layer of lower permeability, further downward movement is controlled by the less permeable layer. The water builds a mound of saturated rock and spreads laterally above the less permeable layer (Marmion, 1962, especially Fig. 9; Prill and Aaronson, 1973). Because the less permeable bed is not impermeable, lateral flow stops when leakage equals supply of water at the top and a steady state develops.

We envision the stages of development of an acid-altered area as shown in Fig. 10. Hydrogen sulfide ris-

ing along fractures is oxidized to sulfuric acid at the land surface, combines with rain and condensed steam, and alters rocks at the surface (Fig. 10a). As alteration of a layer of rock at the surface becomes complete, leaving a highly permeable siliceous residue, newly formed acid moves from the surface directly downward till its drainage is impeded by the argillaceous products of earlier alteration or relatively fresh rock. The acid then flows laterally reacting with the rock minerals present (Fig. 10b-c). This phenomenon continues until the rock is altered down to the water table and all acid is diluted and carried away by ground water (Fig. 10d).

An additional factor in explaining the typical flaring of alteration with depth of acid-altered areas may be the deepening of temperature contours on the borders of active hot spring systems. Because about 90 per cent of rising water vapor will condense at 40°C , and much of the carbon dioxide and hydrogen sulfide present will dissolve in this relatively cool water, a solution of the weak acids carbonic and hydrosulfuric may develop parallel to the flaring temperature contours on the borders of an acid-altered area.

Rising vs descending altering fluids. Another interesting, and perhaps controversial, aspect of the zonation of alteration minerals in acid-altered areas is determining the direction of movement of the altering fluid. In present-day, hot-spring systems that have been adequately studied by drilling, such as Steamboat Springs, Nevada, and Yellowstone Park, Wyoming, there is no doubt that the altering fluid responsible for surficial alteration moves dominantly downward. Less certain is the direction of fluid movement in acid-altered areas that do not exhibit manifestations of hot-spring activity or where the spatial patterns of alteration minerals are obscure.

Iwao (1968) describes a large mass of acid-altered rocks associated with hot springs at Ugusu, Japan. The alteration extends over an area of 10 km^2 and ranges to a depth of 700 m. Zoning of alteration minerals occurs parallel to the rolling topography with silica minerals at the surface followed downward by zones of alunite, kaolin-pyrophyllite, illite-montmorillonite and finally unaltered rock at the bottom. Primary textures and structures of the volcanic rocks are preserved in all zones of alteration. The high TiO_2 content of the silica zone indicates that it is an altered rock residue and is not a deposit of siliceous sinter. Iwao suggests that the vast amount of material removed from these altered rocks moved up to the surface in thermal waters and there either precipitated or left the area.

Several recent descriptions of economic kaolin and silica deposits in Mexico by Keller and Hanson (1968, 1969; Keller *et al.*, 1971; Hanson and Keller, 1966) indicate a mineral zoning similar to that of Steamboat

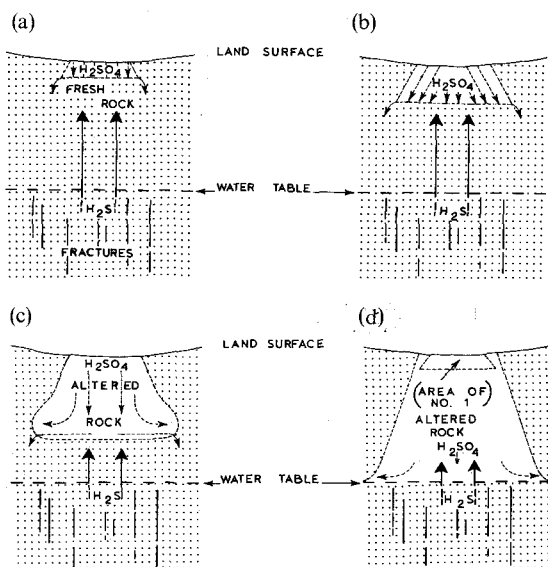


Fig. 10. Hypothetical, four-stage development of acid-altered area showing vertical and horizontal migration of acid.

