

# Desilication of Halloysite and Its Relation to Gibbsite Formation<sup>1</sup>

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**ABSTRACT:** The evidence presented points to the alteration of halloysite to gibbsite. Mineralogical data, as determined by X-ray and differential analysis, verify identification of halloysite and gibbsite. Chemical data confirm the expected lower silica and higher alumina content for samples which are predominantly gibbsitic. It is reasonable to assume from petrographic evidence that gibbsite develops by desilication of halloysite. Halloysite amygdules undergo desilication along the outer peripheries, where acid silica-deficient waters pass, attacking the halloysite by dissolving silica. Halloysite is stable only if it is protected from such solutions, or if the solution passing by is saturated with silica.

Whereas alteration of feldspar to halloysite involves a gain in volume, a loss in volume follows desilication of halloysite. This loss in volume is exemplified by the surface cracks clearly visible in the desilicated halloysite.

IN AN EARLIER PAPER Sherman and Ikawa (1959) described the occurrence of gibbsite amygdules in the Haiku bauxite area of Maui, Hawaii. At that time it was proposed that gibbsite amygdules formed in rock vesicles by rhythmic precipitation of hydrated alumina. Subsequent and more thorough investigation of the same area and elsewhere in the Hawaiian Islands suggests a more complex sequence of events in the development of these gibbsite amygdules. In this paper the results of field and laboratory studies are presented to explain halloysite formation and its subsequent desilication to gibbsite.

Bates (1962) suggested that gibbsite is produced in Hawaii by (1) removal of silica from halloysite, (2) dehydration of aluminum gel, and (3) precipitation from solution. The first mode of formation is of primary interest in this study.

## FIELD DESCRIPTION

All data presented in this work are for samples collected from the Haiku bauxite area described

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by Sherman and Ikawa (1959). Similar features have been observed on the islands of Hawaii, Molokai, Oahu, and Kauai, but the Haiku site represents the most extensive halloysite-gibbsite deposit of this kind. This site is located approximately 2 miles east of Pauwela Village, Maui, and can best be studied along deep roadcuts on the highway leading to Hana.

The soil occurring in this area is mapped as the Pauwela series of the Humic Ferruginous Latosol. Soils of the Pauwela series are found on the island of Maui from sea level to 1,500 ft elevations in areas receiving an annual rainfall of 80–150 inches.

Highly vesicular andesitic pahoehoe probably constituted the parent rock. Pahoehoe lavas are often vesicular and have a rather regular distribution of vesicles; some are cellular to a degree that makes them nearly pumiceous, so that when these vesicles are filled with secondary minerals a larger volume of the rock may be occupied by them.

A description of the Pauwela soil can be found in Cline et al. (1939). Approximately 3–5 ft below the surface there appears a yellowish-brown weathered rock (saprolite) retaining much of the original rock structure. In the area investigated this weathered zone persists even in the deepest portion exposed by the roadcut, although occasional unweathered cores also may be seen.



FIG. 1. Fragments of halloysitic veins from Haiku, Maui. Dark coatings are surface manganiferous deposits. Scale units in mm.

Closer examination of the saprolytic material reveals numerous milky-white, spherical bodies (Figs. 2, 3). In distribution and dimension they appear to be vesicle fillings, and henceforth will be referred to as amygdules. Similarly, joints and crevices in the rock have become filled with this material (Fig. 1) and appear as veins. Differential dispersion of the matrix by rain, and protrusion of amygdules and veins give these features exaggerated prominence. In selected hand specimens, however, as much as 50–75% of the volume may be occupied by these amygdules.

#### RESULTS

Halloysite and gibbsite were identified as the two important crystalline minerals in the amygdules and veins by X-ray diffraction analyses. Halloysite was in the form of the fully hydrated ( $4\text{H}_2\text{O}$ ) form, indicated by the appearance of the  $10 \text{ \AA}$  ( $8.8^\circ 2\theta$ ) spacing.

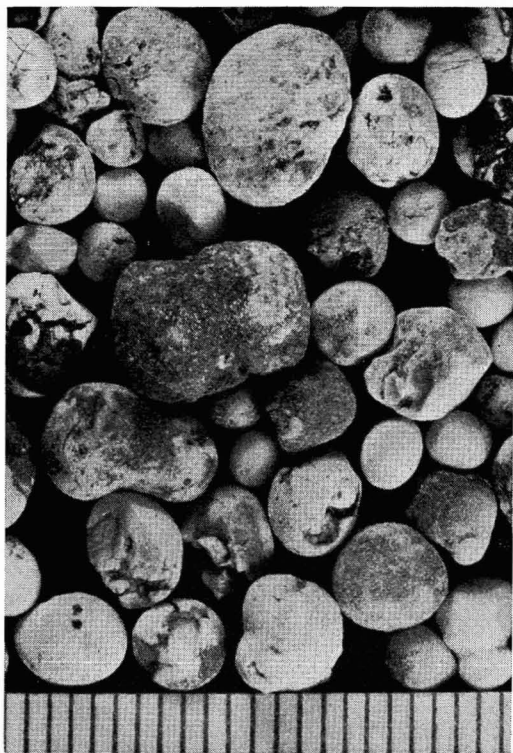


FIG. 2. Halloysitic amygdules from Haiku, Maui. Note relatively smooth surface. Scale units in mm.

