

# Scarbroite, $\text{Al}_5(\text{OH})_{13}\text{CO}_3 \cdot 5\text{H}_2\text{O}$ , compared with gibbsite and hydrotalcite

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**SUMMARY.** The composition of scarbroite, written in the form  $\text{Al}_5(\text{OH})_{13}\text{CO}_3 \cdot 5\text{H}_2\text{O}$ , suggests close crystal-chemical relations to gibbsite and to hydrotalcite and kindred minerals. Parametral relations  $a(S) \approx 2b(G)$  and  $3b(S) \approx 5a(G)$ ,  $S$  = scarbroite,  $G$  = gibbsite, are obtained and are consistent with a hydroxy Al layer structure and interlayer carbonate anions and water molecules. Thermal transformations show two discrete hydrated phases with layer spacings near 8.5 and 7.65 Å and a third phase with initial spacing 6.65 Å which decreases progressively to 5.5 Å over the temperature range 100°–250 °C as decomposition proceeds. No clear break is observed between dehydroxylation and decarbonation.

ALTHOUGH scarbroite was recognized as a distinct mineral by Vernon (1892), it received little detailed attention until Duffin and Goodyear (1957, 1960) reported X-ray diffraction, chemical, infrared and thermal data, and Brindley and Comer (1960) in a parallel study provided electron microscope and single crystal electron diffraction data. By combining the X-ray and the electron diffraction results, Duffin and Goodyear derived a triclinic unit cell with  $a$  9.94,  $b$  14.88,  $c$  26.47 Å,  $\alpha$  98.7°,  $\beta$  96.5°,  $\gamma$  89.0°. With these parameters, a good agreement was obtained between observed and calculated lattice spacings for fifteen observed reflections. A possible structure for scarbroite was not obtained, but Duffin and Goodyear (1960, p. 361) remarked that it was 'tempting to postulate a layer structure for scarbroite consisting of  $\text{Al}(\text{OH})_3$  layers as found in gibbsite . . .', but they carried the enquiry no further.

A renewed interest in scarbroite has been stimulated by a possible close relationship to hydrotalcite. From the chemical data provided by Duffin and Goodyear, and the recognition of simple parametral relations between scarbroite and gibbsite, it seems likely that the structure of scarbroite contains hydroxy aluminum layers with interlayer carbonate anions and water molecules analogous to the hydroxy Mg, Al- layers with interlayer carbonate anions and water molecules in hydrotalcite. To explore this possible relationship further,

the variation of  $d(001)$  for scarbroite, which will be called the basal spacing, with temperature has been examined and results similar to those for hydrotalcite have been obtained. However, these similarities must not obscure some important dissimilarities. Hydrotalcite contains positively charged hydroxy layers because  $\text{Al}^{3+}$  ions replace  $\text{Mg}^{2+}$  ions in the brucite-like layers; scarbroite cannot generate positively charged layers by a similar mechanism. The possibility that scarbroite may be a dioctahedral equivalent of the hydrotalcite group of minerals is an interesting question.

Several references to scarbroite have been made in recent literature. Serna *et al.* (1978*a, b, c*) have mentioned scarbroite in discussions of carbonate-containing hydroxy-aluminum antacids for pharmaceutical purposes. Bardossy and White (1979) have suggested that scarbroite may play a role in modifying the crystallization of aluminum hydroxides in bauxites and have mentioned that Nemeč and Varju (1967) found scarbroite or a similar material at the contact of a footwall dolomite and a clayey bauxite in Hungary.

*Scarbroite compared with gibbsite.* The  $a$  and  $b$  parameters of scarbroite are related to those of gibbsite by the following relations:

$$\begin{aligned} a(S) \ 9.94 \text{ \AA} &\approx 2b(G) = 2 \times 5.078 = 10.16 \text{ \AA} \\ 3b(S) \ 44.64 \text{ \AA} &\approx 5a(G) = 5 \times 8.684 = 43.42 \text{ \AA} \\ 3ab(S) \ 443.7 \text{ \AA}^2 &\approx 10ab(G) = 441.1 \text{ \AA}^2 \end{aligned}$$

