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# X-ray study on polymorphism of ilvaite, $HCaFe_2^{2+}Fe^{3+}O_2[Si_2O_7]$

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*Polymorphism / Ilvaite*

**Abstract.** The crystal structure of the monoclinic form of ilvaite has been investigated. A crystal from Tsumo, Japan, was characterized by space group $P2_1/a$, with $a = 13.009(1)$ Å, $b = 8.8008(3)$ Å, $c = 5.8589(2)$ Å, $\beta = 90.324(9)°$, whereas a crystal from Techukhe, Siberia, had $P2_1/a$, $a = 13.013(3)$ Å, $b = 8.8197(6)$ Å, $c = 5.8424(5)$ Å, $\beta = 90.03(1)°$. In the structure, the octahedra formed by oxygen atoms about Fe(11) and those about Fe(12) are alternately linked together, sharing edges to form a chain of octahedra parallel to $c$. The monoclinic symmetry of ilvaite is characterized by ordering of $Fe^{2+}$ and $Fe^{3+}$ which are distributed over these two Fe sites with a ratio of 1 : 1. The atomic contents in the Fe(11) site, estimated from mean Fe(11)–O length, are: *Tsumo ilvaite* 0.85 $Fe^{2+}$ and 0.15 $Fe^{3+}$, and *Techukhe ilvaite* 0.53 $Fe^{2+}$ and 0.47 $Fe^{3+}$. From these atomic occupancies, the order parameter, $\sigma$, of Tsumo ilvaite is calculated to be 75 %, while that of Techukhe ilvaite 6 %. From the two cases of monoclinic ilvaites, a relation between $\beta$ and $\sigma$ has been deduced; the result permits predicting $\beta \approx 90.45°$ for an ilvaite crystal having $\sigma = 100$ %. The orthorhombic form of ilvaite may be defined as a form of ilvaite having $\sigma = 0$.

## Introduction

Kokkoros (1936) first provided orthorhombic crystallographic data of ilvaite; the cell dimensions are $a = 8.76$ Å, $b = 13.04$ Å, $c = 5.82$ Å and space group is *Pbnm*. The orthorhombic crystal structure of ilvaite, which was described by Belov and Mokeeva (1954), consists of $Si_2O_7$ groups. The chemical formula may then be written by $CaFe_2^{2+}Fe^{3+}Si_2O_7O(OH)$. The Fe atoms are located at two distinct sets of equivalent positions; one is eightfold $8d$ and the other fourfold $4c$. The former has a point symmetry 1 and the latter *m*. Belov and Mokeeva (1954) assumed that the $8d$ positions were occupied by $Fe^{2+}$ and $4c$ by $Fe^{3+}$. The interatomic distances, which were later obtained (Baur, 1971; Beran and Bittner, 1974; Haga and Takéuchi, 1976), however, favor the following distribution scheme of Fe: statistical distribution of $Fe^{2+}$ and $Fe^{3+}$ at $8d$, and location of $Fe^{2+}$ at $4c$. By means of neutron diffraction study, Haga and Takéuchi (1976) revealed that the Mn atoms, commonly contained in ilvaite in minor amount, are preferentially located at $4c$ substituting for $Fe^{2+}$. The hydrogen-bonding in ilvaite was studied by Beran and Bittner (1974) and Haga and Takéuchi (1976).

Further advancement of structural knowledge of ilvaite is due chiefly to studies by means of X-ray powder diffraction. Noting broadenings and splits in powder diffraction lines, Bartholomé and Duchesne (1968) brought out the existence of monoclinic ilvaite with orthorhombic *a* as the unique axis; the $\beta$ angle deviated only slightly from 90°. They gave the monoclinic cell dimensions, $a = 13.00$ Å, $b = 8.81$ Å, $c = 5.85$ Å, $\beta = 90.25°$. Dietrich (1972) also described monoclinic ilvaites. Recently, employing X-ray powder diffractometry, Bunno (1980) made an extensive survey of ilvaites from 36 localities, mainly in Japan, and found that they were mostly monoclinic and rarely orthorhombic. A salient feature was that their $\beta$ angles showed a spectrum of values from $90.34_4°$ down to 90.00°; samples from only three localities gave the latter value within the limit of experimental accuracy and were considered to be orthorhombic. He showed that such a scattering in the value of $\beta$ was correlated not with chemistry but with the difference in the physical condition of crystal formation. As the monoclinic symmetry of ilvaite is presumably due to ordering of $Fe^{2+}$ and $Fe^{3+}$ (Bartholomé and Duchesne, 1968) in the $8d$ positions of the orthorhombic structure, the above feature of the $\beta$ angle would imply the existence of ilvaite crystals having a variety of order parameters. Bunno (1981) described in detail the mode of occurrence of monoclinic ilvaite from the Tsumo mine, Japan.