Figure 4 shows the X-ray diffraction diagrams of the veins and amygdules ranging in mineralogy from essentially pure halloysite to pure gibbsite.

Table 1 gives the chemical composition of these same samples. Halloysite is normally given the formula  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$  and, therefore, should have a mole  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 2. The values given in Table 1 are all less than the theoretical value of 2. This is understandable since both the X-ray and differential thermal data (Fig. 5) show traces of gibbsite even in the predominantly halloysitic samples. Even when no gibbsite can be detected, Hawaiian halloysites, in general, never attain a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 2 (Nakamura and Sherman, 1963).

Pure gibbsite should be free of silica, but the sample containing the largest quantity of gibbsite still retains 6.55%  $\text{SiO}_2$ . The 02 (hk) reflection for halloysite which appears at  $20^\circ 2\theta$  in the X-ray diagram is masked by a major

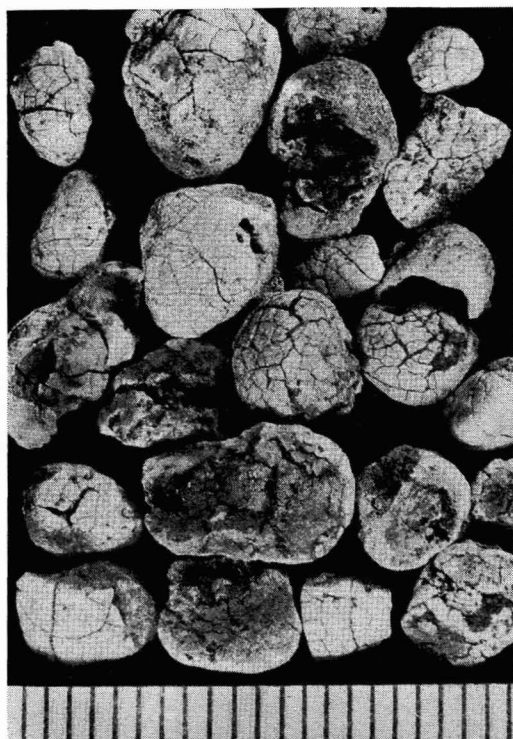


FIG. 3. Gibbsite or desilicated halloysite. Note characteristic cracked surface. Scale units in mm.

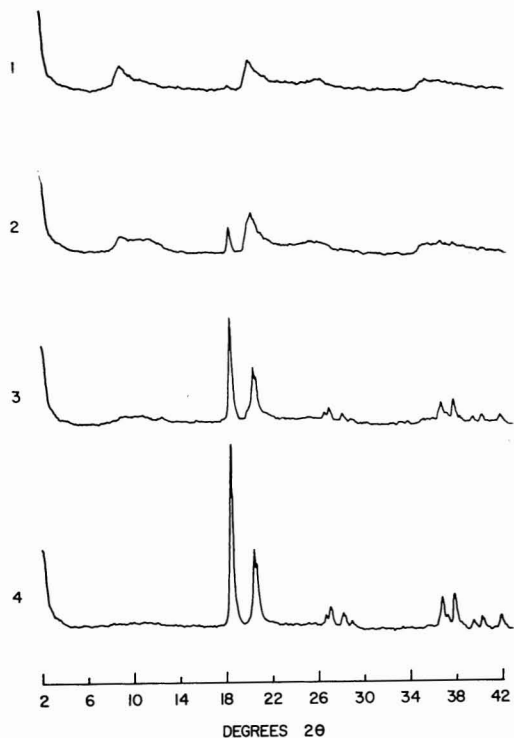


FIG. 4. X-ray diffraction (nickel-filtered, copper  $K\alpha$  radiation) diagram of veins (sample 1) and amygdules (samples 2-4) from Haiku, Maui.

gibbsite line, and detection of trace amounts of halloysite by this method in the presence of gibbsite is difficult at best. Differential thermal analysis of this sample, however, confirms identification of halloysite by the  $550^{\circ}$ – $600^{\circ}$  endotherm characteristic of halloysite which appears in all four samples.

Examination of thin sections merely confirmed the X-ray and thermal data, but clarified the genetic relation of gibbsite to halloysite. Figure 6 shows a vesicle nearly filled with halloysite. The matrix feldspar has also been altered to this mineral and there is no evidence for gibbsite.

