Carbonate Inhibits the Crystallization of Aluminum Hydroxide in Bauxite

Abstract. *Although the role of anions such as nitrate, chloride, and sulfate in inhibiting the crystallization of aluminum hydroxide in soils and geological deposits is generally accepted, the dramatic effect of the carbonate ion in maintaining aluminum hydroxide gel in the amorphous form has been overlooked by most earth scientists. Examination of bauxite occurrences suggests that the inhibiting effect of carbonate is quite apparent in the smaller grain size of gibbsite in karstic bauxite deposits as compared to that in lateritic bauxite. Scarbröite, a crystalline aluminum hydroxy carbonate, has been observed in rare instances. It is suggested that the highly reactive carbonate-containing aluminum hydroxide gels used as pharmaceutical antacids are amorphous or poorly crystalline forms of scarbröite. The effect of the sulfate anion is also apparent in certain bauxite deposits where dissolution of gibbsite by sulfuric acid has resulted from the oxidation of pyrite, with subsequent reprecipitation of gibbsite.*

Increasing concern about nonrenewable resources has sparked new interest in the occurrence of $Al(OH)_3$ in soils and mineral deposits. Under intense weathering conditions, such as those responsible for the formation of lateritic soils and bauxite, the end product of the reaction sequence initiated by the dissolution of aluminum and the precipitation of amorphous $Al(OH)_3$ is the crystalline phase gibbsite or, more rarely, norstrandite. Mild weathering conditions and associated factors may produce amorphous or poorly crystalline $Al(OH)_3$ in the form of coatings or hydroxy aluminum polymers.

The role of anions such as Cl^- and SO_4^{2-} in inhibiting the crystallization of amorphous $Al(OH)_3$ has been demonstrated (*1*). Organic acids such as citric acid also inhibit the crystallization of $Al(OH)_3$ (*2*).

The possible role of the dissolved carbonate species in inhibiting the polymerization of $Al(OH)_3$ appears to have been overlooked by most earth scientists, even though CO_3^{2-} and HCO_3^- are among the most common components of the soil-air-water interface. Although HCO_3^- may be more abundant in the *p*H range likely to occur in most natural waters, carbonate complexes can readily occur in the presence of either CO_3^{2-} or HCO_3^-. Recent work on $Al(OH)_3$ gels used as pharmaceutical antacids (*3-5*) has established the influence, not only of Cl^- and SO_4^{2-}, but also of CO_3^{2-} on the reactivity and stability of these systems. In particular, White and Hem (*6*) have provided spectroscopic evidence that a considerable proportion of the carbonate in highly reactive carbonate-containing $Al(OH)_3$ gels is bound to the aluminum in a unidentate complex (that is, aluminum forms a covalent bond with one oxygen of CO_3^{2-}). Even though HCO_3^- solutions were used in the preparation of these $Al(OH)_3$ gels, the infrared spectra indicated that CO_3^{2-} is the only dissolved carbonate species present in significant amounts in the $Al(OH)_3$ gel. For this reason, CO_3^{2-} was considered to be the agent responsible for inhibiting the crystallization of this gel.

Neither Cl^- nor SO_4^{2-} is as effective as CO_3^{2-} in stabilizing the $Al(OH)_3$ gel, and the reactivity of the gel with protons may decrease to 25 percent of the theoretical reactivity during aging at 25°C for 6 months (*4, 5, 7*). On the other hand, carbonate-containing gels, even after aging for several years, are fully reactive (dissolve completely in $0.1N$ HCl in 1 hour at 37°C) and have a relatively rapid reaction rate as measured by the T_{50}, the time required to add 50 percent of the total $1.0N$ HCl needed to neutralize the aluminum hydroxide gel in a *p*H-stat titration (*4, 8*).

The aging or polymerization process is accelerated by treatments such as the removal of anions, dehydration, and heating. As a consequence, the sampling and preparation techniques commonly used in studies of soils and mineral deposits preclude measurement of the properties of highly reactive amorphous $Al(OH)_3$ present in the sample in the natural state. Until precautions are taken to prevent such alterations, interpretation of measurements intended to characterize the amorphous and poorly crystalline forms of $Al(OH)_3$ present in the sample in the natural state is highly questionable.