In order to elucidate the structural characteristics underlying the monoclinic symmetry of ilvaite, we have undertaken the structural analyses of two ilvaites having different $\beta$ angles. The purpose of the present paper is to describe the result and discusses the monoclinic symmetry of ilvaite. As ilvaite is a mixed valence compound of iron, it has been a target of study with Mössbauer spectroscopy. A number of works, along this line, up to 1979 are summarized by Nolet and Burns (1979). Yamanaka and Takéuchi (1979) reported a novel magnetic feature of ivaite at low temperatures.

## Experimental

### Material

From a collection of the University Museum of the Universitty of Tokyo, crystals from Tsumo, Japan (# 21311) and those from Techukhe, USSR (# 23801) were chosen and used for the present study. According to Bunno's measurement (1980), the former have $\beta = 90.30°$ and the latter $\beta = 90.00°$ (the monoclinic set of axes, mentioned previously, will be used throughout this paper regardless of symmetry). Their chemical compositions obtained by electron microprobe analyses (Bunno, 1980) showed that the Tsumo specimen contained 0.05 Mn and Techukhe specimen 0.29 Mn atoms per quarter unit-cell. These Mn contents will be discussed later in the light of bond lengths.

For X-ray study, crystals of both ilvaites were ground to spheres, each having a radius of 0.125 mm. Unit-cell dimensions were measured with a Rigaku AFC-5 single-crystal diffractometer at 24°C, using graphite-monochromated Mo*K*α radiation, $\lambda = 0.71069$ Å. The cell dimensions, obtained by least-squares procedures applied to sin $2\theta$ values of 25 reflections are listed in Table 1. The $\beta$ angles of both ilvaites are slightly larger than the corresponding values obtained by Bunno (1980). The significance of the deviation from 90° of the $\beta$ angle of Techukhe ilvaite will be discussed later.

### Intensity data collection

The $\omega - 2\theta$ scan technique was used to measure, on the above-mentioned single-crystal diffractometer, quarter the number of the Mo*K*α diffraction

**Table 1.** Crystal data and intensity-study data of Tsumo and Techukhe ilvaites

| | Tsumo | Techukhe |
|---|---|---|
| Cell dimensions | | |
| $a$ | 13.009(1) Å | 13.013(3) Å |
| $b$ | 8.8008(3) | 8.8197(6) |
| $c$ | 5.8589(2) | 5.8424(5) |
| $\beta$ | 90.324(9)° | 90.03(1)° |
| $V$ | 670.79(8) Å$^3$ | 670.5(2) Å$^3$ |
| Number of reflections | | |
| measured | 7464 | 7471 |
| used for refinement | 6297 | 6201 |
| $R$ (%) | 3.23 | 3.51 |
| wt. $R$ (%) | 3.34 | 3.57 |

**Table 2.** Statistics of the number of observed $h0l$ and $0kl$ reflections of Tsumo ilvaite. Corresponding reflections of the orthorhombic structure are given in the second column

| Reflections | Orthorhombic structure | Number of observed reflections | | | |
|---|---|---|---|---|---|
| | | Total | | | Fraction |
| $h0l$ | $0kl$<br>($k = 2n$ only) | 321 | $h = 2n$ | 276 | 86% |
| | | | $h \neq 2n$ | 45 | 14 |
| $0kl$<br>($l \neq 0$) | $h0l$<br>($h + l = 2n$ only) | 91 | $k + l = 2n$ | 39 | 43 |
| | | | $k + l \neq 2n$ | 52 | 57 |
| $0k0$ | $h00$<br>($h = 2n$ only) | 10 | $k = 2n$ | 9 | 90 |
| | | | $k \neq 2n$ | 1 | 10 |

intensities up to $2\theta = 100°$ with the bisecting mode. The number of reflections collected for each sample is listed in Table 1 (the intensity data of Techukhe ilvaite were collected with the monoclinic mode). Each set of intensities was corrected for Lorentz and polarization factors and reduced to structure factors. Spherical absorption correction was also applied to the intensity data. Reflections whose intensities were greater than $2\sigma(I)$ were used for subsequent structural study.

