

# Reports

## Transformation of Gibbsite to Chlorite in Ocean Bottom Sediments

**Abstract.** Numerous grains of gibbsite surrounded by zones of chlorite were found in six samples of sediment taken from Waimea Bay off the coast of Kauai, Hawaii. The chlorite has formed from the gibbsite, and growth bands in the chlorite either are parallel to chlorite-gibbsite interfaces or are concentric around small remnants of gibbsite. Aggregates were found that appeared to be composed of two or more gibbsite grains surrounded by chlorite bands that have grown together. The index of refraction of the chlorite ranged from 1.58 to 1.60 and the chlorite displayed anomalous blue interference colors. The gibbsite was formed on land under conditions of strong weathering and strong leaching. When transported to the sea, the gibbsite was deposited in a solution containing silicic acid, magnesium, potassium, and hydrogen ions, in which it is unstable. Chlorite, a stable mineral in this solution, replaced the gibbsite.

The mineral gibbsite,  $\text{Al}(\text{OH})_3$ , occurs in soils and weathered rocks throughout the state of Hawaii. It is formed by weathering of trachyte, andesite, basalt, ultrabasic igneous rocks, and andesitic volcanic ash under humid tropical conditions. It occurs in almost all Hawaiian soils formed under a mean annual rainfall greater than 1700 mm, and it occurs in amounts greater than 20 percent in soils formed from very porous rocks or ash under rainfalls greater than 2500 mm (1).

Recently (2) evidence has been obtained in Hawaii that suggests that gibbsite and kaolin produced by weathering are transformed into mica during soil formation. Most of the evidence relates to kaolin minerals, but transformations involving gibbsite seem to have occurred in very wet areas where mica-rich, gibbsite-poor topsoils are found to overlie gibbsite-rich, mica-free subsoils. Swindale and Uehara (3), following Garrels and Christ (4), have shown that these transformations are thermodynamically feasible, and are related to the values of the parameters  $\log [\text{K}^+]/[\text{H}^+]$  and  $\log [\text{H}_4\text{SiO}_4]$  for interstitial solutions in contact with the mineral phases. Recycling of potassium ions and active silica by the vegetation appears at present to be the process that maintains the relatively high values for  $[\text{K}^+]$  and  $[\text{H}_4\text{SiO}_4]$  necessary to make mica stable and kaolin and gibbsite unstable in these strongly weathered wet soils.

The values given (4) for  $\log$

$[\text{K}^+]/[\text{H}^+]$  and  $\log [\text{H}_4\text{SiO}_4]$  for seawater show that gibbsite should be similarly unstable in the sea. Thus it is to be expected that gibbsite formed by weathering on land and deposited by erosion in the sea should then be converted into kaolin, mica, or other layer silicates. To test this hypothesis, samples of marine sediments were collected in Waimea Bay off the island of Kauai, Hawaii, and opposite the mouth of the Waimea River. The watershed of this river includes soils that contain up to

80 percent gibbsite, although most of the soils and weathered rocks in the watershed are kaolinic. The sediments in the river contain only 1 to 2 percent gibbsite.

Six samples were collected in the bay from R.V. *Teritu* (Hawaii Institute of Geophysics) at depths of 38 to 525 m with a Shipex sampler. Seven samples were collected in the Waimea River from the mouth to a distance of 2.1 km upstream. In the laboratory the samples were washed free of salt and calcium carbonate, treated with  $\text{H}_2\text{O}_2$  to remove organic matter, treated with  $\text{Na}_2\text{S}_2\text{O}_4$  at pH 7.3 in a citrate buffer to remove hydrated iron oxide coatings, boiled in  $\text{Na}_2\text{CO}_3$  to remove amorphous cementing agents, and dispersed at pH 9.5 in a sodium carbonate system (5). The sand and silt and the clay fractions were separated from each other at  $2\ \mu$  with a centrifuge.

Clay fractions from the bay consisted of halloysite and complex interstratified micaceous minerals in which mica, chlorite, vermiculite, and possibly montmorillonite occurred. Gibbsite occurred in trace amounts in only two samples. Clay fractions from the river consisted of halloysite and discrete montmorillonite and mica. Gibbsite occurred in trace amounts in all samples. Comparisons of clay fractions from bay and river sediments suggested that the complex mica system in the bay had developed from montmorillonite and mica carried down by the river.