Springs. The study near San Luis Potosi, Mexico, (1968) presents the resemblance especially well. A nearly horizontal zone of kaolin, containing minor amounts of alunite and cristobalite, underlies a silica zone at the surface. The kaolin grades laterally and downward into less leached parent rock. The authors conclude that the altering fluids were rising, hence hypogene, and that the surficial silica zone, which they call 'silica gossan', represents the last and most feeble alteration reaction in which silica, derived from the clay zone below, precipitated.

Perhaps the most critical detail to consider, in attempting to determine the direction of movement of the altering fluid, is the constructional versus destructional origin of the silica zone. If the siliceous rocks consist of bedded deposits of hot-spring sinter overlying the original land surface, indicating that the thermal water table was at the surface, hypogene alteration probably exists below. If conversely, the siliceous rocks are altered residues of local rocks, alteration by descending acid is indicated.

Additional evidence of supergene alteration is afforded by the unique mineral zonation of silica at the top, kaolin-alunite below, conforming to the position of an ancient water table, underlain by montmorillonite and then, perhaps, by relatively fresh rock. This sequence indicates greatest alteration (H-metasomatism) of the rock at the top and decreasing intensity of alteration downward, away from the site of formation of the altering agent.

Based on application of these criteria to the published descriptions of the acid-altered areas at Ugusu, Japan, and San Luis Potosi, Mexico, we consider it likely that both formed by surficial alteration effected by downward percolating solutions of sulfuric acid.

Montmorillonite type

All the montmorillonitic clays examined in this study yield basal X-ray spacings of about 14 Å when in an air-dry state. This spacing indicates that the dominant exchangeable cation held in the interlayer position is either calcium or magnesium. For basaltic andesite or even granodiorite, the predominance of calcium and magnesium over sodium and potassium in the alteration products is not surprising. The andesite contains 10.7%(w/w) CaO plus MgO vs 6.5%(w/w) Na₂O plus K₂O, and the granodiorite contains 4.9%(w/w) CaO plus MgO vs 6.5%(w/w) Na₂O plus K₂O (White *et al.*, 1964, Table 1). The preference shown by montmorillonite for divalent rather than monovalent cations explains the occurrence of 14 Å montmorillonite in altered granodiorite. The occurrence of 14 Å montmorillonite in acid-altered arkose,

however, where Na₂O and K₂O presumably far outweigh the CaO and MgO, requires an explanation.

We suggest that the composition of the pore water during any stage of acid alteration is not necessarily in direct proportion to the composition of the solid phases present. For instance, in any rock calcium-magnesium silicates break down at a higher pH (hence earlier) than sodium-potassium silicates. Because montmorillonite tends to form at pH levels close to neutral, its aqueous environment is dominated by the products of dissolution of calcium and magnesium silicates. By the time pH levels decrease to the more aggressive hydrogen metasomatism capable of solubilizing sodium and potassium silicates, montmorillonite is no longer stable and kaolinite usually forms.

At Steamboat Springs, montmorillonites of the 12 Å (sodium-potassium) variety dominate the deep hypogene alteration regardless of rock type, either as a pure phase or interlayered with illite (Sigvaldason and White, 1961; Schoen and White, 1965, 1967). The predominance of 12 Å montmorillonites in an environment saturated with thermal water containing 700–800 mg/l sodium plus potassium and about 10 mg/l or less calcium plus magnesium, suggests that the composition of the hypogene fluid swamps out the compositional effect of the altering mineral.

Metahalloysite-kaolinite

Minerals of the kaolin group, which formed during surficial alteration at Steamboat Springs, vary from well ordered kaolinite to moderately ordered kaolinite to poorly ordered kaolinite to metahalloysite. Though the evidence is only qualitative, consisting of the spatial distribution of types of ordering with respect to the center of alteration, there is an indication that metahalloysite may be a metastable precursor to poorly ordered kaolinite which in turn may be metastable to well ordered kaolinite. Conversely, the attack of sulfuric acid on well ordered kaolinite may form lesser ordered kaolin minerals before complete solution occurs.

