REFERENCES

CLARK, C. D., R. W. DITCHBURN AND H. B. DYER (1956) *Proc. Roy. Soc. (London) Ser. A.,* **234,** 363.
DUGDALE, R. A. (1953) *Brit. J. Appl. Phys.* **4** (11) 334.
DYER, H. B., AND L. DU PREEZ (1965). *J. Chem. Phys.* **42** (6), 1898.
ELLIOT, R. J. (1960) *Proc. Phys. Soc.,* **76,** 787.
EVANS, T., AND C. PHAAL (1962) *Proc. Roy. Soc. (London) Ser. A.,* **270,** 538.
KAISER, W., AND W. L. BOND (1959) *Phys. Rev.,* **115,** 857.
ROBERTSON, R., J. J. FOX AND A. E. MARTIN (1934) *Trans. Roy. Soc. (London) Ser. A.,* **232,** 463.

ABOUT THE STRUCTURE OF IOWAITE[1]

R. ALLMANN, *Universität Marburg, Germany,* AND J. D. H. DONNAY, *The Johns Hopkins University, Baltimore, Maryland 21218.*

ABSTRACT

Iowaite, which weathers to pyroaurite and is similar to it in crystal data and powder-line intensities, should be isostructural with it and be reformulated as $[Mg_4Fe(OH)_{10}]^+ \cdot [Cl(H_2O)_{x-1}]^-$, $x=4$, $Z=3/5$.

Kohls and Rodda (1967, to be referred to as KR) have recently described the new mineral iowaite, $4Mg(OH)_2 \cdot FeOCl \cdot xH_2O$ ($x \leq 4$). All the data reported by them indicate a strong similarity (Table 1) between iowaite and pyroaurite. The latter is one of two polymorphic modifications, described as pyroaurite I and pyroaurite II by Aminoff and Broomé (1930). Frondel (1941), who established the presence of CO_3 in the chemical formula, called the hexagonal modification sjögrenite, reserving the term pyroaurite for the rhombohedral one. Allmann and Lohse (1966) determined the crystal structure of sjögrenite with structural formula $[Mg_6Fe_2(OH)_{16}]^{2+} \cdot [CO_3(H_2O)_4]^{2-}$ and, for pyroaurite, proposed a layer sequence that was later confirmed by two structure determinations independent of each other (Ingram and Taylor, 1967; Allmann, 1968).

In view of the similarities in crystal data (Table 1) and in powder-line intensities, further supported by the fact that iowaite alters to pyroaurite on weathering (KR), it would seem that the structures of these two

[1] Work supported by NSF grant GA 1343 to The Johns Hopkins University.

TABLE 1. COMPARISON OF EXPERIMENTAL DATA

	Iowaite[a]	Pyroaurite[b]
X-ray space group	R ?	$R\bar{3}m$
a (Å)	3.119 ± 5	3.1094 ± 2[b]
c (Å)	24.52 ± 2	23.412 ± 1[b]
V (Å³)	204.3	196.02[b]
D_m (g/cm³)	2.11 ± 2	2.13 ± 1[b]; 2.14[c]
ω	1.543 ± 5	1.564 ± 3[c]
ϵ	1.533 ± 5	1.543 ± 3[c]
Fe/(Fe+Mg) from formula[d]	0.20	0.25[c]
from analysis[d]	0.225	0.248[c]

[a] After Kohls and Rodda (1967).
[b] After Allmann (1968).
[c] After Frondel (1941).
[d] Atomic ratio.

minerals should also be similar. This hypothesis requires rewriting the formula of iowaite as $[Mg_4Fe(OH)_{10}]^+ \cdot [Cl(H_2O)_{x-1}]^-$ and taking $Z = 3/5$ instead of $Z = 1$ as assumed by KR. With $x = 4$, D_x becomes 2.02 for the idealized formula and 2.04 for the actual formula (see below) derived from the analysis published by KR. These values are in better agreement with D_m than the D_x of 2.77 which was obtained for $Z = 1$ and $x = 0$ (KR). It is possible (KR) to decrease D_x from 2.77 to 2.11 by assuming that all the water is adsorbed surface water with its own volume. We suggest that D_x can be increased from 2.04 to 2.06 by taking into account the 4.61 wt. % of admixed serpentine, whose density is 2.65. Structural considerations do not demand that x be smaller than 4; they only require that it be less than 5. For $x = 4.56$ D_x will be equal to 2.11.

Under the assumption that iowaite and pyroaurite are isostructural, a structure consisting of three brucite-like layers and three disordered interlayers (Table 2) is proposed for iowaite.