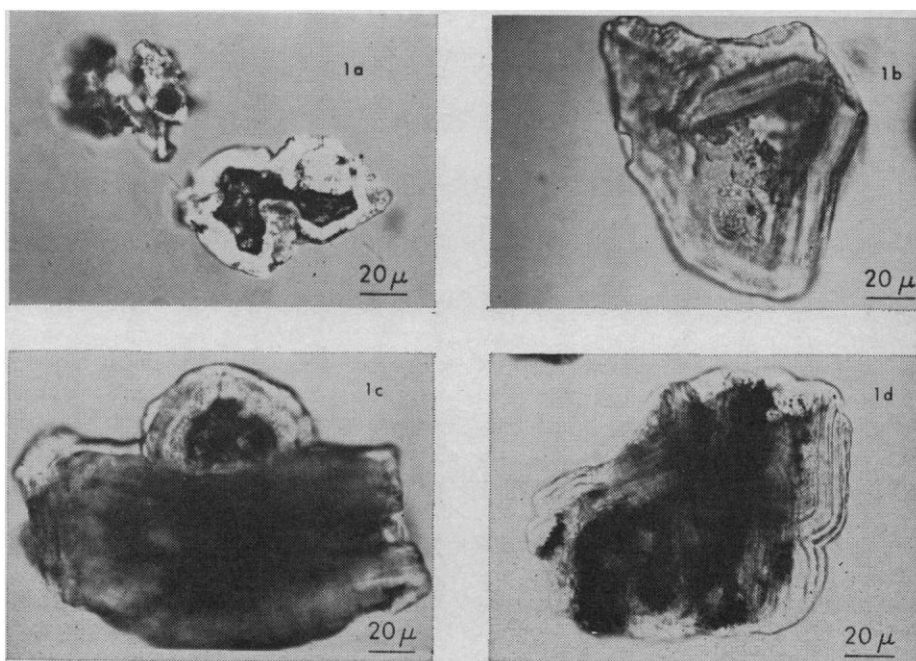


Fig. 1. Photomicrographs showing gibbsite surrounded and penetrated by authigenic chlorite. (a) Crossed nicols. (b) Plain light. (c) Crossed nicols. (d) Plain light.

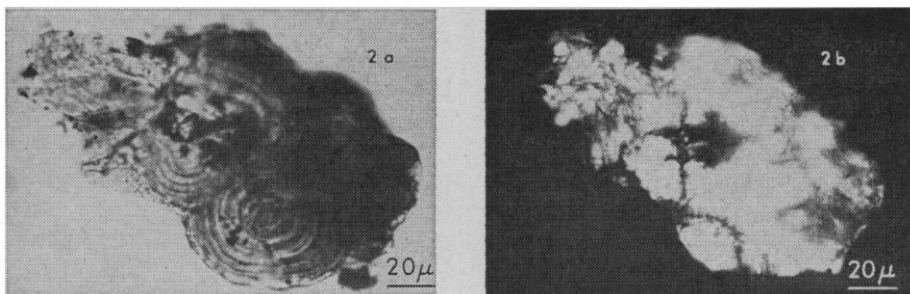


Fig. 2. Photomicrograph of a gibbsite-chlorite aggregate in plain light (a) and under crossed nicols (b).

Occasional grains of gibbsite that were stained red with iron oxides but otherwise unaltered were found in the sand and silt fractions. Most gibbsite grains, however, showed extensive alteration to chlorite. Figure 1a shows, under crossed nicols, two gibbsite-iron oxide grains, each surrounded by authigenic chlorite. One gibbsite-iron oxide grain appears black and pitted. The other appears mainly as a region of high relief. The chlorite appears as a clear zone surrounding each gibbsite-iron oxide grain and is everywhere contiguous to it. In a U-shaped area near the bottom and middle of the larger grain, the chlorite is shaded by what appear under high magnification to be growth lines. Figure 1b shows in plain light an altered gibbsite grain in which the chlorite occurs as a zone on the right-hand edge and also penetrates into the gibbsite, presumably along what was originally a crack. Growth bands occur in the chlorite. They are dark at the gibbsite-chlorite interface, then light, then dark again, and clearly follow the contour of the interface. Figure 1c shows under crossed nicols an aggregate in which two gibbsite grains appear to have become cemented together by the fusing together of chlorite zones. Growth bands are not obvious in the larger portion of the aggregate in which the gibbsite-chlorite interface is diffuse, but are clear in the chlorite surrounding the smaller gibbsite grain. The bands again follow the contour of the gibbsite-chlorite interface, but some smoothing of the contour is obvious. Growth bands are particularly clear in Fig. 1d, which was taken in plain light. Here they may represent different stages of growth. The cusp near the center of the right-hand edge probably results from the growth bands following a crack or embayment in the gibbsite crystal.