where  $S$  = scarbroite,  $G$  = gibbsite, and the gibbsite parameters are those given by Saalfeld and Wedde (1974). The areas  $3ab(S)$  and  $10ab(G)$  are practically identical so that a close similarity in hydroxyl-packing arrangements can reasonably be expected in the two structures. The 3:5 relationship between  $b(S)$  and  $a(G)$  may be interpreted as follows: In gibbsite the quasi close-packed arrangement of hydroxyl ions is such that they lie more or less in lines parallel to  $a(G)$  at intervals of about  $a/3$ ; the idealized arrangement is shown in fig. 1. A similar close-packed arrangement is possible in

scarbroite with five such intervals in the  $b(S)$  parameter. The distribution of the Al ions, however, cannot be exactly the same in the two structures and will be discussed further in the following section.

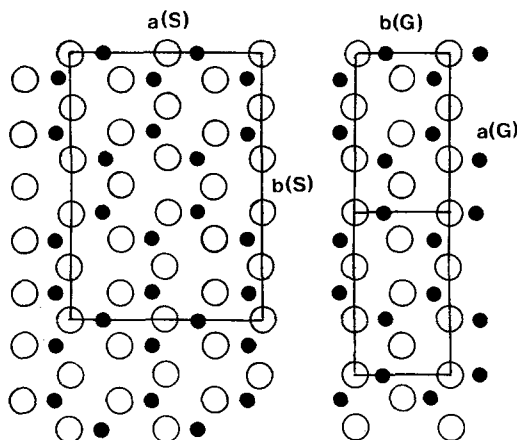


FIG. 1. Comparison of unit cell parameters of scarbroite (left) and gibbsite (right). Large open circles show close-packed plane of hydroxyl ions in gibbsite and a suggested similar arrangement in scarbroite. Small solid circles show the arrangement of Al ions in gibbsite and a possible similar arrangement in scarbroite. Observe that in gibbsite the Al ions form a hexagonal network, but in scarbroite a more densely packed arrangement is suggested (see text).

*The composition of scarbroite.* The empirical formula of scarbroite given by Duffin and Goodyear was based on a chemical analysis by Chalmers for which no details were given. A check has therefore been made on the principle components. A sample of scarbroite was selected which gave the clearest X-ray diffraction pattern. A sample equilibrated under room conditions, temperature near 22 °C and relative humidity near 30%, was analysed for aluminum by Dr A. Tsunashima by atomic absorption analysis using a lithium borate fusion method and 99.99% Al metal as a standard. The result, 47.8%  $\text{Al}_2\text{O}_3$ , is close to that of Chalmers, 45.7%  $\text{Al}_2\text{O}_3$ . The  $\text{CO}_2$  content was determined by Dr P. Deines by a volumetric method using 100% phosphoric acid. Two separate determinations gave 6.9 and 7.2%  $\text{CO}_2$  which are near the previously reported value of 7.9%. A thermogravimetric analysis recorded at 2 °C/min by Mr G. Zimmerman gave a weight loss of 37.5% at 700 °C which can be compared with 44% at 550 °C given by Duffin and Goodyear using longer heating periods, and 45.8% for  $\text{H}_2\text{O} + \text{CO}_2$  found by Chalmers. The present value

is smaller probably because of initial conditions; a weight loss of 11% at 100 °C was obtained as compared with 16% given by Duffin and Goodyear and this difference of 5% accounts for most of the difference found at higher temperatures.

From these results it appears that the empirical formula  $\text{Al}_2(\text{CO}_3)_3 \cdot 12.9\text{Al}(\text{OH})_3 \cdot 15.6\text{H}_2\text{O}$  given by Duffin and Goodyear is substantially correct. This formula can be written in a simple ionic form if  $12.9\text{Al}(\text{OH})_3$  is treated as  $13\text{Al}(\text{OH})_3$ . The formula then becomes  $\text{Al}_{15}(\text{OH})_{39}(\text{CO}_3)_3 \cdot 15\text{H}_2\text{O}$  or  $\text{Al}_5(\text{OH})_{13}\text{CO}_3 \cdot 5\text{H}_2\text{O}$  and is similar to that of hydroxalcite,  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ . This comparison suggests that scarbroite may be a dioctahedral analog of hydroxalcite, with gibbsite-like hydroxide layers in place of trioctahedral, brucite-like layers.

