Carrboydite, a hydrated sulfate of nickel and aluminum: a new mineral from Western Australia

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Abstract

Carrboydite, found at Carr Boyd Rocks in Western Australia, is a green secondary mineral apparently deposited from surface waters carrying components from weathered nickel sulfides. Electron-probe and chemical analyses indicate a composition corresponding to $(Ni, Cu)_{6.90}Al_{4.48}(SO_4,CO_3)_{2.78}(OH)_{21.69} \cdot 3.67 \, H_2O$. Electron and X-ray diffraction patterns indicate a hexagonal unit cell with $a = 9.14$Å and $c = 10.34$ Å. Specific gravity is 2.50 (meas.) and 2.692 (calc.). The mineral is uniaxial negative with refractive indices between 1.54 and 1.56. Inferences drawn from heating and chemical experiments suggest that the structure is a layered one consisting of "double-brucite type" sheets separated by interlayer water molecules.

Introduction

Green secondary nickel minerals are common in the weathered zone overlying many of the nickel sulfide deposits of Western Australia, generally as pore or fracture fillings. Such minerals, reported to date, comprise silicates (pecoraite and talc-like garnierite), carbonates (gaspeite, reevesite, and eardleyite), and hydrated sulfates (retgersite, morenosite and nickel-hexahydrite) (Nickel, 1973; Keele and Nickel, 1974; Nickel and Bridge, 1975; Nickel *et al.,* 1976). This paper describes a hydrated, sulfate-bearing hydroxide of nickel and aluminum that has not previously been characterized.

Carrboydite was discovered by one of the authors (E.H.N.) in the glory hole of the Carr Boyd Rocks nickel mine in August, 1972; subsequently it was found by the other author (R.M.C.) on specimens collected by M. W. Pryce of the Government Chemical Laboratories from surface dumps near the glory hole in March 1973.

The mineral is named after the Carr Boyd Rocks locality. Both mineral and name have been approved by the I.M.A. Commission on New Minerals and Mineral Names. Type material is preserved at Perth, Western Australia, in the mineral collections of the Government Chemical Laboratories and of the Division of Mineralogy of the CSIRO.

Occurrence

The Carr Boyd Rocks mine is located at 30°04′ S, 121°37′ E, on the Gindalbie pastoral station in the Yerilla district of the North Coolgardie Goldfield, some 80 km NNE of Kalgoorlie, Western Australia.

The carrboydite occurs in relatively open fractures, mostly as sheets of tiny concretionary nodules, generally between about 0.5 and 0.1 mm in diameter. The nodules are frequently hollow, and sometimes have shrunken cores of green, amorphous, gel-like material. Electron-scanning micrographs (Figs. 1 and 2) show that the nodules consist of felted masses of crystallites that look like miniature balls of fur at low magnification, but reveal a platy habit at higher magnifications. Some of the carrboydite also occurs as rather featureless amorphous-looking coatings.

The carrboydite has apparently been precipitated from surface waters that have been in contact with oxidizing nickel sulfides in the Carr Boyd Rocks orebody. Purvis *et al.* (1972) report that the sulfides occur in a bronzite-sulfide pegmatoid breccia pipe that cuts a layered complex of mafic and ultramafic
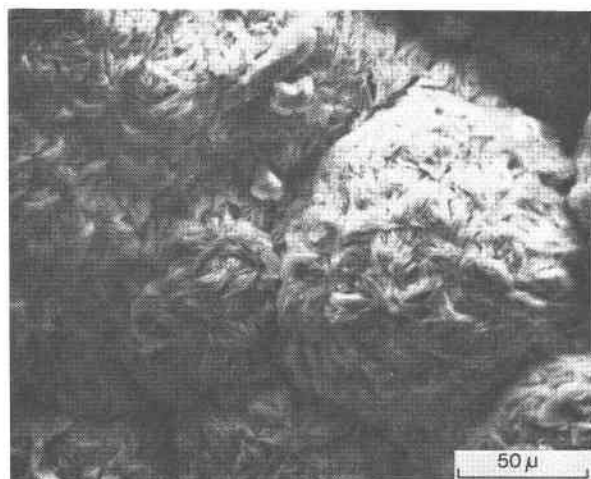
FIG. 1. Electron-scanning micrograph of carrboydite nodules.

rock units. The samples in which carrboydite was found vary from relatively fresh rock consisting essentially of feldspar and amphibole, with varying amounts of biotite, chlorite, and talc, to a bleached, weathered rock consisting of saponite, magnesite, goethite, and natroalunite. Other secondary minerals in the fractures with the carrboydite include malachite, paratacamite, glaukosphaerite, halloysite, eardleyite, chabazite, gypsum, and epsomite.

