TRAVAUX, Proceedings of the 3rd International Congress of ICSOBA , Nice, 17 - 21 September 1973

Geochemistry of gibbsite in lateritic soils and bauxite deposits

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Gibbsite is a major constituent of soils in some areas, but it is rare or absent in other areas subject to the same climate and same degree of weathering. Gibbsite is usually associated with kaolinite, goethite and quartz although quartz and gibbsite, according to physical chemical date, are not mutually stable and should not co-exist.

Two chemical conditions are recognized. Equilibrium may be reached in deeply buried bauxite deposits and in soils below the water table with restricted drainage, but gibbsite is formed only in an open system where weathering products are removed by drainage. The initial formation of gibbsite in soils and weathered rock is apparently a function of the structural chemistry of the parent material, because under humid tropical conditions plagioclase feldspar and microcline alter directly to gibbsite, and orthoclase feldspar alters to kaolinite. In Alabama these two weathering sequences were noted in the same outcrop.

1. INTRODUCTION

Gibbsite is a common constituent of soils in the humid tropics, but it is absent in many areas where climate favors lateritic development. Gibbsite occurs with quartz in some lateritic soils, although thermodynamic data show that gibbsite and quartz are not mutually stable and should not co-exist. In contrast to soils, most bauxite deposits contain practically no quartz, clay mica (illite), or other transitional soil minerals. The purpose of this report is to correlate field observations on lateritic soils and bauxite with conclusions based on laboratory data.

The field data are based on personal investigations that include weathered igneous-metamorphic rocks and soils of the southeast United States, and laterites and lateritic soils in Central and South America. Laboratory data are based on review of literature and water analyses of samples collected in Alabama.

2. CHEMISTRY

Garrels and Christ (1965, p. 352-365) show that gibbsite is relatively insoluble between pH 4.5 and 7.0, and in the K_2O-Al_2O_3-SiO_2-H_2O system they show that gibbsite is stable at

silicic acid concentration of less than log-4.7 mols per liter. They that the K-feldspar and quartz stability fields are separated from the gibbsite stability field by kaolinite. Kittrick (1969) shows gibbsite-kaolinite, kaolinite-montmorillonite-amorphous silica to be stable pairs and amorphous silica-kaolinite, amorphous silica-gibbsite and montmorillonite-gibbsite to be "forbidden pairs". Gardner (1970) calls for minor adjustments in the critical values of pH and silica concentration for formation of gibbsite, showing that gibbsite may form kaolinite only after all quartz has been removed from the system, the infiltrating water reaches a pH of at least 4.2, and the dissolved silica content is less than log -4.6 mols per liter. Haung and Keller (1972) point out that although bauxite deposits are regarded as relatively immobile and the end product of weathering, field evidence, such as gibbsite and boehmite crystals in pisolitic structure and in trails through which solutions have moved, proves the solution and precipitation of aluminum.

