

# Iowaite, a re-investigation

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## Abstract

Iowaite has been re-examined using new, well crystallized material from the Palabora open pit mine, Transvaal. Microprobe, carbon analyser and thermal analyses, powder and single-crystal X-ray diffraction, infrared, UV-visible and mass spectroscopic and optical studies were made. The ideal formula is  $\text{Mg}_6\text{Fe}_2^{\text{III}}(\text{OH})_{16}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ . It is trigonal,  $R\bar{3}m$ ,  $a = 3.1183(9)$ ,  $c = 24.113(8)$  Å,  $V = 203.1(2)$  Å<sup>3</sup>,  $Z = 3/8$ ;  $D_{\text{obs}} 2.09$  g/cm<sup>3</sup>;  $D_{\text{calc}} 2.04$  g/cm<sup>3</sup>; hardness (Mohs) =  $2\frac{1}{2}$ . The interlayer  $\text{Cl}^-$  ions are displaced from the threefold axis. It is uniaxial negative, with  $\omega = 1.561 \pm 0.002$ ,  $\varepsilon = 1.543 \pm 0.002$ ; coloured crystals are intensely pleochroic, due to intervalence charge transfer between the  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  substituting for  $\text{Mg}^{2+}$ , with O pale yellow, E deep blue-green.

KEYWORDS: iowaite, pyroaurite, Palabora mine, Transvaal

## Introduction

IOWAITE was first described by Kohls and Rodda (1967), using material from a borehole core in Iowa. Only a small quantity, of poor quality material, was available, and its formula was concluded to be  $\text{Mg}_4\text{Fe}^{3+}(\text{OH})_8\text{OCl} \cdot 2-4\text{H}_2\text{O}$ . Allmann and Donnay (1969) reviewed Kohls and Rodda's powder X-ray diffraction data of this iowaite, noted its similarity with those of the pyroaurite group of minerals, and suggested that iowaite might be isostructural with pyroaurite. Using Kohls and Rodda's published analysis values they reformulated iowaite as  $\text{Mg}_4\text{Fe}(\text{OH})_{10}\text{Cl} \cdot 3\text{H}_2\text{O}$ . The limitations of this material militated against further studies.

Among a suite of specimens from Palabora open pit mine, Phalaborwa, Transvaal, sent to one of us (R.S.W.B.) for investigation in 1983 were some which were accompanied by notes from the sender, Jon P. Gliddon, asking whether they might be pyroaurite. These consisted of blue-green micaceous crystals, some with colourless zones in cavities in carbonatite, with the associates described below.

The micaceous crystals were very similar in physical properties to pyroaurite, despite their unusual colour. Like pyroaurite, the crystals dissolved easily in dilute hydrochloric acid to give a yellow solution [Fe(III)], but unlike pyroaurite, very little carbon dioxide was evolved. The crystals gave an infrared spectrum much like that of pyroaurite, except that the

strong carbonate  $\nu_3$  absorption present in the spectrum of pyroaurite is greatly weakened. The X-ray powder diffraction pattern was also shown to be close to that of pyroaurite, but with minor differences, e.g. a small expansion of the  $c$ -axis parameter; it is also close to that of iowaite.

Further studies of this new material have shown that it is indeed similar to pyroaurite, but with chloride taking the place of most of the interlayer carbonate in the latter, and despite some differences in analyses and physical properties, seems to be identical with iowaite. The new material from Palabora mine is far superior to the original iowaite in purity, crystal distinction and size; its greater availability has enabled the current studies to be carried out.

#### Description and occurrence

The Palabora open pit works parts of the Phalaborwa alkaline complex, the carbonatite portion of which is mined principally for copper, while the ultramafic rocks of the complex yield economic deposits of apatite and vermiculite (Russell *et al.*, 1955; Forster, 1958; Lombaard *et al.*, 1964; Hanekom *et al.*, 1965; Heinrich, 1970; Palabora staff, 1976).

Iowaite is a late-generation mineral, found in cavities in carbonatite in the lowest current level of the Palabora open pit. The carbonatite here is coarse-grained, and consists mainly of white rhombohedral calcite and dolomite with much magnetite, and also biotite, phlogopite and chondrodite. Cavity minerals associated with the iowaite include well-crystallized magnetite in octahedra, sometimes over 1 mm across, and rarely in graphic textures, also excellent crystals of orange chondrodite occasionally reaching 5 mm in length, fine clinocllore crystals to more than 1 cm across, and smaller amounts of brucite, phlogopite, hydrotalcite, white acicular fluoborite, fluorite, apatite, baryte, celestine and antigorite.