A phase identical in appearance to carrboydite was found on several specimens, associated with poorly-crystalline, dessication-cracked blue-green gel. The X-ray diffraction pattern of the carrboydite-like phase is similar, although distinguishable from carrboydite; it has a basal spacing close to 11 Å, and will therefore be referred to in this paper as the "11 Å phase."
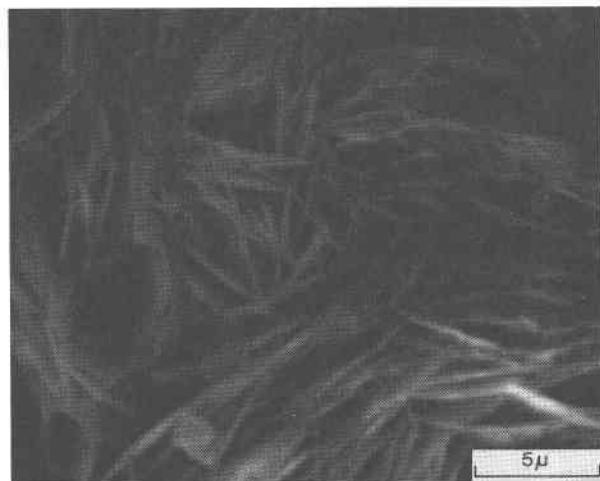
X-ray and electron diffraction analysis

Electron diffraction patterns obtained from flakes of carrboydite (Fig. 3) indicate a hexagonal pattern with a approximately 9.2 Å; intensity variations indicate a pseudo-cell with $a' = 1/3\ a$, Debye-Scherrer X-ray powder diffraction patterns (Table 1) show a strong basal reflection at 10.5 Å, and apparent higher orders at 5.25 and 3.48 Å. Assuming that the lowest-angle basal reflection corresponds to 001 and the higher ones to 002 and 003, respectively, and assuming that the a value approximates 9.2 Å, the X-ray diffraction pattern was indexed as shown in Table 1. The crystallographic parameters obtained by a least-squares refinement of the powder data are $a = 9.14$ Å and $c = 10.34$ Å.

Also shown in Table 1 are the X-ray powder diffraction data for the 11 Å phase and for pattern 17–132 from the J.C.P.D.S. compilation. Both patterns are very similar to each other, but have appreciably higher d values than the carrboydite. Pattern 17–132 is given as woodwardite in the J.C.P.D.S. file,

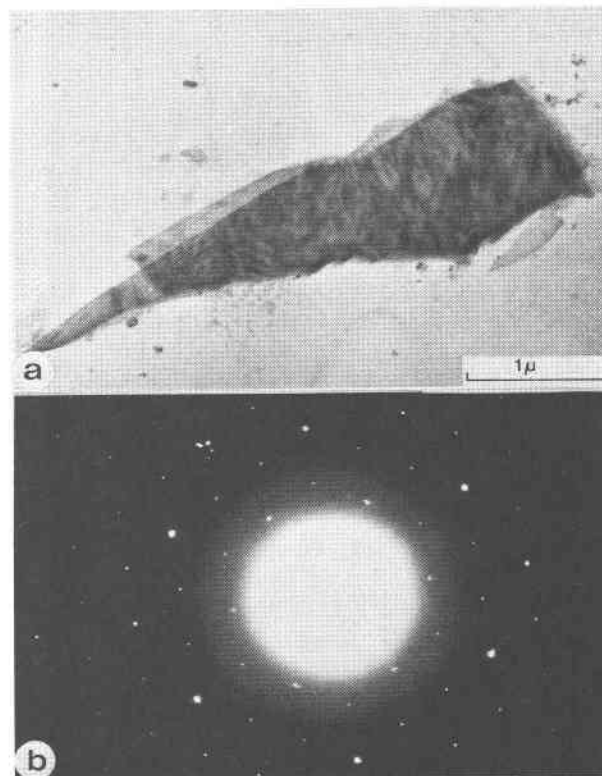FIG. 2. Part of a carrboydite nodule, at higher magnification, showing the platy nature of the crystallites.