TABLE 1

CHEMICAL COMPOSITION (IN %) OF VEINS (SAMPLE 1) AND AMYGDULES (SAMPLES 2-4) FROM HAIKU, MAUI, SHOWING RANGE IN SILICA-ALUMINA RATIO

SAMPLE NO. (as in Figs. 4, 5)	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MnO	L.O.I.	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>
1	39.42	40.58	5.55	1.40	0.13	23.85	1.649
2	36.83	44.32	2.11	0.44	0.03	16.39	1.410
3	15.29	57.33	4.30	0.48	0.08	23.85	0.453
4	6.55	64.14	1.41	0.44	0.02	28.07	0.173

Figure 7 is a photomicrograph corresponding to sample 3 in the X-ray, thermal, and chemical data. All data point to a mixture of halloysite and gibbsite. A thin section, however, shows that the gibbsite exists on the outer periphery of the

amygdules and not as an intimate mixture with halloysite.

Figure 8 represents a thin section of a thoroughly gibbsitized amygdule. Although these are not evident in Figure 8, most gibbsite amygdules are characterized by surface fractures. Figure 3 clearly shows this feature; in Figure 2 the amygdules composed predominantly of halloysite fail to show this.

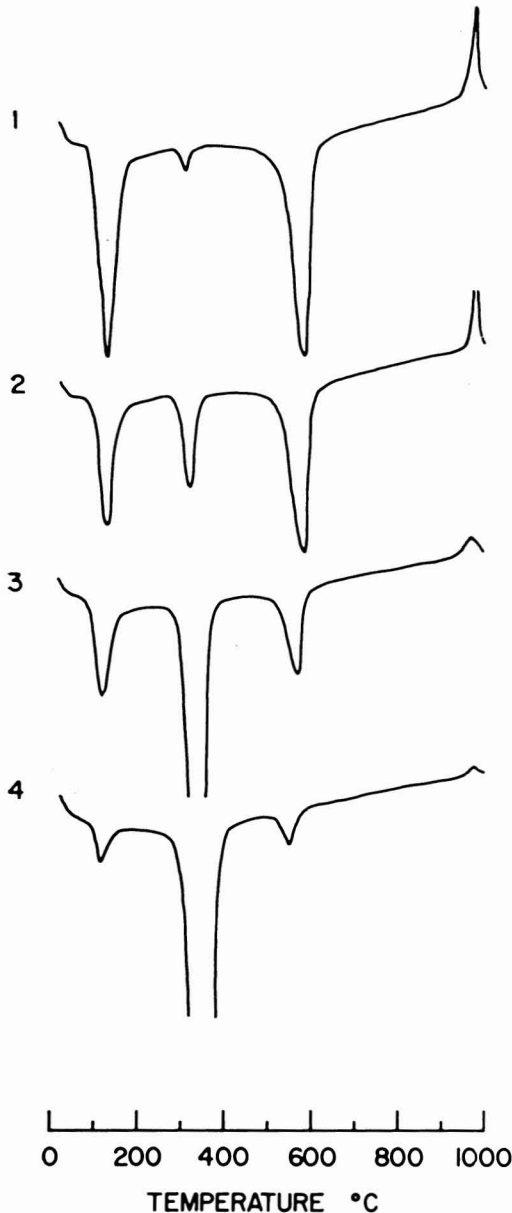


FIG. 5. Differential thermal diagrams of veins (sample 1) and amygdules (samples 2-4) from Haiku, Maui.

#### DISCUSSION

It is often difficult to distinguish halloysite from gibbsite in hand specimen. Therefore, X-ray, differential thermal, or chemical analyses are often necessary to confirm the identification. Differential thermal analysis is probably the best method for making quantitative estimates of these two constituents.

Once the minerals have been identified, op-

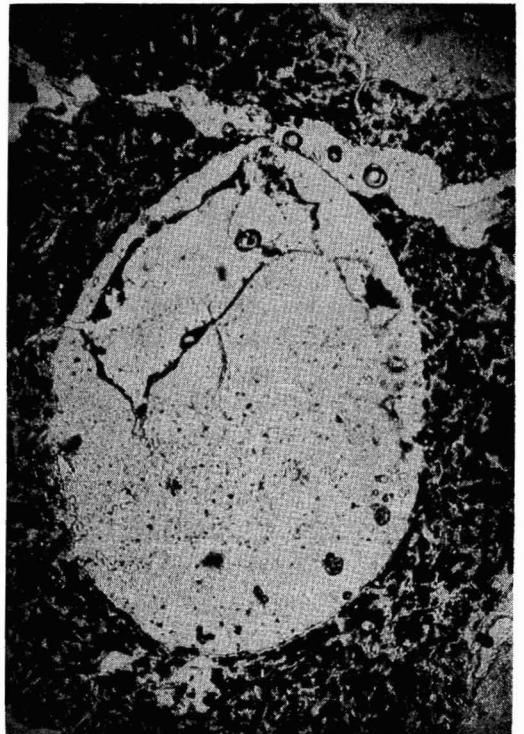


FIG. 6. Vesicle nearly filled with halloysite. Dark areas are residual grains of iron ore; clear areas in surrounding matrix are halloysite clays pseudomorph after feldspar. Plain light,  $\times 320$ .