Support for such a stability series of kaolin-group minerals appears to be offset by those that disclaim such a series (Deer *et al.*, 1962, p. 209). Synthesis experiments by Parham (1969a) support the hypothesis that metahalloysite is an early organizational stage in the formation of kaolinite. Parham (1969a, p. 19) observed that metahalloysite is more abundant in modern weathering products and concluded that it would change to kaolinite within relatively short geologic times (Parham, 1969b).

The crude zoning noted at Steamboat Springs of better ordered kaolin minerals toward the center of

alteration is, however, not just related to age. Temperature appears to decrease outward from the center of alteration, but again, only in a crude way with many irregularities. It may be that degree of ordering among the kaolin minerals is directly related to temperature as well as age.

Several pieces of evidence support the importance of temperature. Well ordered kaolinite occurs near the center of alteration at the clay quarry where areas of hot ground still exist, whereas moderately to poorly ordered kaolinite lies close to the edge of alteration. Well ordered kaolinite that formed from Holocene alluvium in auger hole 8, where temperatures at present measure 70–95°C, contrasts with poorly ordered kaolinite in auger hole 9, also in Holocene alluvium but at a present-day temperature of 34°C. Schoen and White (1967, p. B116) noted that core from drill hole GS-6 contained well ordered kaolinite from the bottom of the hole up through the sample at 155 ft but contained poorly ordered kaolinite at a depth of 133 ft and above. We now realize that the presence of the water table at a depth of 148 ft may indicate that hot water (temperature near boiling) aided crystallization or recrystallization of kaolinite in submerged samples by accelerating the reaction and allowing part of the process to occur in solution. It is also notable that at the Sombrerete kaolin deposit in Mexico, Keller and Hanson (1969, p. 11) found that well ordered kaolinite, near the center of a volcanic pipe, graded outward into halloysite (their endellite) near the cooler intruded country rock. They proposed that temperature may have been important in causing this zoning.

Alunite

At Steamboat Springs, supergene alunite coexists with all other alteration minerals, but is much more abundant in association with kaolinite, in accord with geologic observations in other areas and with the implications of mineral stability studies by Hemley *et al.* (1969) (Fig. 11). Alunite forms during alteration in a sulfate-rich system under conditions of strong hydrogen metasomatism and is, therefore, more often associated with a phase representing complete removal of the alkali cations such as kaolinite. Figure 11 shows that a minimal activity (or concentration) of hydrogen ion is necessary before alunite can form with either K-mica or K-feldspar at relatively high K^+ activities or with kaolinite at relatively low K^+ activities.

Conditions under which alkali ion concentrations might rise to sufficiently high values to stabilize alunite with alteration minerals other than kaolinite could, of course, occur locally in geologic systems. Such conditions might exist on the fringes of more intense alunite-

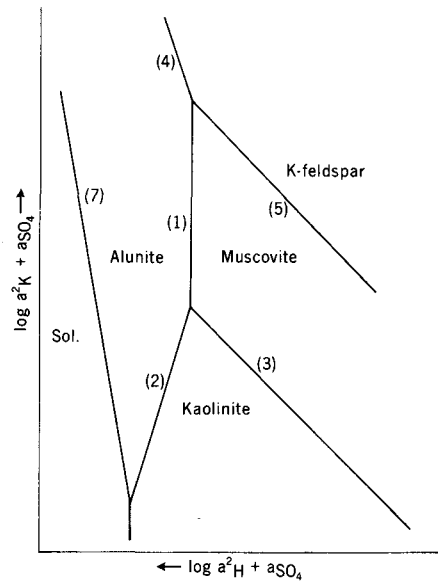


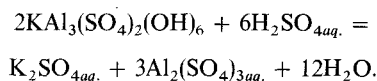
Fig. 11. Stability relations of alunite as a function of H_2SO_4 and K_2SO_4 activities (modified from Hemley *et al.*, 1969). Numbers on boundaries refer to equilibrium reactions given in original reference.