FIG. 3. (a) Electron micrograph of carrboydite flake; (b) electron diffraction pattern obtained from the flake.

TABLE 1. X-ray powder diffraction data

hkl	Carrboydite a=9.14; c=10.34			J.C.P.D.S. No. 17-132		11Å Phase a=9.74; c=10.80	
	d. calc.	d obs.	I	d	I	d	I
001	10.34	10.5	vs	10.9	100	10.8	vs
002	5.17	5.25	s	5.46	60	5.40	s
003	3.45			3.66	50	3.60	ms
112	3.424	3.48	m				
300	2.638						
203	2.599	2.62	w				
004	2.585						
301	2.557	2.55	ms	2.613	40	2.59	m
302	2.350	2.36	wB	2.454	20B	2.44	mB
303	2.095					2.21	wB
222	2.090	2.07	wB			1.96	wB
005	2.068						
320	1.816	1.82	wB				
116	1.612	1.61	vw				
323	1.607						
331	1.507						
315	1.505	1.51	m	1.535	5B	1.51	m
420	1.496						

Ni-filtered Cu radiation; 57.8 mm Debye-Scherrer camera.

but recent work (Nickel, 1976) has shown that the mineral does not correspond to woodwardite although, like woodwardite, it is a hydrated sulfate of copper and aluminum.

Chemical composition

Carbon and hydrogen analyses were made on a 3 mg hand-picked sample by R. D. MacDonald of CSIRO's Division of Applied Organic Chemistry, using a microgravimetric procedure (MacDonald, 1974). The other constituents were determined in polished section by one of the authors (E.H.N.) using an electron-probe microanalyzer. The instrument used was the M.A.C. microanalyzer, equipped with LiF and RAP crystal spectrometers. Metal standards were used for all elements, with the exception of sulfur, for which a pyrite standard was used. Corrections were made by means of Colby's MAGIC IV computer program.

The silicon content was shown by probe analysis to be quite variable, and since no extraneous X-ray diffraction lines of quartz or silicates were detected, it can be assumed that the silicon is most likely due to the presence of amorphous silica in the carrboydite. This assumption was supported by X-ray fluorescence analysis of an X-ray amorphous residue obtained after dissolving carrboydite in hot HCl. The presence of amorphous silica in the carrboydite is not entirely unexpected, since siliceous plates and flakes are a common impurity in layered minerals generally (Faust et al., 1973). Therefore the probe analysis with the lowest silicon content is assumed to represent the purest carrboydite, and is shown in Table 2.

The atomic proportions derived from the carr-

boydite analysis have been recalculated to 36 oxygen atoms, based on the assumed structure, discussed more fully below. Sulfur and carbon were calculated as SO_4 and CO_3, respectively, and the amount of OH was taken as that required to balance the ionic charges. The remainder of the hydrogen, left after the OH calculation, was taken as water. These calculations give the formula: $(Ni,Cu)_{6.90}Al_{4.48}(SO_4,CO_3)_{2.78}(OH)_{21.69} \cdot 3.67H_2O$, or approximately $Ni_7Al_{4.5}(SO_4,CO_3)_{2.8}(OH)_{22} \cdot 3.7 H_2O$.

The Ni:Al atomic ratio of the analysis in Table 2 is 1.45; electron-probe analyses of other samples gave ratios varying between 1.05 and 1.80. This variation in Ni:Al ratio requires that there be a charge-compensating mechanism to maintain electrical neutrality. The heterovalent substitution of OH^- by divalent ions such as SO_4^{2-} or CO_3^{2-} is unlikely from size considerations and the fact that no systematic correlation is observed between metal and sulfur contents (the determination of carbon by microprobe was not attempted). The probable charge-balancing mechanism is the development of cation vacancies, as discussed below.

The composition of the 11 Å phase was not determined because of the difficulty in distinguishing it from carrboydite, but its greater basal spacing suggests that it probably contains more H_2O than the carrboydite.

Optical and physical properties

The color of carrboydite varies from yellowish-green to blue-green. In terms of the Ridgway color scheme, most is in the range from "Neuvider Green 37d" to "Chrysoprase Green 37b," with the blue extreme corresponding to "Turquoise Green 41d."