## Space group

As the (010) plane of monoclinic ilvaite corresponds to (100) of orthorhombic ilvaite, the $h0l$ reflections of monoclinic ilvaite will occur only if $h = 2n$ if the $b$-glide of the orthorhombic structure is not suppressed upon distortion from orthorhombic to monoclinic. On the other hand, there will be no missing rule of spectra for $0kl$ reflections, which correspond to $h0l$ of the orthorhombic structure. These situations are summarized in Table 2, which shows statistics of the number of observed $h0l$ and $0kl$ reflections of Tsumo ilvaite. As will be observed in this table, the $n$ glide of the orthorhombic structure is obviously suppressed in Tsumo ilvaite whereas there are 45 $h0l$ reflections with $h \neq 2n$. The intensities of these reflections were relatively very weak and not necessarily reproducible. Those which were found to be reproducible, by repeated measurements, were subjected to examination with the $\psi$-scan technique. From the results, we decided that they were not structural but due to the Renninger effect. The $b$ glide in the orthorhombic structure is thus retained as an $a$ glide in the monoclinic structure. Similarly, the intensities of $0k0$ reflections were found to be significant only if $k = 2n$. The most probable space group of Tsumo ilvaite was then found to be $P2_1/a$.

In the case of Techukhe ilvaite, we recorded 15 $0kl$ reflections, with $k+l \neq 2n$, which could not be ascribed to the Renninger effect. Their intensities were however too weak to permit accurate measurement; their significance is unknown. We nevertheless assumed a space group $P2_1/a$ for the process of structure analysis as will be described later; it was expected that we could find the true symmetry in the final result of the analysis.

## Structure analysis

As mentioned earlier, the monoclinic structure of ilvaite would be effected by a very slight distortion of the orthorhombic structure. It is then anticipated that the former structure can be derived by straightforward refinement of the latter. Upon distortion from *Pbnm* to $P2_1/a$, the Fe(1) site of the orthorhombic structure splits into two distinct fourfold sites: we denote them Fe(11) and Fe(12). While, the fourfold Fe(2) site in the orthorhombic structure does not split upon its distortion to $P2_1/a$; the notation is retained in the monoclinic structure. The oxygen atoms in the monoclinic structure are likewise denoted according to this notation scheme.

The atomic parameters provided by Haga and Takéuchi (1976) served as initial atomic parameters for structure refinement of Tsumo ilvaite. Five cycles of isotropic refinement using the program LINUS (Coppens and Hamilton, 1970) converged to give $R = 5.16\%$ (wt. $R = 5.48\%$). For this refinement, neutral atomic form factors were used which were provided by *International Tables for X-ray Crystallography* (1974). Further three cycles of anisotropic refinement converged to give $R = 3.65\%$ (wt. $R = 4.06\%$). Bond lengths calculated at this stage suggested that the Fe(11) site was nearly completely occupied by $Fe^{2+}$ and Fe(12) by $Fe^{3+}$. Subsequent refinement was therefore executed based on this ordered model of structure using half-ionized form factors for all atoms; those for $Ca^{1+}$, $Si^{2+}$ were provided by Fukamachi (1971), that for $Fe^{1+}$ by *International Tables for X-ray Crystallography* (1962) and those for others by *International Tables for X-ray Crystallography* (1974). Two cycles of refinement converged to give $R = 3.23\%$ (wt. $R = 3.34\%$) for all reflections used (Table 1); unit weighting scheme was used throughout calculations. The resulting atomic parameters are listed in Table 3.

The structure of Techukhe ilvaite was refined assuming the space group $P2_1/a$; namely, the observed structure factors of both $hkl$ and $\bar{h}kl$ reflections were used for least-squares calculation. The refinement was made in a way which is similar to the above case. As the ordering of $Fe^{2+}$ and $Fe^{3+}$ was not significantly observed during the process of refinement, a form factor corresponding to $Fe^{1.25+}$ was evaluated, from those for $Fe^{2+}$ and $Fe^{1+}$, and used for the Fe atoms at Fe(11) and Fe(12). The final $R$ value is given in Table 1. We give in Table 4 the atomic parameters obtained.