zation. These areas would represent micro systems of lower permeability where solution migration is not sufficiently rapid relative to leaching to immediately sweep away and dissipate the base cations removed from the rock. Therefore, concentrations would be able to build up to values in equilibrium with montmorillonite or other phases. An alternative possibility is that the rare coexistence of alunite with phases other than kaolinite represents metastable persistence of one of the phases.

Supersaturation of the pore water with respect to alunite would be achieved in different ways in different rock and solution environments. As shown in Table 3, most of the aluminum in a rock is not released into solution until the most aggressive stages of hydrogen metasomatism. Calcium, iron and sodium tend to be released early, followed by potassium and eventually aluminum. In most rocks, therefore, sodium and iron will have been completely removed by the time acidity, potassium and aluminum concentrations build up in the pore water to values sufficient for the formation of alunite. These relationships explain the absent or rare association of alunite with calcium minerals and even the uncommon association of alunite and jarosite.

As suggested by Hemley *et al.* (1969, p. 610), the following reaction represents the most extreme environment of hydrogen ion metasomatism in hot-spring

alteration systems, in which alunite dissolves in sulfuric acid:



No boundary was shown for this reaction by Hemley *et al.* (1969, their reaction number 7) because the equilibrium relations were not worked out. The boundary labeled number 7 on Fig. 11 represents a hypothetical boundary for this reaction. The significance of the alunite-solution boundary is that an upper, as well as a lower, limit of acidity is involved in alunite stability, a point also noted by Höller (1967). With the dissolution of alunite, only a silica phase (usually opaline silica) remains in the system and its inversion to the more stable quartz is quite slow, even geologically.

The relatively high sodium content of alunite in sample 128-5 from the silica pit (K:Na atomic ratio = 1.4:1.0) may reflect the presence of anorthoclase feldspar in the basaltic andesite that broke down late in the alteration and supplied abundant sodium as well as potassium to pore waters. The low-sodium alunite from 120 ft depth in GS-7 drill hole (K:Na = 16.2:1.0) may indicate the early removal of all sodium-rich phases from the granodiorite prior to destruction of orthoclase. Additional possible explanations for these large compositional differences between the alunites involve higher potassium contents in alunite formed at higher temperature, and higher sodium contents in alunite formed at higher acidities (Zotov, 1971).

ECONOMIC IMPLICATIONS

Economic products related to surficial alteration at Steamboat Springs include kaolin, glass sand and cinnabar. Though the sizes of these deposits are small, their mode of formation appears to have operated on a larger scale elsewhere in the world. The recent compendium of economic kaolin deposits of the world, (23rd *International Geological Congress*, Vols. 14-16) frequently refers to associated hot-spring activity, volcanism and sulfurous vapors.

In order to form an economic deposit of kaolin by surficial alteration, acid solutions must percolate down through and leach the base cations from rocks containing aluminum and silicon. Kaolin may form from the residual alumina and silica frameworks of the primary rock minerals. Continued attack by strong acid will dissolve the kaolin and provide descending solutions rich in silicon and aluminum. Neutralization of these solutions by reaction with unstable minerals or dilution at the water table may cause supersaturation with respect to kaolin and consequent precipitation. If kao-

lin formed from residual alumina and silica frameworks is present together with descending solutions supersaturated with respect to kaolin, it is likely that kaolin will precipitate directly on the residual seed crystals. A slow lowering of the water table may increase the thickness of the kaolin deposit but only if downward percolating acid can get through the kaolin blanket without destroying much of the kaolin. A rising water table or a cessation of emission of hydrogen sulfide will allow preservation of the kaolin deposit.