In contrast with the Iowa material, the Palabora iowaite is well crystallised, displaying a variety of habits, reminiscent of members of the chlorite group, most commonly six-sided plates, but occasionally rhombohedra, sometimes terminated by basal planes. The platy crystals are usually between 3 mm and 1 cm across, but vary considerably in thickness. A few crystals are completely colourless, but most contain blue-green zones or are completely coloured. Some crystals show a brown alteration rim. Some cavities in the carbonatite are found completely filled with a confused mass of thin plates; in other cases the cavity walls are lined with clusters of thicker, brilliant-faced crystals. A few opaque, dark-coloured plates reach 2 cm across. Elongated rhombohedral or bipyramidal crystals up to approximately 1 mm in length are occasionally found scattered on matrix surfaces, and these display obvious pleochroism due to their presenting a lateral aspect, as do sprinklings of tiny equant rhombohedra <1 mm across. On a few specimens, iowaite is overlain thinly by calcite, but it is not otherwise overgrown by other species. Many crystals contain inclusions of sharp magnetite octahedra.

#### Optical and physical properties

The refractive indices were determined by conventional immersion methods. The crystals (all from the same cavity) which were measured, displayed pronounced colour zoning, with a wide blue-green core surrounded by a narrow yellowish zone and an outer colourless rim. Iowaite is optically uniaxial negative, with  $\omega = 1.561 \pm 0.002$ , and  $\epsilon = 1.543 \pm 0.002$  (in monochromatic light of  $\lambda = 589$  nm). The yellowish zone has indices approximately 0.003 higher than the core and outer zones. The coloured zones of the crystals show spectacular pleochroism, with O pale yellow and E deep blue-green. Kohls and

TABLE 1. Comparison of lattice parameters of iowaite with those of pyroaurite

	Iowaite Palabora (Present work)	Iowaite (Kohls and Rodda, 1967; Ingram and Allmann and Donnay, Taylor, 1967) 1969*)	Pyroaurite (Ingram and Allmann and Donnay, Taylor, 1967)	Pyroaurite (Allmann, 1968)
$a$ , Å	3.1183(9)	3.119(5)	3.13	3.1094(2)
$c$ , Å	24.113(8)	24.25(2)	23.49	23.4117(9)
$V$ , Å <sup>3</sup>	203.1(2)	204.3(1.5)	199.3	196.02(3)

\*Misprint in Allmann and Donnay, 1969.

TABLE 2. Atomic co-ordinates and vibrational parameters for iowaite.

## Atomic co-ordinates

	x/a	y/b	z/c
Fe,Mg	0	0	0
O(1)	0.33333	0.66667	0.04206(7)
H(1)	0.33333	0.66667	0.0670(10)
O(2),Cl(1)	0.2105(42)	0.7895(42)	0.16667

## Vibrational parameters

	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Fe,Mg	0.0077(5)	0.077(5)	0.0268(6)	0	0	0.0039(3)
O(1)	0.0166(7)	0.0116(7)	0.0191(8)	0	0	0.0058(4)
H(1)	0.010(6) (= U)	-	-	-	-	-
O(2),Cl(1)	0.245(21)	0.232(21)	0.046(3)	0.017(10)	0	0

Rodda (1967) give  $\omega = 1.543 \pm 0.005$  and  $\epsilon = 1.533 \pm 0.005$  for the Iowa material.

The density of Palabora iowaite was measured by flotation, using about ten microscopically selected fragments free from inclusions, and was found to be  $2.09 \text{ g/cm}^3$ . No difference in density between coloured and colourless material was observed.

The Mohs hardness of the Palabora material is  $2\frac{1}{2}$ . Kohls and Rodda (1967) reported  $1\frac{1}{2}$  for their material from Iowa. Iowaite has a micaceous cleavage on {0001}.

## X-ray crystallography

A hexagonal prismatic crystal of dimensions  $0.3 \times 0.3 \times 0.3 \text{ mm}$  was examined using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with a Nicolet R3m/v diffractometer and a graphite monochromator.