In transmitted light the color ranges between "Light blue-green 39d" and "Light yellow-green 31d." The individual crystallites are too small for definitive

TABLE 2. Composition of carrboydite

	Weight %*	Atomic Props. Calculated to 36 Oxygen Atoms	
Ni	30.0		6.502
Cu	2.0		0.401
Al	9.5		4.480
Si	1.2		**
S	5.8	SO_4	2.302
C	0.45	CO_3	0.477
H	2.30	OH	21.688
O (equiv.)	46.63	H_2O	3.673
	97.88		

*Ni, Cu, Al, Si and S determined by electron microprobe; C and H determined by microanalysis; equivalent oxygen calculated to satisfy valencies.
**Si excluded from calculation of atomic proportions.

optical characterization, but some useable interference figures were obtained that indicate a uniaxial negative character (some particles appear to be biaxial negative with a small 2V); this is in agreement with length-slow orientation observed for on-edge flakes. Birefringence is low to moderate, and refractive indices fall between 1.54 and 1.56.

The specific gravity, determined by the sink-float method in bromoform diluted with acetone, is 2.50 ± 0.05; the density of the matching liquid was measured by pycnometer. This is substantially below the calculated density of 2.692, but perhaps the discrepancy can be attributed to the porous nature of the aggregates on which the specific gravity was performed, and the presence of intergrown amorphous silica.

An infrared spectrum of carrboydite is shown in Figure 4. The high-frequency end of the spectrum is dominated by the H_2O stretching band at about 3400 cm^{-1}, which effectively swamps possible bands attributable to the less intense OH vibrations. Other high-frequency absorption bands are attributed to H_2O (bending), CO_3, and SO_4 vibrations, as shown in Figure 4. (Some carrboydite spectra lack the CO_3 bands, which indicates that CO_3 is not essential to the carrboydite formulation.) The lower-frequency bands are due to various cation–anion interactions, and cannot be assigned on present knowledge.

Results of thermal and chemical treatment

T.G.A. and D.T.A. spectra are rather poorly resolved and do not show any prominent features; consequently they are not reproduced here. Quadrupole mass spectrographic analyses of the gases given off during the D.T.A. heating experiments show the evolution of water throughout the low-temperature range, culminating in a peak at about 450°C. The evolution of CO_2 and SO_2 is represented by peaks at 580°C and 840°C, respectively.

X-ray diffractometry of carrboydite on a heated stage shows that the basal spacing is reduced from the original 10.4 Å to 8.6 Å at a temperature between 60°C and 90°C; subsequent cooling to room temperature in a normal laboratory atmosphere causes the basal spacing to expand more or less to its original value. Using a Guinier high-temperature X-ray diffraction camera, all diffraction lines disappear between 150–200°C. Debye-Scherrer film of material heated in a temperature-controlled furnace and then cooled to room temperature showed, however, that the carrboydite pattern was retained to somewhat over 200°C. This apparent discrepancy may be due to imprecise fixing of the temperature in the Guinier device, but both sets of results indicate disruption of the structure at about 200°C.

Carrboydite is virtually insoluble in water, but dissolves in hot 0.5M HCl, leaving an amorphous residue shown by X-ray fluorescence analysis to consist largely of silica. Immersion in boiling water converts the carrboydite to the "11 Å phase"; a similar effect is produced by immersion in hydrogen peroxide. Immersion in 1.25M NaOH converts the carrboydite to a phase with a 7.5 Å basal spacing, and an X-ray diffraction pattern similar to nickel hydraluminate; immersion in 3.6M H_2SO_4 converts this phase back to carrboydite.

Discussion

The platy morphology of the carrboydite, as shown by the electron-scanning micrograph (Fig. 2) and the
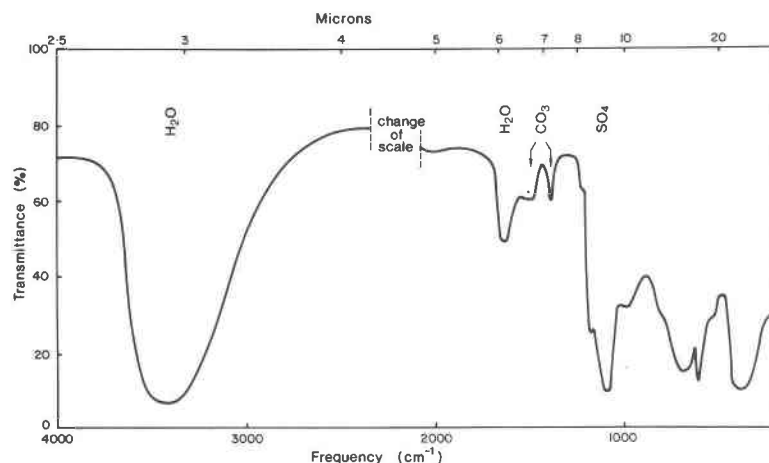