Another aspect of surficial hot-spring alteration of economic potential is possible secondary enrichment at the water table of metals leached from overlying rocks. This mechanism of enrichment is similar to the classical supergene enrichment of oxidized sulfide ore deposits. Neverov and Khvedchemya (1966) propose such an origin for deposits of copper, mercury, molybdenum, arsenic and iron sulfides containing small amounts of lead, silver and gold, beneath solfatara fields in the Kurile Islands.

White (1955b, 1967) described the frequent association of mercury deposits with hot springs. The opalite-type deposit shows a clear resemblance to the surficial alteration at Steamboat Springs. Of critical distinction is the blanketlike, nearly horizontal form of the opalite, that grades laterally into unaltered rock and cuts across steeply dipping, primary rock-structures. Considered for many years to be hot-spring sinter, detailed studies in the 1940's showed the residual nature of opalite.

One final economic consideration of surficial, hot-spring alteration concerns the potential for contamination of streams and destruction of man-made structures by acid effluents from acid-altering areas. This problem does not appear to be of great concern in the United States, though the National Park Service has been forced to specify vitreous tile or stainless steel for roadway conduits in many parts of Yellowstone Park (Environmental Science and Technology, December 1967, p. 971). In Japan, acid contamination of streams and rivers seems to be more widespread. A related world-wide problem is the drainage of acid from many sulfide-bearing metal and coal mines. That even this problem, when fully understood, can be changed into an asset is indicated by the recovery of large amounts of uranium from acidic wastes draining from several shut-down, Canadian mines (MacGregor, 1969).

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Résumé—Steamboat Springs, Nevada, localité où l'on trouve des sources thermales en activité, illustre clairement la dépendance génétique de certains dépôts de kaolin vis-à-vis de l'activité thermique. L'andésite, la granodiorite et les sédiments arkosiques sont altérés localement à la surface du paysage en résidus siliceux consistant en du quartz et de l'anatase primaire, plus de l'opale provenant des silicates primaires. Les résidus siliceux ont en général les caractéristiques texturales et structurales de leurs équivalents non altérés. Sous les résidus siliceux, le kaolin et l'alunite remplacent les silicates primaires et remplissent les espaces vides en formant comme un dépôt de recouvrement. Sous la zone à kaolin-alunite, la montmorillonite communément accompagnée de pyrite, remplace les silicates primaires. A la surface, les mêmes zones d'altération du minéral peuvent être délimitées en partant du résidu siliceux; toutefois c'est l'hématite plutôt que la pyrite qui accompagne la montmorillonite.

L'analyse chimique indique que l'acide sulfurique est l'agent actif dans l'altération. L'acide se forme à partir de l'hydrogène sulfuré qui se dégage de l'eau thermale profonde, puis qui passe au-dessus de la nappe et qui est oxydé par les bactéries thio oxydantes qui vivent près de la surface du sol. L'acide se dissout dans l'eau de pluie ou dans la vapeur d'eau condensée et percole vers le bas en détruisant la plus grande partie des minéraux primaires ce qui produit le résidu siliceux. La coïncidence de la nappe avec la transition inférieure entre le résidu siliceux et la mélange kaolin-alunite signifie que le métasomatisme par l'hydrogène diminue à cause de la dilution de l'acide qui percole par l'eau du sol.

Dans les zones de sources thermales, les lits de travertin siliceux déposé à la surface par l'eau thermale de profondeur, ressemblent, superficiellement, à des zones d'altération acide de surface. Les caractéristiques diagnostiques d'une telle altération sont les structures de la roche restante, constituées par un résidu siliceux et une zone à kaolin et alunite en mélange située immédiatement dessous.