Least-squares refinement on the setting angles of 17 accurately centred reflections yielded the following rhombohedral cell parameters:  $a = 3.1183(9)$ ,  $c = 24.113(8) \text{ \AA}$ ,  $V = 203.1(2) \text{ \AA}^3$ ,  $Z = 3/8$ . The 844 reflections ( $0^\circ \leq \theta \leq 27^\circ$ ), including those forbidden by rhombohedral centring, were measured using  $\omega$  scans. There were no significant exceptions to the rhombohedral condition, and rotation photographs did not reveal any weak super-lattice reflections. No additional systematic absences were found, and space group  $R\bar{3}m$  was selected by comparison with pyroaurite (Ingram and Taylor, 1967; Allmann, 1968). Table 1 gives a comparison of cell dimensions with those of pyroaurite and the Iowa iowaite.

Absorption, Lorentz and polarization corrections were applied prior to merging ( $R_{\text{int}} = 0.028$ ) to give 78 unique reflections ( $F \geq 3\sigma(F)$ ). Three intensity standards measured repeatedly during data-collection showed no deterioration.

A difference Fourier analysis with brucite layer positions taken from those of pyroaurite and the Mg:Fe ratio from our chemical analyses revealed a diffuse interlayer peak at  $1/3$ ,  $2/3$ ,  $1/6$ . Interpretation of this peak as a combination of  $\text{Cl}^-$  and variable O ( $\text{OH}^-$ ,  $\text{H}_2\text{O}$ ), with occupancies fixed at the analysis value and variable, respectively, led to very high vibrational spread ( $U_{11}$ ). A better refinement resulted when the  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$  'atom' was allowed to leave the threefold axis, with a final  $R = 0.017$  and  $R_w = 0.025$ , with  $w = 2.6022/(\sigma^2(F) + 0.00016F^2)$ . Final positional and vibrational parameters are presented in Table 2 and weighted structure factors in Table 3 (deposited). The calculated density of  $2.11 \text{ g cm}^{-3}$  based on this model ( $\text{CO}_3^{2-}$  ignored,  $\text{OH}^-$  fixed at 0.48 and  $\text{H}_2\text{O}$  at 5.5) was close to the measured density of  $2.09 \text{ g cm}^{-3}$  and the value of  $2.04 \text{ g cm}^{-3}$ , for the cell contents from our chemical analyses, suggesting that a higher water content is required in the chemical formula.

The indexed powder patterns presented in Table 4 were recorded using a 57.3 mm Debye-Scherrer camera and Cu-K $\alpha$  radiation filtered with Ni, without standards, intensities being measured using a microdensitometer. Attempts to obtain better results by using a diffractometer were not successful. This was because of problems with pronounced preferred orientation effects due to particle orientation, this despite trying a number of techniques designed to overcome this problem.

TABLE 4. X-ray powder diffraction data for iowaites

Kohls and Rodda (1967)*			Present work				<i>h</i>	<i>k</i>	<i>l</i>
<i>d</i> <sub>obs</sub> Å	<i>I</i> <sub>meas</sub>	<i>d</i> <sub>calc</sub> Å	Type specimen		Palabora				
			<i>d</i> <sub>obs</sub> Å	<i>I</i> <sub>meas</sub>	<i>d</i> <sub>obs</sub> Å	<i>I</i> <sub>meas</sub>			
8.109	100	8.083	7.900	10	8.043	10	0	0	3
4.047	40	4.042	3.943	4	4.040	5	0	0	6
2.697	<1	2.694					0	0	9
2.639	17	2.637	2.625	4	2.637	4	0	1	2
2.363	27	2.360	2.341	4	2.353	4	0	1	5
2.019	23	2.017	1.987	4	2.014	4	0	1	8
1.805	4	1.804	1.773	>1	1.791	<1	1	0	10
1.710	5	1.708	1.677	>1	1.705	1	0	1	11
1.560	8	1.560	1.552	1	1.566	1	1	1	0
1.530	13	1.531	1.524	1	1.536	2	1	1	3
1.453	5	1.455	1.444	>1	1.455	<1	1	1	6
1.345	2	1.342			1.348	<1	2	0	2
1.324	3	1.322			1.319	<1	1	0	16
1.299	3	1.301	1.291	1	1.307	<1	2	0	5
1.233	3	1.234			1.238	<1	2	0	8
1.179	<1	1.180					0	2	10
1.154	2	1.154			1.155	<1	1	0	19
1.016	<1	1.017					1	2	2
1.007	<1	1.008					0	2	16
0.998	1	0.999					1	2	5
0.967	1	0.968					1	2	8
0.940	<1	0.941					2	1	10
0.927	3	0.928					1	1	21
		0.928					0	2	19
0.901	<1	0.900					0	3	0

To 0.900 Å; as modified by Allmann and Donnay (1969).