FIG. 4. Infrared absorption spectrum of carrboydite.

strong basal reflections exhibited by the X-ray diffraction patterns indicate that the structure of carrboydite is probably a layered one. An analogy can be drawn with brucite, $Mg(OH)_2$, which consists of layers of magnesium ions octahedrally coordinated by hydroxyl ions. Brucite has $a = 3.12$ Å, which corresponds closely to the a' pseudocell of carrboydite (3.1 Å). The close similarity between the a dimensions suggests that the carrboydite structure also consists of layers of octahedrally-coordinated cations, although the true a dimension, which is three times the size of a', suggests some atomic ordering.

The large basal spacing (10.34 Å) of carrboydite can theoretically be derived from the brucite structure, which has a basal spacing of 4.73 Å (Fig. 5A), in two different ways. The first is simply by inserting interlayer material between the brucite layers, as in pyroaurite (Allmann, 1968). The second is by postulating a double hydroxide layer that contains two layers of cations, as has been proposed by Longuet-Escard (1950) for a synthetically-produced nickel hydraluminate, plus the addition of some interlayer material.

Considering the first possibility, a segment of the brucite structure corresponding to the a dimensions of carrboydite (9.14 Å) contains 18 OH ions and 9 cations. To expand the basal spacing from that of brucite ($c = 4.73$ Å) to that of carrboydite ($c = 10.34$ Å) requires a thickness of interlayer material measuring 5.6 Å, which corresponds approximately to two layers of water molecules each 2.8 Å thick. The number of water molecules that can be accommodated in one layer is about 9, assuming spherical molecules with a "packing diameter" of 2.8 Å. Two layers could therefore accommodate 18 such molecules, which would give a H_2O/cation ratio of 2. However, carrboydite has only 3.67 water molecules per unit cell,

which gives a H_2O/cation ratio of only 0.32, and it is extremely doubtful if this small number could somehow provide the observed interlayer thickness. In the 10.6 Å member of the hydrocalumite group, for instance, in which the structure is interpreted as consisting of brucite layers separated by two interlayers of water molecules (Dosch, 1967), the H_2O/cation ratio corresponds to the ideal, fully-packed value of 2.0. In pyroaurite, which has a H_2O/cation ratio of 0.50, *i.e.*, greater than that of carrboydite (see Table 3), there is only one layer of water molecules and a corresponding interlayer thickness of 2.9 Å (Allmann, 1968). The doubly-charged anions (SO_4 and CO_3) in carrboydite cannot be invoked as being responsible for the large interlayer thickness since pyroaurite has a greater proportion of these than carrboydite. It seems, therefore, that this type of structure is unlikely for carrboydite.

The second possibility is based on the structural proposal for a 7.8 Å nickel hydraluminate precipitate (Longuet-Escard, 1950), illustrated diagrammatically in Figure 5B. The structure of the hydraluminate is regarded as consisting of sheets comprising three layers of OH ions between which are sandwiched two layers of cations. It can be visualized as two brucite layers sharing a common layer of hydroxyls. If an interlayer of water molecules 2.8 Å thick is inserted between each of the multiple layers, as shown in Figure 5C, this gives a basal spacing of 10.6 Å, which is somewhat greater than the measured carrboydite c-parameter, but if some "shrinkage" due to cation vacancies is assumed, then the agreement is reasonable. As shown below, this postulated structure is supported by evidence from the dehydration experiments.

Assuming hexagonal close-packing of oxygen atoms, a hexagonal unit cell of $a = 9.14$ Å and $c = 10.34$ Å can accommodate 4 layers of oxygen atoms. This can be expected to apply approximately, regardless of whether the oxygen atoms exist as individual ions or whether they are combined into water molecules or multi-element anions such as OH^-, SO_4^{2-} or CO_3^{2-}. The number of possible cation sites in a unit cell of this structure is 18.