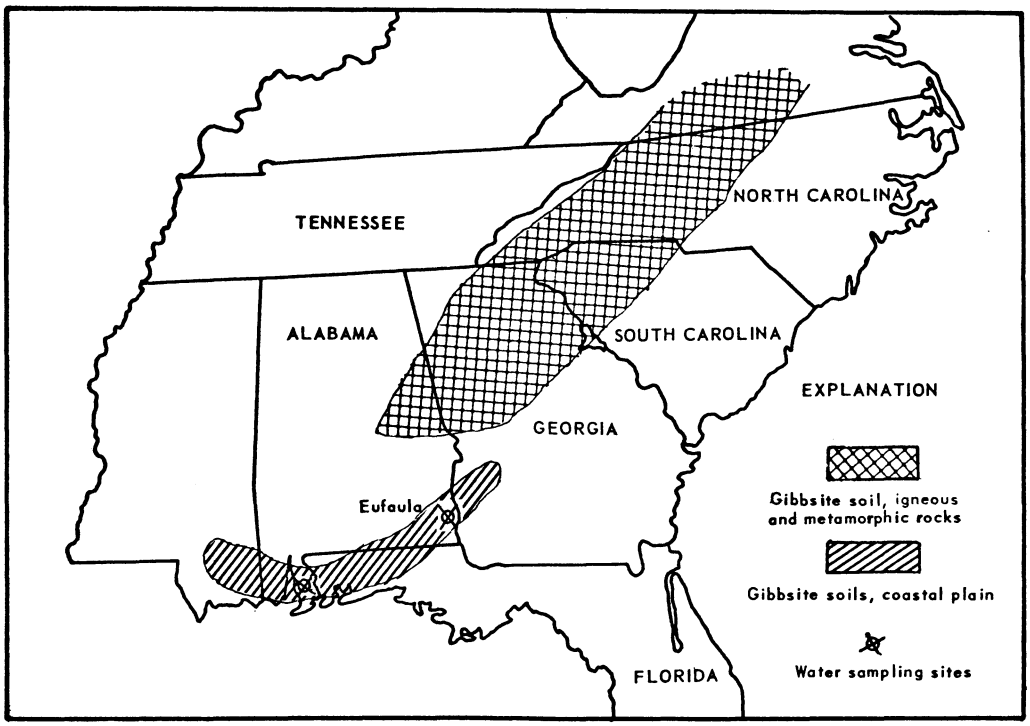
Ground-water and streams draining humid tropical soils are generally slightly acid unless there has been buffering action from limestone or other alkaline rocks. The acidity is attributed to carbonic acid formed by solution of carbon dioxide from the air and soil, and to organic acids, generally described as "humic" acids, formed during decay of organic matter (Patterson, 1971). Ong, Swanson and Bisque (1970) show that organic acids decrease the solubility of aluminum between pH 4 and 7. Their report does not show the effect of organic acids below pH 4. Baker (1973) shows high solubility of calcium and base metals such as copper, lead, and zinc in humic acids, but he shows iron to be relatively insoluble as compared to other metals, and aluminum to be less soluble than iron. Solutions used had pH of 3.0 to 3.4.

3. GIBBSITE IN RESIDUAL SOILS, SOUTHEASTERN UNITED STATES

Saprolite containing gibbsite and kaolinite has been investigated as a potential alumina source in the southeastern United States (Patterson, 1967). Prospects located in northwest North Carolina containing less than 7 percent gibbsite in quartz mica schist were referred to several aluminum manufacturing companies in 1952. The investigation reached a peak in 1957-1958, when two companies leased and drilled property near Greenville, South Carolina that contained 10 to 30 percent gibbsite. The reconnaissance investigation covering the southeast quarter of the United States involved collecting and analyzing thousands of samples from highway exposures and shallow drill holes. Clarke (1972) reports that gibbsite concentration is controlled by mineral composition of the parent rock and by topography. Gibbsite replaces plagioclase feldspars in well-drained upland soils; whereas, orthoclase subjected to the same weathering conditions alters to kaolinite. This is clearly illustrated in one outcrop where orthoclase in a small pegmatite has partly altered to kaolinite and plagioclase in the quartz diorite gneiss host rock has altered largely to gibbsite. Quartz veinlets and quartz crystals in the weathered gneiss show evidence of leaching, but quartz remains the predominant mineral. This paragenesis substantiated Harrison's (1931) classic work on rock weathering.

No significant difference was noted in weathering of the sodium and calcium plagioclase. Both alter to gibbsite in the well-drained soils. Although orthoclase feldspars alter to kaolinite, microcline feldspars alter directly to gibbsite. The formation of gibbsite from microcline without passing through a kaolinite stage was noted in deeply weathered granite gneiss at Lake Toxaway, North Carolina, in the Blue Ridge highlands. Correia Neves, Lopez Nunes, and Lucus (1969) also reported microcline in pegmatites of Zambezia weathering directly to gibbsite.

In the Arkansas bauxite district orthoclase feldspar in weathered syenite has altered to kaolinite, with the degree of weathering ranging from kaolinite coating on crystal faces



Location of gibbsite soil in southeast United States

to complete kaolinization. Gibbsite is restricted to the bauxite zone that was controlled by the early Eocene surface and drainage.

In Alabama clay mica (illite) and interlayered vermiculite-illite occur with gibbsite in the saprolite derived from the more mafic rocks such as biotite gneiss, quartz diorite and diabase. Field relationship indicates they are transition minerals and yield kaolinite on prolonged weathering.