The *d*-spacings obtained from the type specimen (off NMNH 121706) correspond to a unit cell of *a* = 3.104(1) and *c* = 23.65(4) Å, which indicates a shrinkage (of *a* by 0.5% and *c* by 2.5%) since Kohls and Rodda's (1967) measurements, suggesting a slight loss of material from the interlayer region, probably because of dehydration.

### Chemistry

Both colourless and blue-green iowaites dissolve slowly in cold dilute hydrochloric acid with slight effervescence to give a yellow solution due to the presence of Fe(III). They also dissolve in cold dilute nitric acid, and then afford a dense white precipitate with aqueous silver nitrate, indicating the presence of halide ions.

Wavelength-dispersive electron microprobe scans indicated the absence of elements with *Z* > 9 apart from Fe, Mg and Cl, and mass-spectrometry indicated the absence of elements

with *Z* < 10 other than H, O, small amounts of C and traces of F (see below).

Blue-green material was quantitatively analysed using electron microprobe, carbon analyser and thermogravimetric analysis methods.

An ARL-SEM-Q electron microprobe, utilizing an operating voltage of 15 kV and a sample current of 0.025 µA, measured on brass, was used to determine iron, magnesium and chlorine. A hornblende standard was used for the Fe and Mg determinations, and scapolite for the Cl determination, and the data were corrected using a suitable program. Carbon was determined using a Leco carbon analyser. Water, total volatiles and residue were determined by TGA (see below).

The results of these analyses agree well with those calculated for a formula of (Mg<sub>5.9</sub>Fe<sub>2.1</sub>)Fe<sub>2</sub><sup>3+</sup>(OH)<sub>16</sub>[Cl<sub>1.4</sub>OH<sub>0.48</sub>(CO<sub>3</sub>)<sub>0.06</sub>]·4H<sub>2</sub>O and are shown in Table 5 (*cf.* those reported for the Iowa material of Mg<sub>4</sub>Fe<sup>3+</sup>(OH)<sub>8</sub>OC1.2–4H<sub>2</sub>O (Kohls and Rodda, 1967) and Mg<sub>4</sub>Fe(OH)<sub>10</sub>-Cl(H<sub>2</sub>O)<sub>3</sub> (Allmann and Donnay, 1969) and that of pyroaurite, Mg<sub>6</sub>Fe<sub>2</sub><sup>3+</sup>(OH)<sub>16</sub>CO<sub>3</sub>·4H<sub>2</sub>O).

TABLE 5. Analyses of iowaite

	1	2
MgO	35.3	34.9
Fe <sub>2</sub> O <sub>3</sub> *	24.6	24.6
Cl	7.0	7.3
CO <sub>2</sub>	0.4	0.4
H <sub>2</sub> O to 200°C	11	10.6
Total volatiles	41	40.2

\*FeO calculated as Fe<sub>2</sub>O<sub>3</sub>

1. Found

2. Calculated for (Mg<sub>5.9</sub>Fe<sub>0.1</sub>)Fe<sub>2</sub>(OH)<sub>16</sub>(Cl<sub>1.4</sub>OH<sub>0.48</sub>(CO<sub>3</sub>)<sub>0.06</sub>)·4H<sub>2</sub>O

#### Mass spectrometry

A sample of the new iowaite was submitted to SIMS (Secondary Ion Mass Spectrometry) using FAB (Fast Atom Bombardment). A single crystal, mounted on gold foil, was etched by fast argon atom bombardment for 10 mins. using 40 μA at 4 keV, to remove contaminated surface layers, and then submitted to further FAB at 5 mA emission at 2 keV, the positive and negative secondary ions emitted being analysed separately by mass spectrometry. The results show that the only elements present with  $Z < 10$  are H, O, small amounts of C and traces of F. Fluorine is therefore not an important constituent in the chloride site. The presence of major Cl, Fe and Mg were also confirmed.

#### Thermal analysis

Samples of the Palabora iowaite were submitted to thermogravimetric analysis with a heating rate of 15°C per minute, in a Pt holder, in a static air atmosphere, using a Stanton Redcroft TG 770 thermogravimetric balance fitted with a Pt-Rh thermocouple. After initial problems with decrepitation were overcome, a 5.93 mg sample showed an initial weight loss levelling out near 200°C at 11.0% loss. Further fairly steep weight loss, showing indications of overlapping losses, to about 400°C was followed by a slow loss, which by 1000°C had reached about 41%.