If a modification of the Longuet-Escard structure is accepted for carrboydite, then it is reasonable to assume that the charged anions will be accommodated largely in the double-layered sheets containing the cations, and that the water molecules are contained in the interlayer part of the structure. Since water molecules are uncharged, it should be relatively easy to develop vacancies in the interlayer portion so
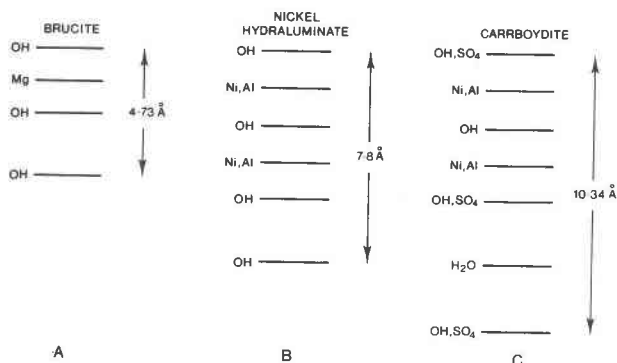

Fig. 5. Diagrammatic representation of the layering in brucite (A), nickel hydraluminate (after Louër *et al*, 1973) (B), and the inferred structure of carrboydite (C).

TABLE 3. Interlayer thickness, and ratios of anions and water molecules per cation for brucite, carrboydite, pyroaurite, and 10.6 A hydrocalumite

	X^{2-}/cation	H_2O/cation	Interlayer Thickness*
Brucite	0	0	0
Pyroaurite	0.375	0.50	3.1
Carrboydite	0.240	0.32	5.6
10.6Å Hydrocalumite	0	2.00	5.9

*Obtained by subtracting the thickness of a brucite layer (4.73Å) from the basal spacing of the mineral in question.

that the actual number of oxygen atoms in the unit cell of the mineral may fall below the ideal number of 36. This would reduce the specific gravity appreciably. For example, a calculation based on 34 oxygen atoms per unit cell gives a calculated density of 2.55 g/cc, which is very close to the measured value.

In a double-layer structure such as the one proposed here, not all of the 18 potentially-available octahedral cation sites would be occupied, by virtue of the fact that the middle layer of OH ions is shared by two layers of cations, thereby effectively reducing the ionic charge of the layer. Furthermore, charge-balancing constraints will tend to promote cation vacancies. The anionic charge of the unit-cell formula, −27.25, is balanced by 6.50 Ni^{2+}, 0.40 Cu^{2+}, and 4.48 Al^{3+}, giving a total of 11.38 cations. Presumably a higher Al: Ni ratio, as indicated by some of the probe analyses, would reduce the cation occupancy still further.

The proposed structure of carrboydite is supported by the dehydration experiments. The collapse of the structure to 8.6 Å on heating to 60–90°C can be attributed to loss of the weakly-bonded water molecules. That the structure does not collapse down to the brucite structure confirms that the structure is probably a double-layered one rather than consisting of brucite layers separated by two layers of water. It might be expected that expulsion of the water would cause the structure to collapse down to a basal spacing of 7.8 Å (i.e. nickel hydraluminate, Fig. 5B), but it seems likely that the larger anions (SO_4^{2-} and CO_3^{2-}) in the double layer increase the effective thickness of the layer. An analogous behaviour has been described by Louër et al. (1973) for the nitrate ions in hydroxynitrates of nickel and zinc.

The chemical experiments indicate that the interlayer material is easily displaced and is therefore only lightly bonded to the compound sheets. The compound sheets themselves, although more stable than the interlayer material, nevertheless decompose at a relatively low temperature, much lower, for example,

than is the case for eardleyite (Nickel et al., 1976), a Ni–Al member of the pyroaurite group. This suggests that the double-layer sheets proposed here are less structurally stable than the brucite-like sheets in pyroaurite-type minerals.

The nature of the 11 Å phase associated with some of the carrboydite is not known, since it was not possible to obtain enough of the material for chemical analyses or other tests. However, it seems reasonable to conclude that this phase consists of the same kind of compound sheet, but with somewhat more interlayer water. This would make it a slightly hydrated form of carrboydite.

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