The subtle changes produced in amorphous $Al(OH)_3$ by sampling and preparation techniques are not readily detected by the usual x-ray diffraction or infrared techniques. Thus, a lack of sensitivity in detection techniques has helped to obscure the presence of reactive amorphous $Al(OH)_3$ in soils and geological deposits.

The rate of reaction of $Al(OH)_3$ with protons, used in the pharmaceutical evaluation of antacids (*9*), has been shown to be a sensitive method for continuously monitoring the changes in the $Al(OH)_3$ gel that take place with aging. Kerkhof *et al.* (*8*) have recently described an even more sensitive method for following the stages of crystallization in $Al(OH)_3$ gels produced by aging. On the basis of the foregoing statements, $Al(OH)_3$ occurring in environments having significant concentrations of SO_4^{2-} and CO_3^{2-} or HCO_3^- would be expected to show evidence of the inhibition of polymerization or crystallization.

In a recent study of gibbsite in more than 100 bauxite samples from the major bauxite deposits of the world, Bárdossy *et al.* (*10*) showed that there is a great difference in the grain size and crystallinity of gibbsite in young karstic and lateritic bauxites. Examination by transmission electron microscopy and scanning electron microscopy showed that the grain size of gibbsite in young uncovered karstic deposits (Jamaica, Haiti, and the Dominican Republic) varies from 0.05 to 0.5 μm, the most common values being from 0.1 to 0.25 μm. In the so-called "high level" lateritic bauxites—that is, deposits occurring at altitudes from 400 to 2000 m above sea level (India, Guinea, Ghana, and Brazil)—the grain size varies from 10 μm to 1 to 2 mm. Both groups are essentially gibbsitic bauxites. In the "low level" type lateritic bauxite deposits such as those at Weipa, Australia, the gibbsite grain size is somewhat smaller, ranging from 0.5 to 20 μm.

We suggest that the small grain size of gibbsite in the karstic bauxites is the result of the inhibition and retardation of the crystallization of the $Al(OH)_3$ gel caused by the dissolved carbonate species in the water percolating through the bauxite deposits. Differences in the crystallinity of gibbsite that may be attributed to this effect have been reported by Bárdossy *et al.* (*11*).

The formation of large, well-crystallized gibbsite particles in high-level deposits appears to be favored by extremely good drainage conditions under neutral to slightly acid *p*H values and negligibly small concentrations of dissolved carbonate species. The occurrence of amorphous material in bauxites is rather rare; Bárdossy (*12*) observed the greatest amounts of amorphous $Al(OH)_3$ in the youngest karstic bauxite deposits of the Pacific (Loyalty Islands and Niué Island, south of Samoa).

Amorphous or very poorly ordered $Al(OH)_3$ can also be produced by SO_4^{2-}.

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Such material occurs as secondary nests in some bauxite deposits, and it forms in an acid environment. When the overburden is eroded from pyrite-bearing bauxite deposits, strong oxidation of this iron sulfide mineral takes place and sulfuric acid is formed. This acid dissolves most of the iron minerals and in some places even part of the alumina minerals. As the downward-percolating solution is neutralized several meters below, Al(OH)$_3$ gel precipitates and forms white nests within the lower part of the deposit. Bárdossy (*12*) found such nests 2 to 5 cm in diameter below oxidized pyrite-bearing bauxites in mines at Szõc and Nyirád, Hungary. They contained 10 to 60 percent amorphous Al(OH)$_3$ gel together with poorly crystallized gibbsite. Similar precipitations occur at the contact of the footwall limestone or dolomite at Sümeg and Cserszegtomaj, Hungary. The amorphous material forms nests in the precipitated gibbsitic layer 2 to 10 cm thick; here the neutralizing effect of the carbonate rocks is quite obvious.