Figure 2 shows a gibbsite-chlorite aggregate in plain light and under crossed nicols. The aggregate appears

to be composed of four gibbsite grains, now almost completely replaced, surrounded by fused zones of chlorite. Concentric growth bands in the chlorite around gibbsite centers show up clearly in plain light (Fig. 2a), but are barely visible under crossed nicols (Fig. 2b). Growth bands in the bottom right-hand portion of the aggregate (Fig. 2a) have a discontinuity running down through them—similar to a fault trace in sedimentary bedding. The discontinuity is marked by particles of opaque minerals. It appears also under crossed nicols (Fig. 2b) as a line of extinction crosses. Growth bands are not obvious under plain light in the right-hand half of the aggregate, and this region is finely cross-hatched by extinction lines under crossed nicols. Presumably, along the discontinuity and in the right-hand half of the aggregate, the chlorite is fractured, and the continuous mineral is replaced by very fine, virtually isotropic micro-aggregates.

Some grains not shown in the figures showed many stringers of chlorite penetrating into the gibbsite and small clear patches of chlorite in the interior of the grains surrounding and surrounded by gibbsite. Most grains, however, showed centers of gibbsite and outside zones of chlorite with growth bands as has been shown in the figures. The growth bands may be due to cyclic concentrations of iron in the growing chlorite, although the birefringence across the chlorite is generally very uniform. The bands generally do not appear to be due to different stages of growth in the chlorite.

The gibbsite when clear had a  $\eta_x \approx \eta_y$  of 1.57 and a  $\eta_z$  of 1.59 and a positive optic sign (6). Optical properties of the chlorite were difficult to determine because the orientation was generally controlled by the gibbsite. On one band that appeared to be oriented along  $b$ ,  $\eta_b$  was equal to 1.58. Refractive indices on other chlorite zones varied from 1.58 to 1.60. Bands

with the higher indices were usually associated with gibbsite coated by iron oxide. Positive elongation signs were obtained on the extinction of the fine-grained chlorite. The clear zones showed the anomalous blue interference color so characteristic of chlorite. Pleochroism from colorless or green to dark brown was observed in some chlorite zones.

The genesis of the chlorite is readily explained. Gibbsite formed under conditions of strong weathering and strong leaching when deposited in the sea is surrounded by a solution in which it is unstable. It has been suggested (4, p. 364) that the concentrations of silicic acid, magnesium ions, potassium ions, and hydrogen ions in seawater are only slightly more than those required for the stability of numerous layer silicates including kaolin, mica, and chlorite. Thus it is not easy to predict into which layer silicate or silicates the gibbsite will be transformed, except that it is certain to be one or more of these. The environment of Waimea Bay appears to favor chlorite. Bonatti and Arrhenius (7) have reported an apparent transformation of iron oxide to chlorite in the Pacific off Baja California, Mexico.

The results given in this study provide no evidence for the rate of transformation of gibbsite to chlorite. The fact that gibbsite is seldom reported in ocean bottom sediments and never in large quantities (8) suggests that the transformation is rapid.

L. D. SWINDALE

Hawaii Agricultural Experiment  
Station, University of Hawaii, Honolulu  
POW-FOONG FAN  
Hawaii Institute of Geophysics,  
University of Hawaii, Honolulu

#### References and Notes

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6.  $\eta_x$ ,  $\eta_y$ , and  $\eta_z$  represent the index of refraction along the optical directions  $x$ ,  $y$ , and  $z$ , respectively; F. D. Bloss, *An Introduction to the Methods of Optical Crystallography* (Holt, Rinehart and Winston, New York, 1961), pp. 200-201.
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