**Table 3.** Atomic parameters for Tsumo ilvaite

Positional parameters

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Ca | 0.18724(2) | 0.37015(3) | 0.24603(5) | 0.535 Å$^2$ |
| Fe(11) | 0.10986(2) | 0.04931(2) | 0.99276(4) | 0.491 |
| Fe(12) | 0.11010(2) | 0.05228(2) | 0.50717(4) | 0.468 |
| Fe(2) | 0.44100(2) | 0.24028(2) | 0.24832(4) | 0.499 |
| Si(1) | 0.04048(3) | 0.36892(5) | 0.75110(8) | 0.334 |
| Si(2) | 0.32055(3) | 0.22714(5) | 0.74743(8) | 0.347 |
| O(1) | 0.49011(9) | 0.4700(1) | 0.2664(2) | 0.554 |
| O(21) | 0.06257(8) | 0.2726(1) | 0.9840(2) | 0.508 |
| O(22) | 0.06486(9) | 0.2730(1) | 0.5186(2) | 0.515 |
| O(3) | 0.22255(8) | 0.1090(1) | 0.7419(2) | 0.481 |
| O(41) | 0.32861(9) | 0.3272(1) | 0.9808(2) | 0.527 |
| O(42) | 0.32956(9) | 0.3318(1) | 0.5181(2) | 0.521 |
| O(5) | 0.41504(8) | 0.1008(1) | 0.7460(2) | 0.489 |
| O(6) | 0.39855(9) | 0.0265(1) | 0.2472(2) | 0.708 |
| O(7) | 0.20216(8) | 0.1091(1) | 0.2575(2) | 0.525 |
| H | 0.258(3) | 0.068(5) | 0.260(8) | 0.776 |

Anisotropic thermal parameters ($\times 10^3$)

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Ca | 0.723(9) | 1.21(2) | 5.39(5) | −0.12(1) | −0.04(2) | −0.02(3) |
| Fe(11) | 0.725(7) | 1.34(2) | 4.12(4) | 0.003(9) | −0.15(1) | −0.23(2) |
| Fe(12) | 0.661(7) | 1.29(1) | 4.07(4) | −0.034(8) | 0.05(1) | 0.19(2) |
| Fe(2) | 0.830(8) | 1.15(2) | 4.21(4) | −0.068(9) | −0.04(1) | −0.04(2) |
| Si(1) | 0.51(1) | 0.87(3) | 2.79(8) | 0.00(2) | −0.06(3) | 0.00(4) |
| Si(2) | 0.52(1) | 0.96(3) | 2.88(8) | −0.05(2) | −0.03(3) | 0.08(4) |
| O(1) | 0.82(4) | 1.62(8) | 4.4(2) | 0.15(4) | −0.15(7) | −0.1(1) |
| O(21) | 0.84(4) | 1.61(8) | 3.3(2) | 0.12(4) | −0.07(7) | 0.4(1) |
| O(22) | 0.93(4) | 1.37(8) | 3.6(2) | 0.13(4) | 0.12(7) | −0.2(1) |
| O(3) | 0.58(3) | 1.44(8) | 4.4(2) | −0.28(4) | −0.03(7) | 0.0(1) |
| O(41) | 0.95(4) | 1.52(8) | 3.4(2) | −0.11(4) | −0.03(7) | −0.4(1) |
| O(42) | 0.95(4) | 1.33(8) | 3.7(2) | −0.16(4) | 0.04(7) | 0.4(1) |
| O(5) | 0.49(3) | 1.32(8) | 5.3(2) | 0.06(4) | −0.08(7) | 0.2(1) |
| O(6) | 0.90(4) | 1.38(8) | 7.9(3) | 0.29(4) | 0.10(8) | 0.3(1) |
| O(7) | 0.70(3) | 1.61(8) | 4.4(2) | −0.04(4) | 0.07(7) | 0.1(1) |
| H | – | – | – | – | – | – |

The expression used for the anisotropic thermal parameters was
$\exp[-(\beta_{11} h^2 + \beta_{22} k^2 + \beta_{33} l^2 + 2\beta_{12} hk + 2\beta_{13} hl + 2\beta_{23} kl)]$