In view of the fact, established by KR, that the interlayer water is very mobile and can be removed (without the structure being destroyed) by heating to 280°C, the disordered interlayers are inferred to be liquid-like in character. By this term we mean that the water molecules are migrating within the interlayer and that the hydrogen bonds H_2O . . . HO between interlayer and main layer are not fixed but change with time as in liquid water. The water in iowaite thus cannot be considered "adsorbed water". With the water molecules removed, the chlorine ions prevent the crystal structure from collapsing. As in the related Mg-Al

TABLE 2. CRYSTAL STRUCTURE PROPOSED FOR IOWAITE IN $R\bar{3}m$

		x	y	z
3 (Mg, Fe)	in 3(a)	0	0	0
6 OH	in 6(c)	0	0	0.376
3 $[Cl_{0.2}(H_2O)_{0.6}\square_{0.2}]$	in 3(b)	0	0	1/2[a]

[a] The water molecules are probably shifted randomly out of 3(b) by about 0.5 Å.

compound (Ross and Kodama, 1967), the c length can be expected to decrease with decreasing water content and to take up its original value again after rehydration, so that the interlayer water may be called zeolitic. The free surface of the water-free interlayers, that is the area not occupied by chlorine, is calculated to be equal to about 350 m²/g, as compared with the measured value of 12.7 m²/g obtained by the method of nitrogen adsorption (KR). (Presumably nitrogen can fill only the area near the rim of the interlayers.)

The chlorine ions can likewise be removed, provided other anions are introduced to maintain the balance of charge. This is what happens when iowaite weathers to pyroaurite. Iowaite should be formulated, not as an oxychloride, but as a hydroxychloride because free O^{2-} ions are not likely to coexist with H_2O molecules. The formula will thus be written

$$[Mg_{0.775}Fe(II)_{0.022}Fe(III)_{0.203}(OH)_2]^{0.203+}\cdot[Cl_{0.203}(H_2O)_{0.6}]^{0.203-}$$

with $Z=3$, *i.e.* three metal atoms per cell.

The measured single-crystal intensities of pyroaurite, which should be similar to those of iowaite, indicate that some of the lines in the powder pattern (Table 3 of KR) should be reindexed[1] (Table 3).

One possible objection to the proposed iowaite structure is that the

TABLE 3. REINDEXING OF POWDER LINES OF IOWAITE

$d(hkl)$ (measured)[a]	$d(hkl)$ (old indexing)[a]	$d(hkl)$ (new indexing)[b]
2.019	d(00.12) 2.021	d(01.8) 2.017
1.345	d(11.9) 1.345	d(20.2) 1.342
1.007	d(21.4) 1.007	d(02.16) 1.008
0.895	d(21.13) 0.896	d(03.3) 0.895
0.879	d(12.14) 0.880	d(01.26) 0.882

[a] After Kohls and Rodda (1967).

[b] Interplanar distances calculated by Kohls (priv. commun., 1968).

[1] The calculated d(00.3) is misprinted in KR (*instead of* 0.083, *read* 8.083).

electron-diffraction pattern (Fig. 3 of KR) shows, besides strong $hk0$ reflections with $h-k=3n$, weaker ones with $h-k \neq 3n$. This fact may be explained by postulating that the thin platy crystal used was only some ten layers thick, each iowaite layer being 8.1 Å thick. This number of layers is far from infinity, which is assumed in the idealized diffraction theory. The spots in reciprocal space will, therefore, be elongated along c^*; it also follows that reflections with $l = \pm 1$ will appear on the electron-diffraction pattern.

References

ALLMANN, R. (1968) The crystal structure of pyroaurite. *Acta Crystallogr.* B **24**, 972–974.

ALLMANN, R., AND H.-H. LOHSE (1966) Die Kristallstruktur des Sjögrenits und eines Umwandlungsproduktes des Koenenits (= Chlor-Manasseits). *Neues Jahrb. Mineral., Monatsh.,* **1966**, 161–181.

AMINOFF, G., AND B. BROOMÉ (1930) Contributions to the knowledge of the mineral pyroaurite. *Kgl. Svenska Vetenskapsakad. Handl.,* **9**, 23–48.

FRONDEL, C. (1941) Constitution and polymorphism of the pyroaurite and sjögrenite groups. *Amer. Mineral.,* **26**, 295–315.

INGRAM, L., AND H. F. W. TAYLOR (1967) The crystal structures of sjögrenite and pyroaurite. *Mineral Mag.,* **36**, 465–479.

KOHLS, D. W., AND J. L. RODDA (1967) Iowaite, a new hydrous magnesium hydroxide ferric oxychloride from the Precambrian of Iowa. *Amer. Mineral.,* **52**, 1261–1271.

ROSS, G. J., AND H. KODAMA (1967) Properties of a synthetic magnesium-aluminum carbonate hydroxide and its relationship to magnesium-aluminum double hydroxide, manasseite and hydrotalcite. *Amer. Mineral.,* **52**, 1036–1047.

ON THE VALENCE OF IRON IN TRIPUHYITE: A MÖSSBAUER STUDY

U. GAKIEL[1] AND M. MALAMUD,[2] *Department of Electronics, the Weizmann Institute of Science, Rehovoth, Israel.*

Abstract

Mössbauer spectra show iron in tripuhyite is ferric, giving the formula $FeSbO_4$.

In recent years, the use of Mössbauer spectroscopy has developed into a remarkable tool in many branches of physics, chemistry and biology. One of the most important parameters studied is the so-called isomer shift, also referred to as the "chemical shift". The isomer shift is the position (in energy) of the center of gravity of the spectrum. The relevant

[1] Present address: Dpartment of Physics, Carnegie-Mellon University, Pittsburgh, Pa. 15213. On leave from the Weizmann Institute of Science.

[2] Present address: I.A.E.C., Nuclear Research Center, Negev, P.O.B. 9001, Beer Sheva, Israel.