4. GIBBSITE IN COASTAL PLAIN SOILS

Gibbsite and kaolinite also occur as soil minerals in weathered arkosic sand of the Citronelle Formation of Pliocène age in the Alabama and west Florida Gulf coastal plain (Clarke, 1971). The gibbsite-kaolinite ratio is zoned regionally. Gibbsite is the main clay-size mineral in an arc-shaped central zone and kaolinite is the most abundant clay mineral in the ring surrounding the gibbsite zone. A mixed clay containing vermiculite-illite and clay mica is associated with the gibbsite soils, but these are regarded as transition minerals because they occur as minor constituents in the main gibbsite zone and major constituents beyond the kaolin rim. Montmorillonite has not been identified in the gibbsite soil profile.

The coastal plain gibbsite soils are characterized by an extremely thick A2 soil horizon above the gibbsite soil that ranges from about 20 centimeters to more than 3 meters thick. This is a leached zone consisting of light-gray sand containing very little organic matter. The gibbsite soil horizon is generally a brownish red (5 R4/6 to 10 R4/6), 2 to 4 meters thick, slightly indurated, and overlies loose sand. Most of the gibbsite occurs in the clay-size fraction, but gibbsite concentrations do occur in some outcrops.

There is no observed relationship between the iron and gibbsite content. Iron occurs generally as hematite and occasionally as goethite in lateritic up-land soils found throughout the entire coastal plain.

5. LATERITIC SOILS AND LATERITES, CENTRAL AND SOUTH AMERICA

The gibbsite residual soils in Guatemala, Costa Rica, Panama and Colombia are similar to the residual gibbsite soils of the southeast United States, except in degree of weathering. They were derived from volcanic ash ranging from andesitic to basaltic composition. There is less quartz in these soils, which reflects both the degree of weathering and mineral composition of the parent rock. These soils are composed of gibbsite, kaolinite and goethite or hematite. Gibbsite occurs both as concretions and in the clay-size fraction. No hard iron laterites were found.

In Panama, weathered marine shales were sampled. Although the shale had been subjected to the same weathering as the gibbsite soils derived from volcanic ash, they contained practically no gibbsite.

6. FIELD OBSERVATIONS — BAUXITE MINES

In Eufaula, Alabama, the bauxite ore occurs in a series of bauxite-kaolin deposits where laterization was suspended by rapid marine submergence and the district was then covered by sediments. The deposits were in various stages of laterization and none of the deposits can be considered the end product of leaching. The bauxite was formed from clay deposited in karst lakes at the end of the Paleocene and beginning of the Eocene time (Clarke, 1966). The weathered igneous-metamorphic rocks of the southeast United States were the original source of the sediments.

The general structure of the bauxite deposits is an elongated, tabular bauxite core that grades outward through bauxitic clay to kaolin. The kaolin grades laterally to sandy clay. Sand surrounds, underlies, and separates the clay core from the limestone. The bauxite center is composed of gibbsite with a minor amount of kaolinite; the bauxitic clay contains more kaolinite than gibbsite, but neither the bauxite or bauxitic clay contains a significant amount of quartz. Gibbsite and kaolinite are the only aluminum-bearing minerals that have been identified in the bauxite-bauxitic clay zone.

The surrounding and underlying clays are a mixture of kaolinite and clay mica (illite) with minor amounts of quartz sand and muscovite. There is a gradation of clay mixtures from sandy clay to nearly pure kaolinite. Quartz grains in the clay adjacent to the kaolin show evidence of solution. Gibbsite was not detected in any sample containing quartz or any clay minerals other than kaolinite.

7. GROUND WATER SAMPLING

Patterson (1971, p. 29, 35) collected six water samples from Hawaii saprolite where alumina is accumulating as a gel. The water is slightly acid, with pH ranging from 4.6 to 5.6,