FIG. 7. Isotropic halloysite desilicating to birefringent gibbsite along periphery of amygdule. Crossed nicols,  $\times 320$ .



FIG. 8. Completely gibbsitized amygdule. Dark area represents opaque iron oxide and pore space. Crossed nicols,  $\times 320$ .

tical methods can give insight to the relationship of these minerals to one another by their arrangement and distribution in a specimen. Thin-section studies suggest that halloysite and gibbsite are not necessarily synthesized independently of each other, but follow a predictable pattern of formation.

The source of silica and alumina for synthesis of halloysite is mainly in the feldspars. In the feldspars the aluminum ion, as well as the silicon ion, is tetrahedrally coordinated. Each tetrahedrally coordinated aluminum substituted in the three-dimensional silica network imparts to it a negative charge, which is satisfied by either sodium or calcium. Halloysite, on the other hand, consists of a sheet of tetrahedrally coordinated silica joined to an octahedrally coordinated alumina sheet through common oxygen linkages.

When a feldspar is altered directly to halloysite, forming pseudomorphs after feldspars, neither hydrated silica nor alumina need move more than a few atomic diameters to recrystal-

lize in the form of halloysite. Nevertheless, all the sodium and calcium, and a considerable portion of the silica must be removed from the volume occupied by the feldspar to accommodate the new mineral. Water incorporated into the crystal lattice of halloysite more than makes up for loss of the metallic cation and silica.

Implicit in the assumption that halloysite precipitates in vesicles is the movement of aluminum into these voids. Alumina probably moves early in the weathering of the rock as the anion  $Al(OH)_4^-$ , when the sodium ion concentration is still relatively high. In an acid environment the tetrahedrally coordinated anion is incorporated octahedrally into the halloysite lattice. Since the tetrahedrally coordinated alumina can be stabilized in acid media by silica (Iler, 1955), it is not unlikely that octahedral alumina sheet is the nucleus to which the silica sheet is joined. In systems retaining sodium and calcium, the secondary mineral is a zeolite rather than

halloysite. There is evidence in certain Hawaiian soils that zeolites do in fact weather to halloysite.

Bates et al. (1950) long ago proved the morphology of halloysite to be tubular; Hawaiian halloysites (Nakamura and Sherman, 1963) are often more closely related morphologically to the spheroidal, Japanese allophanes described by Sudo and Takahashi (1955). Critical electron microscope examination of Hawaiian halloysites should be extremely interesting.

One might expect the gibbsite content to increase with increasing proximity to the soil surface. However, samples 4, 3, 2, and 1, showing increasing halloysite content in the order given, were obtained at approximately equal depths below the surface. Mineralogical variability can be readily explained on the basis of certain weathering factors.

The gibbsite content in any unit volume of the weathering profile depends on a number of factors. In general, the gibbsite content increases with increasing proximity to the soil surface, where weathering is most intense. However, even at depths quite distant from the surface, zones exist which are highly gibbsitic by virtue of their proximity to an internal drainage channel. All other factors being equal, the permeability of the rock also controls rate of weathering.

In general, any differential volume undergoing weathering may be treated as an open system. Two distinct volumes might be given special consideration here: (1) the volume occupied by a feldspar crystal, and (2) the voids or vesicles. From the moment atmospheric pressure and temperatures are attained, the feldspar is subject to decomposition by  $\text{CO}_2$ -saturated leaching waters. If the feldspar occurs near the surface of a lava flow, the  $\text{CO}_2$  concentration is high and the reaction will be relatively rapid. At greater depths, the leaching solution is saturated with silica, alumina, sodium, and calcium, and is depleted of  $\text{CO}_2$ . This saturated solution accumulates in voids, and precipitates in the form of an appropriate secondary mineral.

The rate at which this process takes place will depend on the amount of water passing through this unit volume. In an open system, the difference between the concentration of the outgoing and of the incoming solution gives a measure of the weathering rate. In an open system, a void in the rock gains constituents early in its history; but, in the final stages of weathering, even this volume suffers loss of certain material. Gibbsite as a final weathering product is extremely stable and will resist further decomposition; thus, it accumulates to form some of the world's bauxite deposits.

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