Kurzreferat—Steamboat Springs, Nevada, ein Gebiet mit noch heute tätigen heißen Quellen, ist ein deutliches Beispiel für die genetische Abhängigkeit einiger Kaolin-Lagerstätten von der Aktivität heißer Quellen. Andesite, Granodiorite und arkosische Sedimente sind lokal an der Erdoberfläche zu kieseligen Rückständen umgewandelt worden, die aus primären Quarzen und Anatase sowie aus Opal von primären Silicaten bestehen. Diese kieseligen Rückstände weisen gewöhnlich in Textur und Struktur Merkmale ihrer unveränderten Äquivalente auf. Unterhalb der kieseligen Rückstände ersetzen Kaolin und Alunite die primären Silicate, füllen offene Hohlräume aus und bilden eine deckenartige Ablagerung. Unter der Kaolin-Alunit-Zone ersetzt Montmorillonit, gewöhnlich mit Pyrit vergesellschaftet, die primären Silicate. An der Bodenoberfläche kann von dem kieseligen Rückstand aus die gleiche Veränderung der Mineralzonen verfolgt werden. Jedoch ist Montmorillonit hier eher mit Hämatit als mit Pyrit vergesellschaftet.

Die chemische Analyse zeigt, daß Schwefelsäure die aktive umwandelnde Komponente ist. Die Säure bildet sich aus Schwefelwasserstoff, der sich aus tiefem Thermalwasser löst, über die Grundwasser-oberfläche aufsteigt und durch schwefeloxidierende Bakterien, die nahe der Bodenoberfläche leben, oxidiert wird. Diese Säure löst sich in Niederschlägen oder kondensiertem Wasserdampf und perkoliert abwärts, wobei die meisten primären Silicate zerstört werden und einen kieseligen Rückstand bilden.

Das Zusammenfallen der Grundwasser-oberfläche mit dem unteren Übergang von kieseligen Rückständen zu Kaolin-Alunit kennzeichnet die infolge der Verdünnung der abfließenden Säure durch Grundwasser abnehmende Wasserstoff-Metasomatose.

In Gebieten mit heißen Quellen sehen Betten von kieseligem Sinter, die an der Oberfläche durch oberirdisches Thermalwasser abgelagert worden sind, auf den ersten Blick wie Gebiete einer sauren Umwandlung an der Oberfläche aus. Diagnostische Merkmale für eine oberflächliche Umwandlung sind die relik-tischen Gesteinsstrukturen der kieseligen Rückstände und die unmittelbar darunter gelegenen Kaolin-Alunit-Zonen.

Резюме — Стимбот источники, район современных горячих источников, ясно иллюстрируют генетическую зависимость некоторых залежей каолина от деятельности горячих источников. Осадки андезина, гранодиорита и аркозита на поверхности земли изменяются в кремнистые отложения, состоящих из первичного кварца и анатаза, плюс опал из первичного кремния. Эти кремнистые отложения обычно выявляют текстурные и структурные свойства своих неизмененных эквивалентов. Под кремниевыми отложениями, каолин и алунит замещают первичный кремний и заполняют пустые места, образуя одеялообразное отложение. Под зоной каолина-алунита, монтмориллонит, обычно сопровождаемый пиритом, заменяет первичный кремний. На поверхности земли наружу от кремнистых отложений заметны те же самые изменения минеральных зон; однако, монтмориллонит сопровождается не пиритом а гематитом.

Химический анализ указывает, что серная кислота является активным фактором изменения. Кислота образуется из сероводорода, который выходит из глубокой термоводы, поднимается над водной поверхностью и окисляется бактериями окисляющими серу, живущими вблизи поверхности земли. Эта кислота растворяется при осаждении или в конденсированных парах воды и просачивается вниз уничтожая почти все первичные минералы, образуя кремнистые отложения. Совпадение уровня грунтовых вод с переходом вниз из кремнистого отложения в каолин-алунит означает уменьшающийся метасоматизм водорода вследствие разбавления опускающейся кислоты почвенной водой.

В районах горячих источников, пласты кремнистого туфа, отложенные на поверхности гипогенной горячей водой, выглядят, поверхностно, как площади измененные кислотой. Диагностическими чертами поверхностного изменения являются: структура кремнистых отложений в виде реликтовых скал и непосредственно под ними зона каолинита-алунита.