**Table 4.** Atomic parameters of Techukhe ilvaite

Positional parameters

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Ca | 0.18721(2) | 0.37036(4) | 0.24959(6) | 0.571 Å$^2$ |
| Fe(11) | 0.10977(2) | 0.05063(3) | 0.99240(4) | 0.553 |
| Fe(12) | 0.10980(2) | 0.05086(3) | 0.50752(4) | 0.553 |
| Fe(2) | 0.44035(2) | 0.23975(3) | 0.24973(4) | 0.564 |
| Si(1) | 0.04073(3) | 0.36862(5) | 0.75046(8) | 0.373 |
| Si(2) | 0.32047(3) | 0.22720(5) | 0.74975(8) | 0.364 |
| O(1) | 0.4906(1) | 0.4722(1) | 0.2513(3) | 0.863 |
| O(21) | 0.06353(9) | 0.2723(1) | 0.9839(2) | 0.553 |
| O(22) | 0.06377(9) | 0.2724(1) | 0.5168(2) | 0.571 |
| O(3) | 0.22271(9) | 0.1091(1) | 0.7496(2) | 0.597 |
| O(41) | 0.32914(9) | 0.3296(1) | 0.9820(2) | 0.562 |
| O(42) | 0.32928(9) | 0.3301(1) | 0.5183(2) | 0.587 |
| O(5) | 0.41525(9) | 0.1011(1) | 0.7496(2) | 0.550 |
| O(6) | 0.3978(1) | 0.0243(1) | 0.2505(3) | 0.807 |
| O(7) | 0.20177(9) | 0.1094(1) | 0.2502(2) | 0.577 |
| H | 0.236(4) | 0.081(7) | 0.26(1) | 1.642 |

Anisotropic thermal parameters ( × 10$^3$)

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Ca | 0.68(1) | 1.45(2) | 5.87(6) | −0.12(1) | 0.01(2) | 0.08(3) |
| Fe(11) | 0.709(8) | 1.67(2) | 4.82(4) | 0.0(1) | −0.14(1) | −0.27(2) |
| Fe(12) | 0.711(8) | 1.67(2) | 4.80(4) | −0.01(1) | 0.18(1) | 0.32(2) |
| Fe(2) | 0.841(8) | 1.56(2) | 4.68(4) | −0.03(1) | 0.04(1) | −0.10(2) |
| Si(1) | 0.47(1) | 1.41(4) | 2.65(8) | 0.06(2) | 0.07(3) | 0.05(4) |
| Si(2) | 0.46(1) | 1.13(3) | 3.12(8) | −0.06(2) | 0.02(3) | 0.02(4) |
| O(1) | 1.06(5) | 2.0(1) | 9.1(3) | 0.10(6) | −0.1(1) | −0.2(1) |
| O(21) | 0.92(4) | 1.80(9) | 3.5(2) | 0.15(5) | −0.07(7) | 0.6(1) |
| O(22) | 0.89(4) | 1.97(9) | 3.6(2) | 0.21(5) | 0.27(7) | −0.3(1) |
| O(3) | 0.61(4) | 1.77(9) | 6.1(2) | −0.19(5) | −0.02(8) | −0.2(1) |
| O(41) | 0.86(4) | 1.71(9) | 4.2(2) | −0.11(5) | 0.12(8) | −0.6(1) |
| O(42) | 0.95(4) | 1.81(9) | 4.0(2) | −0.15(5) | −0.01(8) | 0.3(1) |
| O(5) | 0.53(4) | 1.67(9) | 5.6(2) | −0.03(4) | 0.03(7) | −0.1(1) |
| O(6) | 0.99(4) | 1.9(1) | 8.5(3) | 0.46(5) | −0.10(9) | −0.2(1) |
| O(7) | 0.72(4) | 1.82(9) | 5.0(2) | 0.05(5) | −0.07(8) | 0.2(1) |
| H | – | – | – | – | – | – |

## Discussion

### *Monoclinic structure of Tsumo ilvaite*

Although the mode of polyhedral links of the monoclinic structure of Tsumo ilvaite is essentially the same as that of the orthorhombic form, we illustrate the structure in Figure 1 for the convenience of subsequent discussions. The Fe atoms in the structure are octahedrally coordinated by six oxygen atoms. The octahedra about Fe(11) and those about Fe(12) are alternately linked together, sharing edges, to form a chain along *c*. A pair of such chains are laterally joined together, sharing edges, and form a double chain of octahedra, which is flanked by the octahedra about Fe(2). These composite chains, or columns, of octahedra about Fe are linked together by non-magnetic cations such as Ca and Si to complete the continuity of the structure.