A possible correlation of the scarbroite formula with a gibbsite-like hydroxy-aluminum layer structure can now be attempted. Gibbsite contains 4Al and 12(OH) ions per layer per unit cell, and with the same packing density the unit cell of scarbroite would contain 13.33 Al and 40(OH) ions per layer (see fig. 1). These numbers are close to  $\text{Al}_{15}(\text{OH})_{39}$  as given by the composition of scarbroite. Possible layer and interlayer compositions for scarbroite are as follows: Layer composition,  $[\text{Al}_{15}(\text{OH})_{39}\square]^{6+}$ ; interlayer composition,  $[3(\text{CO}_3) \cdot 15\text{H}_2\text{O}]^{6-}$ . Alternatively a layer composition of  $[\text{Al}_{14}(\text{OH})_{39}\square]^{3+}$  and an interlayer composition of  $[\text{Al}(\text{CO}_3)_3 \cdot 15\text{H}_2\text{O}]^{3-}$  can be considered and fig. 1 shows a possible distribution with  $\text{Al}_{14}$  per unit cell. A vacant or  $\text{H}_2\text{O}$ -filled position in the layer structure seems necessary to give layer and interlayer charges of the form  $3n$ . At present, no clear choice can be made between the two suggested arrangements, or other possible but less simple arrangements. The first arrangement, with  $[\text{Al}_{15}(\text{OH})_{39}\square]$  in the layer structure, gives an interlayer involving only carbonate anions and water molecules similar to that in hydroxalcite. The second arrangement with  $[\text{Al}_{14}(\text{OH})_{39}\square]$  in the layer structure requires less deviation from a gibbsite-like layer and a lower layer charge, but one Al ion is transferred to an interlayer position. On the basis of the parametral relations and the mineral composition, it is not possible at present to go further than to suggest that scarbroite probably contains positively charged, gibbsite-like hydroxy layers with interlayer carbonate anions and water molecules similar to the arrangement in hydroxalcite.

*Thermal behaviour of scarbroite.* A sample of scarbroite in a thin layer on a glass slide was heated for periods of about 2 hr at progressively higher steady temperatures at intervals of about 10 °C. The possibility of rehydration in hydrous atmospheres also

was studied. Samples were examined by X-ray diffraction at room temperature immediately after each thermal treatment. Above 500 °C, samples were heated in platinum crucibles and then examined by X-ray diffraction.

The results are summarized in fig. 2, where fig. 2A shows the observed basal spacings and fig. 2B the variations of X-ray peak intensities in relation to temperature. The results broadly confirm the earlier data of Duffin and Goodyear, and also provide additional information which shows interesting similarities to data for hydrotalcite obtained by Brindley and Kikkawa, to be published later, and for pyroaurite by Rouxhet and Taylor (1969). Pyroaurite has the ideal formula  $Mg_6Fe_2(OH)_{16}CO_3 \cdot 4H_2O$ . Duffin and Goodyear recorded two phases in scarbroite with basal spacings 9.00 Å and 8.74 Å prior to any heat-treatment. The 9.00 Å phase converted irreversibly to the 8.74 Å phase when left in the open air for several weeks. This phase was not observed in the present work probably because the material had been stored in the laboratory for almost 20 years. Exposure to water and to hydrous atmospheres did not expand the mineral to the 9.00 Å spacing.

The initial phase observed in the present study has a nearly constant basal spacing of 8.50 Å in the temperature range 20–110 °C. This spacing corresponds to  $d(001)/3$  with respect to the unit cell given by Duffin and Goodyear; in other words, there are three structural layers per unit cell. Unfortunately, the only basal reflections clearly seen are 003, 006, and possibly 0,0,12 so that a one-

dimensional Fourier synthesis is not practicable. The calculated density of scarbroite based on  $a = 9.94$ ,  $b = 14.88$ , and a layer spacing of 8.50 Å and a layer composition  $3[Al_5(OH)_{13}CO_3 \cdot 5H_2O]$  is  $2.00 \text{ g cm}^{-3}$  which agrees very well with the result obtained by Duffin and Goodyear (1960, p. 354),  $2.01 \pm 0.01$ , which they regarded as 'probably the most reliable'.