The weight loss to 200°C is accounted for by the loss of interlayer water, and the subsequent losses to overlapping loss of hydroxide water, carbon dioxide and hydrogen chloride. Magnesium hydroxychlorides are known to lose hydrogen chloride on heating. The residue is of a golden yellow-brown colour with no black

material visible and is magnetic, so it is probably a mixture of MgO with magnesioferrite, MgFe<sub>2</sub>O<sub>4</sub>, rather than with magnetite.

#### Infrared spectroscopy

The infrared spectra of several samples of Palabora iowaite and of brucite were measured in Nujol and hexachlorobutadiene mulls, between KBr plates, over the range 400–4000 cm<sup>-1</sup>, using a Perkin-Elmer PE 397 grating spectrophotometer.

The spectra resemble those of the related minerals of the hydrotalcite and manasseite groups (*cf.* Mumpton *et al.*, 1965), with characteristically broad absorption bands. The O–H stretching absorption, with maximum near 3400 cm<sup>-1</sup>, ranges from about 2500 to 3900 cm<sup>-1</sup>. The absorption maximum of the broad H–O–H symmetrical 'scissor' deformation vibration is near 1630 cm<sup>-1</sup>. The carbonate ν<sub>3</sub> unsymmetrical stretching absorption is much weaker than in the carbonate members of the group, of course, and shows a maximum at 1375 cm<sup>-1</sup> and a weaker one near 1450 cm<sup>-1</sup>. A further extremely broad absorption stretches from about 1100 to 480 cm<sup>-1</sup>, with maximum near 570 cm<sup>-1</sup>, is present in the spectrum of brucite but with maximum near 450 cm<sup>-1</sup>, and is therefore ascribed to metal–oxygen vibrations of the brucite layer. No difference was observed between the infrared spectra of the blue-green and colourless zones of the iowaite.

The oriented infrared spectra of very thin cleavage flakes of iowaite and of brucite were measured along their *c*-axes. The O–H stretching absorption of iowaite in randomly oriented mull samples has much stronger absorbance than that of the H–O–H 'scissor' vibration, but measured along the *c*-axis the stretching absorbance is reduced to approximately the same as that of the H–O–H vibration. In the spectrum of brucite, the strong and very sharp O–H stretching absorption at 3700 cm<sup>-1</sup> for randomly oriented material is reduced to practically zero in *c*-axis oriented measurements. This infrared pleochroism is due to the orientation of the vibrating dipoles of the brucite layer hydroxyls parallel to the *c*-axis, thus minimising absorption along this axis. The residual broad O–H stretching absorption in *c* oriented iowaite spectra must be due to that of the interlayer water, oriented across the *c*-axis. The strong broadening of the O–H stretching absorptions observed in the spectra of iowaite and the other members of the hydrotalcite and manasseite groups is due to strong hydrogen bonding between the interlayer water and the hydrogens of the brucite layer. The O–H stretching vibration of

brucite is contrastingly very sharp because hydrogen bonding is not possible between brucite layers.

### Electronic spectroscopy

The visible-ultraviolet spectra of blue-green and colourless iowaites were measured over the range 200–900 nm along the *c*-axis (the optic axis), using a Beckmann Acta M IV double-beam spectrophotometer. A mosaic of thin cleavage plates of the relevant material was stuck to a strip of transparent sticky tape, and a similar strip of tape alone was placed in the reference beam. This technique excludes the measurement of extinction coefficients, but good graphic profiles of the spectra were obtained (Fig. 1).

The colour of the blue-green iowaitite is seen to be mostly due to a strong broad absorption at 670 nm, typical of an  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  intervalence charge transfer band, responsible for similar colours in many materials. In addition, a series of bands is seen in the ultraviolet with maxima in the 275–345 nm region and at 375 and 440 nm, which are probably ligand-metal charge transfer bands. Colourless iowaitite displays only one absorption band, with maximum at 285 nm, so most of the absorptions must be due to the excess ferrous iron replacing some magnesium in the brucite layers. The weaker absorption at 495 nm is not likely to be a crystal field transition of  $\text{Fe}^{3+}$  (those of  $\text{Fe}^{2+}$  lie at longer wavelengths) as the d–d transitions of  $\text{Fe}^{3+}$  are spin forbidden as well as Laporte forbidden, and therefore probably too weak to be visible on our spectra.