Now, as will be observed in Table 5, the mean of Fe(11) – O bond lengths is significantly larger than that of Fe(12) – O, suggesting that Fe(11) is mainly occupied by $Fe^{2+}$ and Fe(12) by $Fe^{3+}$. The over-all mean of Fe(11) – O and Fe(12) – O lengths give a value of 2.081 Å. According to Ghose (1969), average M – O lengths for six-coordinated $Fe^{2+}$ and that for $Fe^{3+}$ in silicates are 2.135 Å and 2.025 Å, respectively. An average of 2.080 Å of these two values agree well with the above value of 2.081 Å for Tsumo ilvaite. It is then reasonable to adopt Ghose's values to estimate the atomic contents in Fe(11) and Fe(12): the contents of Fe(11) are 0.85 $Fe^{2+}$ and 0.15 $Fe^{3+}$, and those of Fe(12) are 0.15 $Fe^{2+}$ and 0.85 $Fe^{3+}$. The order parameter, $\sigma$, of Tsumo ilvaite was then evaluated to be ca. 75 %. The parameter, $\sigma$, is defined by $|OP\text{-}50|/50$, where OP is the atomic % occupancy of one of the two kinds of atoms occupying either Fe(11) or Fe(12).

The ordering of $Fe^{2+}$ and $Fe^{3+}$ necessarily gives rise to a distortion of the $\beta$ angle from 90°. This situation can readily be recognized from the O(3) – O(7) *n* ($= l_1$) edge of the octahedron about Fe(11) and the O(3) – O(7) ($= l_2$) edge of the octahedron about Fe(12) as given in Figure 1 (ii); the former has a length of 3.034 Å and the latter 2.849 Å. The zigzag line, which is formed by an alternate link of $l_1$ and $l_2$ as shown in Figure 1 (ii), is very closely in a plane parallel to (010) and defines the direction of the double chain of octahedra to which $l_1$ and $l_2$ are associated; namely, the zigzag line defines the direction of *c*. If Fe(11) and Fe(12) were equivalent and consequently $l_1$ and $l_2$ were related by a mirror parallel to (001), the direction as defined by the zigzag line would be normal to the *a* axis. As $l_1$ and $l_2$ are in the actual case different in length, the direction defined by the zigzag line becomes oblique to *a*, as shown in Figure 1 (ii).

### *Definition of the orthorhombic form of ilvaite*

The difference in length between $l_1$ and $l_2$ varies depending on the contents of Fe(11) and Fe(12). The value of the $\beta$ angle can therefore be regarded as a