Water analyses in parts per million

Season, sample number	*Temp. °C*	*pH*	*SiO_2*	*Al^3*	*Mg*	*Na*	*K*	*Description, location*
Winter								
1	8.0	6.4	3.8	0.0	0.6	4.4	1.0	Gibbsite soil, SW Ala.
2	11.7	5.9	3.2	.0	.4	1.0	1.8	Gibbsite soil, Eufaula
3	17.8	5.5	3.3	.0	.4	.8	1.0	Gibbsite soil, Eufaula
Summer								
4	33.3	5.8	3.6	.0	.3	2.0	.2	Gibbsite soil, SW Ala.
5	26.7	5.4	3.4	—	.5	3.1	.3	Gibbsite soil, SW Ala.
Winter								
6	10.5	6.1	4.4	.1	.6	3.0	.6	Spring, SW Ala.
7	17.2	5.6	4.4	.0	.3	.7	.5	Spring, Eufaula
Summer								
8	28.4	6.0	6.1	.0	.4	2.1	.3	Spring, SW Ala.
9	18.6	5.2	5.0	.0	.3	.7	.1	Spring, Eufaula
Summer								
10	24.6	3.9	5.3	.1	.9	2.7	.1	Swamp, SW Ala.
Winter								
11	7.8	5.1	1.9	.0	.3	.6	.4	Dixon No. 2 bauxite mine
12	7.8	3.4	8.0	32	7.0	.8	1.2	Espy No. 51 bauxite mine
Summer								
13	27.8	4.8	2.2	.0	.2	.6	.1	Dixon No. 2 bauxite mine
14	27.8	3.6	5.8	21	4.8	.6	.9	Espy No. 51 bauxite mine

Analyses by E. R. German, U. S. Geological Survey

whereas water collected in the fresh basalt below is alkaline, from pH 7.6 to 7.8. The SiO_2 content of water in the saprolite ranged from 1.2 to 4.1 parts per million (ppm), averaging 2.7 ppm, the Al_2O_3 ranged from 0.01 to 0.12 ppm, averaging 0.05 ppm. Water collected from the unweathered basalt after passing through the soil horizons contained 32 to 42 ppm silica with no increase in alumina.

A series of water samples was collected in south Alabama from seepages in the gibbsite soil, springs, swamps and abandoned bauxite pits. Samples were collected in winter and summer to reflect difference in climate. Part of the samples were collected in Baldwin County in southwest Alabama near the west end of the coastal plain gibbsite soil belt and the rest of the samples came from the Eufaula bauxite district. The gibbsite soils were collected at a higher topographic and stratigraphic horizon than the bauxite. The sample results are given in table 1.

Samples 1 through 5 represent seepage in gibbsite soils collected two days after heavy rains. The alumina content was below detection limits and the silica content ranged from 3.2 to 3.8 ppm. No difference was noted between samples collected in summer and winter. Samples 6 through 9 were collected from springs where the water had passed through the gibbsite soil zone and moved through a loose sand horizon to a clay bed. The samples showed an increase in silica compared to the seepage samples, and the samples collected in the summer contained significantly more silica.

Sample 10, collected from a ditch draining a swamp, had a reddishbrown tint due to organic acids (humic acids). It contained a detectable amount of aluminum; more than the springs that contained no humic acids.

Samples 11 and 13 were collected from a bauxite pit in the Eufaula district where the ore is a mixture of gibbsite and kaolinite containing less than 1 percent iron and no lignite. Samples 12 and 14 were collected from a pit where the water was in contact with bauxite overlain by lignite containing abundant pyrite. The pyrite was oxidizing, causing an acid condition.

DISCUSSION

Gibbsite occurs with quartz, clay mica and mixed clay minerals only in well-drained soils. This is an open system where there is movement of water transporting the products of leaching out of the system, and more silica is leached than alumina.

Only one analysis of water collected in the Hawaiian soils (Patterson, 1971, p. 29) plotted within the gibbsite field of the kaolinite-gibbsite stability diagram given by Garrels and Christ (1965, p. 361). The other samples and the water samples collected in the gibbsite soils of Alabama contained higher silica concentrations than the log —4.7 silicic acid limits of Garrels and Christ or the —4.6 limits computed by Gardner (1970). Gibbsite in the soils should be altering to kaolinite at these concentrations, but water collected from springs that has passed through the gibbsite soil horizons contained considerably more silica and no significant increase in alumina.

Water analyses and mineral assemblages present in gibbsite soils indicate that in an open system the ability of leaching solutions to dissolve additional silica is more important than the total silica in solution. Also, in an open system, gibbsite may occur with quartz, clay mica, and interlayered vermiculite-illite, but in a closed system where there is restricted drainage, gibbsite does not occur with these same minerals. Mineral assemblages of most bauxite deposits that are now below the water table, with restricted drainage, indicate a state of equilibrium or a closed system.

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Publication authorized by State Geologist, Alabama Geological Survey