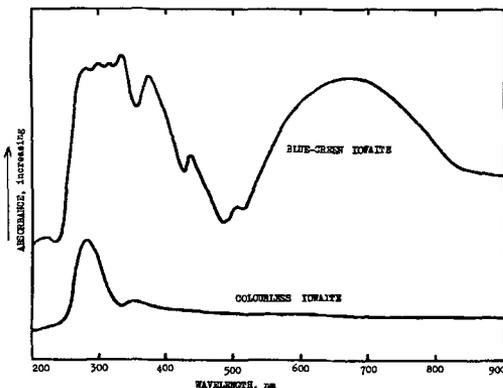


FIG. 1. Electronic absorption spectra of iowaites, viewed along the optic axis (*c*).

### Cause of the pleochroism

The shortest line between two metal ions in the brucite layer passes midway between two oxygen atoms in the coordination octahedron, and thus lies along the directions of the lobes of the  $t_{2g}$  orbitals. The electron involved in  $\text{Fe}^{2+}$ – $\text{Fe}^{3+}$  intervalence charge transfer lies in a  $t_{2g}$  orbital. In the structure of iowaitite, one  $\text{Mg}^{2+}$  in four is replaced by an  $\text{Fe}^{3+}$  ion. Replacement of even a small proportion of the remaining  $\text{Mg}^{2+}$  ions by  $\text{Fe}^{2+}$  would give rise to a situation in which  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are sometimes nearest neighbour cations, with adjacent lobes of their  $t_{2g}$  orbitals aligned along the metal–metal axis, and thus ideally situated for charge-transfer to take place. Charge-transfer, being an allowed transition, gives rise to very strong absorption, and a small population of  $\text{Fe}^{2+}$  ions would be enough to produce a visible blue-green colour. Charge transfer could not conceivably take place between the separated brucite layers, and is therefore directionally restricted to transitions in the plane of the brucite layers, giving rise to the intense pleochroism observed.

### Discussion and conclusion

Iowaitite is the chloride analogue of pyroaurite, of ideal formula  $\text{Mg}_6\text{Fe}_2(\text{OH})_{16}\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ .

Pyroaurite is a member of the trigonal-rhombohedral (3R) hydrotalcite group of minerals (Taylor, 1969, 1973; Fleischer and Mandarino, 1991) with general formula  $M_6^{2+}M_2^{3+}(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ , in which  $M^{2+}$  is commonly Mg but may be Ni or Fe, and  $M^{3+}$  is Fe, Al, Cr or Mn. The interlayer carbonate may be replaced by other anions, e.g.  $\text{OH}^-$  in meixnerite (*cf.* hydrotalcite) or  $\text{SO}_4^{2-}$  in honessite (*cf.* reevesite). Some members of this group have hexagonal (2H) polytypes (the manasseite group, Taylor, 1969, 1973; Fleischer and Mandarino, 1991). Chlormagaluminite,  $(\text{Mg},\text{Fe})_4\text{Al}_2(\text{OH})_{12}(\text{Cl}_2,\text{CO}_3) \cdot 2\text{H}_2\text{O}$  is a hexagonal mineral structurally related to the manasseite group in which some of the carbonate is replaced by chloride (Kashaev *et al.*, 1982) as in iowaitite. Other related hexagonal minerals, in which the carbonate is replaced partially or wholly by sulphate include carrboydite, glaucocerinite, honessite, hydrohonessite, motukoreaitite, mountkiethite, and wermlandite (Fleischer and Mandarino, 1991; see also Drits *et al.*, 1987). The interlayer cations in this group of minerals are fairly loosely held, and can be replaced by ion-exchange, as evidenced by experiments in which the carbonate groups in takovite and hydrotalcite were readily exchanged

with suitable anions such as chloride, hydroxide, sulphate and nitrate. It was noted that replacement of carbonate by chloride increased the *c*-spacing by about 0.2 Å (Bish, 1980). Thus pyroaurite, also known from Palabora, may be expected to be converted to iowaite by the action of chloride-rich solutions, while excess of carbonate in solution should prevent or reverse this process. Primary pyroaurite, formed in the carbonate-rich carbonatite crystallization phase, could be replaced by iowaite in a later, chloride-carrying hydrothermal phase.

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