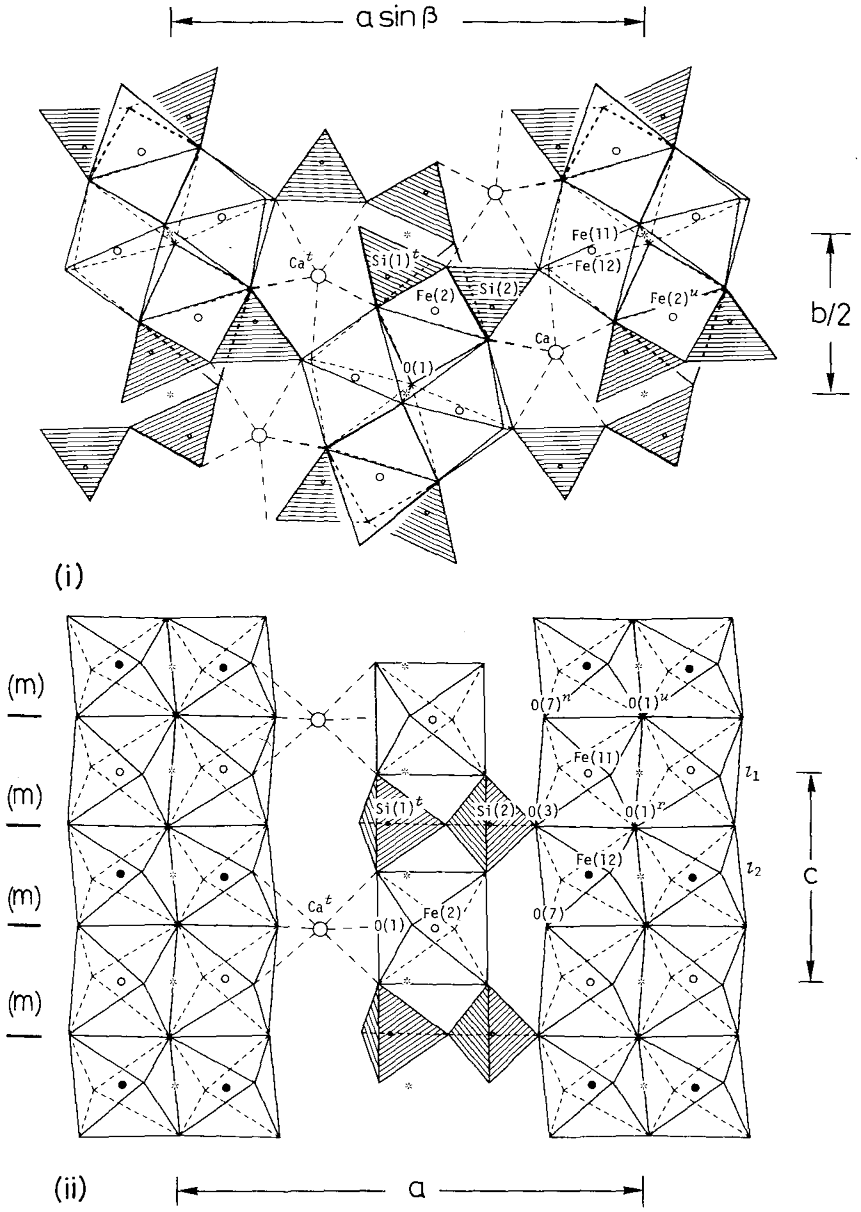

**Fig. 1.** The crystal structure of Tsumo ilvaite. (i) Projection along the *c* axis, showing half cell. (ii) Projection along the *b* axis, showing double chains of octahedra passing through the origin. Fe(11) and Fe(12) are represented by open circles and solid circles, respectively. Some of the polyhedra or cations between the two double chains are omitted [see Fig. 1 (i)]. Pseudo-mirror planes are indicated by (*m*). In both projections, the tetrahedra about Si are ruled. Stars indicate centers of symmetry

**Table 5.** Bond lengths and edges (Å), and bond angles (°) of polyhedra about cations in the structure of Tsumo ilvaite. Symmetry code is given in Table 7

| Central cation | Neighbors | Bond lengths | Edges | Edge lengths | Angles subtended by the edges |
|---|---|---|---|---|---|
| Ca | O(21)p | 2.387(1) | O(21)p–O(22) | 3.132(2) | 81.37(4) |
| | O(22) | 2.418(1) | O(21)p–O(41)p | 3.494(2) | 92.66(4) |
| | O(3)q | 2.408(1) | O(21)p–O(5)q | 3.305(2) | 86.71(4) |
| | O(41)p | 2.444(1) | O(21)p–O(7) | 2.811(2) | 73.57(4) |
| | O(42) | 2.460(1) | O(22)–O(42) | 3.482(2) | 91.12(4) |
| | O(5)q | 2.427(1) | O(22)–O(5)q | 3.286(2) | 85.41(4) |
| | O(7) | 2.307(1) | O(22)–O(7) | 2.764(2) | 71.58(4) |
| Average | | 2.407(1) | O(3)q–O(41)p | 3.041(2) | 77.61(4) |
| | | | O(3)q–O(42) | 2.953(1) | 74.68(4) |
| | | | O(3)q–O(5)q | 2.505(1) | 62.40(4) |
| | | | O(41)p–O(42) | 3.148(2) | 79.89(4) |
| | | | O(41)p–O(7) | 3.008(2) | 78.51(4) |
| | | | O(42)–O(7) | 2.982(2) | 77.38(4) |
| | | | Average | 3.070(2) | |
| Fe(11) | O(1)r | 2.112(1) | O(1)r–O(1)w | 3.177(2) | 93.51(4) |
| | O(1)w | 2.248(1) | O(1)r–O(21) | 3.114(2) | 96.58(4) |
| | O(21) | 2.060(1) | O(1)r–O(3) | 3.025(2) | 90.50(4) |
| | O(3) | 2.147(1) | O(1)r–O(41)s | 2.959(2) | 88.77(4) |
| | O(41)s | 2.118(1) | O(1)w–O(21) | 2.864(2) | 83.22(4) |
| | O(7)n | 2.026(1) | O(1)w–O(41)s | 3.299(2) | 98.11(4) |
| Average | | 2.118(1) | O(1)w–O(7)n | 2.846(2) | 83.33(4) |
| | | | O(21)–O(3) | 2.907(1) | 87.39(4) |
| | | | O(21)–O(7)n | 2.811(2) | 86.97(4) |
| | | | O(3)–O(41)s | 3.041(2) | 90.96(4) |
| | | | O(3)–O(7)n | 3.034(2) | 93.24(4) |
| | | | O(41)s–O(7)n | 2.873(2) | 87.79(4) |
| | | | Average | 2.996(2) | |
| Volume of the polyhedron (octahedron) | | | 12.55(2) Å$^3$ | | |
| Fe(12) | O(1)r | 2.001(1) | O(1)r–O(1)u | 2.798(2) | 85.83(5) |
| | O(1)u | 2.107(1) | O(1)r–O(22) | 3.036(2) | 97.71(5) |
| | O(22) | 2.031(1) | O(1)r–O(3) | 3.025(2) | 96.19(5) |
| | O(3) | 2.063(1) | O(1)r–O(42)r | 2.838(2) | 87.57(5) |
| | O(42)r | 2.099(1) | O(1)u–O(22) | 2.772(2) | 84.11(5) |
| | O(7) | 1.961(1) | O(1)u–O(42)r | 3.179(2) | 98.20(4) |
| Average | | 2.044(1) | O(1)u–O(7) | 2.846(2) | 88.71(5) |
| | | | O(22)–O(3) | 2.823(2) | 87.20(4) |
| | | | O(22)–O(7) | 2.764(2) | 87.66(5) |
| | | | O(3)–O(42)r | 2.953(1) | 90.39(4) |
| | | | O(3)–O(7) | 2.849(2) | 90.10(4) |
| | | | O(42)r–O(7) | 2.804(2) | 87.29(5) |
| | | | Average | 2.891(2) | |
| Volume of the polyhedron (octahedron) | | | 11.26(2) Å$^3$ | | |