There are no reported minerals which exhibit infrared spectra identical to that of carbonate-containing Al(OH)$_3$ gel. However, Duffin and Goodyear (*13*) have reported data for scarbröite, a crystalline aluminum hydroxy carbonate with a formula Al$_2$(CO$_3$)$_3$ · 12Al(OH)$_3$. Nemecz and Varju (*14*) found scarbröite occurring in small nests at the contact of the footwall dolomite in the deposit of clayey bauxite at Pilisvörsösvar, Hungary. Serna *et al.* (*15*) have reported that the infrared spectrum of scarbröite is similar to that of carbonate-containing Al(OH)$_3$ gel. They suggested that the difference between carbonate-containing Al(OH)$_3$ gel and scarbröite is particle size along with very slight differences in ordering, and noted that scarbröite had been found associated with gibbsite, the final crystalline form in the aging of Al(OH)$_3$ gel.

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Djurleite (Cu$_{1.94}$S) and Low Chalcocite (Cu$_2$S): New Crystal Structure Studies

Abstract. *Additional x-ray structure studies on low chalcocite generally confirm the previously reported structure but show that either disorder is present or the true space group is not* P2$_1$/c *but* Pc, *four of the 96 copper atoms in the monoclinic unit cell taking on twofold (linear) coordination. The crystal structure of djurleite has been solved in space group* P2$_1$/n, *the monoclinic cell having parameters* a = *26.897,* b = *15.745, and* c = *13.565 angstroms; β = 90.13°; and a content of 248 copper and 128 sulfur atoms. Of the 62 different copper atoms in the structure, 52 are in threefold, triangular coordination with sulfur, nine in tetrahedral, and one in linear coordination.*

Chalcocite, a major ore mineral of copper having the essential composition Cu$_2$S, has long been the subject of structure study, but only in 1971 was its complex crystal structure finally revealed (*1*). A second phase of closely related chemical composition Cu$_{1.96}$S, which was discovered in an x-ray study of the Cu-S system by Djurle in 1958 (*2*), was established as the mineral species djurleite in 1962 (*3*). Since then, much of what was formerly considered to be chalcocite has been found to be actually djurleite; the two minerals are both very common and frequently intermixed. In the field of solid-state physics, the significance of the phase relationship of chalcocite and djurleite in the function of cadmium sulfide solar cells has been emphasized (*4*). Thus, the structures and crystal chemistry of these phases, which are very complex, are of considerable interest in many areas. I previously reported the structure of low chalcocite (*1*); I now report the determination of the crystal structure of djurleite. The essential results of the structure determination are given below.

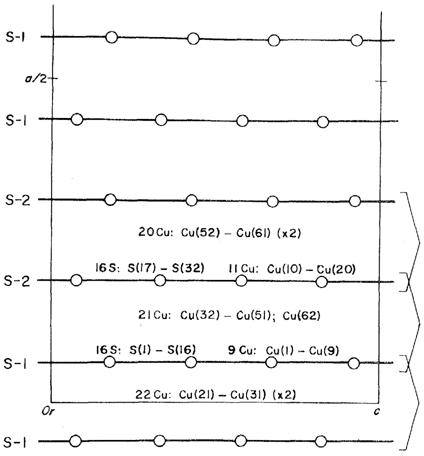

Fig. 1. View of the djurleite structure along the *b* axis, showing schematically the two types of hexagonal-close-packed sulfur layers S-1 and S-2 (on edge). The distribution of the 32 sulfur and 62 copper atoms is indicated.

My determination of the crystal structure of low chalcocite was based on a monoclinic unit cell containing 96 Cu$_2$S (*1*). Continued study of this complex structure has shown that although the reported structure is generally correct, either there is disorder in the structure or the true space group is *Pc* rather than *P*2$_1$/*c*. This ambiguity is brought about by the behavior of two of the 24 copper atoms in the asymmetric unit of the structure in *P*2$_1$/*c*, each of which splits into two types of atom, one having triangular coordination and one having linear (twofold) coordination. A very similar situation was found in the synthetic compound Bi$_2$Cu$_3$S$_4$Cl by Lewis and Kupčík (*5*). The best conventional reliability index *R* that could be attained (with absorption corrections) for a centrosymmetric, isotropic model for low chalcocite is 0.157; the centrosymmetric anisotropic model refined to 0.107. The latter refinement revealed extreme anisotropy for Cu(15) and Cu(19), strongly indicating a dual nature for these atoms.

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