In the temperature range 60°–125 °C, a second phase occurs with a spacing of 7.70–7.65 Å and a maximum reflected intensity at about 90 °C. This phase, which was not recorded by Duffin and Goodyear, rehydrates very easily to the 8.50 Å phase, and corresponds almost exactly with the spacings of hydrotalcite and pyroaurite.

A third phase with a spacing 6.65 Å occurs in the temperature range 100°–240 °C, with a maximum observed intensity at 140 °C. With increased temperature the spacing and the reflected intensity both diminish to a minimum spacing of about 5.5 Å at 240 °C, above which the reflection is no longer recorded. In the initial stages, when the spacing is still near 6.6 Å, rehydration to 8.5 Å is still possible. In the temperature range 20–140 °C, the observed changes are probably due to loss of molecular water; this conclusion is consistent with the thermogravimetric curves given by Duffin and Goodyear, and found in the present work. The molecular water is probably arranged in a rather specific (but unknown) way because the layer spacings are discrete, and do not change in a continuous manner from 8.50 to 6.65 Å.

Above 140 °C, general decomposition of the

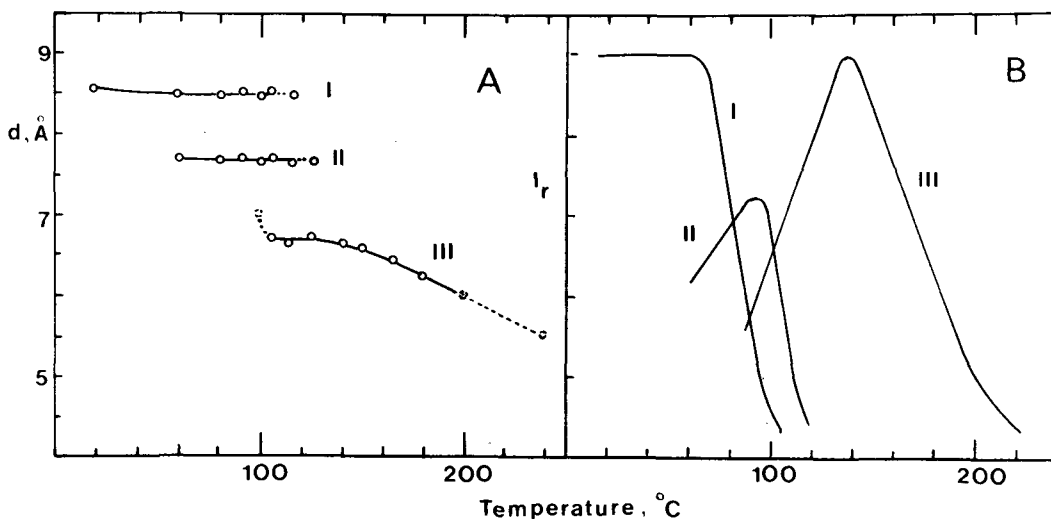


FIG. 2. Layer spacings of scarbroite phases vs. temperature (left) and diffracted intensities  $I_r$  from the first observed basal reflection, 003. Spacings in Å, intensities in arbitrary units. Dotted lines indicate uncertain extensions of the full lines where the reflections were broad and the spacings less accurate.

structure occurs, i.e. both dehydroxylation and decarbonation. Rouxhet and Taylor (1969) in their detailed study of the thermal decomposition of pyroaurite, were unable to find any sharp distinction between these processes. Hydrotalcite and pyroaurite are stable to about 220–240 °C, whereas scarbroite begins to decompose at a lower temperature, around 140 °C. The higher thermal stability of hydrotalcite can be related to the brucite-like layer structure and the lower stability of scarbroite to the gibbsite-like layer structure. Brucite is stable to about 350 °C, but fine-grained gibbsite dehydrates in the temperature range 140–200 °C (Brindley and Choe, 1961).

*Conclusions.* The formula of scarbroite, written in the form  $\text{Al}_5(\text{OH})_{13}\text{CO}_3 \cdot 5\text{H}_2\text{O}$ , suggests a close relationship to gibbsite  $\text{Al}(\text{OH})_3$  and to hydrotalcite  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ . Close relations are shown between the layer parameters of scarbroite and gibbsite. The layer spacing,  $d(001)/3$ , and the thermal behaviour of scarbroite are similar to corresponding data for hydrotalcite and the analogous mineral, pyroaurite.

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