**Table 5.** (Continued)

| Central cation | Neighbors | Bond lengths | Edges | Edge lengths | Angles subtended by the edges |
|---|---|---|---|---|---|
| Fe(2) | O(1) | 2.123(1) | O(1)–O(21)v | 2.864(2) | 82.42(4) |
| | O(21)v | 2.223(1) | O(1)–O(22)t | 2.772(2) | 78.50(4) |
| | O(22)t | 2.256(1) | O(1)–O(41)p | 2.959(2) | 84.61(4) |
| | O(41)p | 2.270(1) | O(1)–O(42) | 2.838(2) | 79.78(4) |
| | O(42) | 2.297(1) | O(21)v–O(22)t | 3.132(2) | 88.75(4) |
| | O(6) | 1.961(1) | O(21)v–O(41)p | 3.168(2) | 89.66(4) |
| Average | | 2.188(1) | O(21)v–O(6) | 3.177(2) | 98.64(5) |
| | | | O(22)t–O(42) | 3.197(2) | 89.21(4) |
| | | | O(22)t–O(6) | 3.207(2) | 98.79(5) |
| | | | O(41)p–O(42) | 3.148(2) | 87.16(4) |
| | | | O(41)p–O(6) | 3.202(2) | 98.09(5) |
| | | | O(42)–O(6) | 3.250(2) | 99.21(5) |
| | | | Average | 3.076(2) | |
| Volume of the polyhedron (octahedron) | | | 13.59(2) Å$^3$ | | |
| Si(1) | O(21) | 1.630(1) | O(21)–O(22) | 2.727(2) | 113.23(6) |
| | O(22) | 1.635(1) | O(21)–O(5)u | 2.615(1) | 105.57(6) |
| | O(5)u | 1.654(1) | O(21)–O(6)q | 2.663(2) | 111.16(7) |
| | O(6)q | 1.597(1) | O(22)–O(5)u | 2.615(2) | 105.32(6) |
| Average | | 1.629(1) | O(22)–O(6)q | 2.661(2) | 110.78(7) |
| | | | O(5)u–O(6)q | 2.671(2) | 110.49(6) |
| | | | Average | 2.659(2) | |
| Volume of the polyhedron (tetrahedron) | | | 2.211(4) Å$^3$ | | |
| Si(2) | O(3) | 1.645(1) | O(3)–O(41) | 2.744(2) | 113.85(6) |
| | O(41) | 1.629(1) | O(3)–O(42) | 2.743(1) | 113.53(6) |
| | O(42) | 1.634(1) | O(3)–O(5) | 2.505(1) | 98.66(6) |
| | O(5) | 1.658(1) | O(41)–O(42) | 2.711(2) | 112.39(6) |
| Average | | 1.641(1) | O(41)–O(5) | 2.673(2) | 108.83(6) |
| | | | O(42)–O(5) | 2.671(1) | 108.50(6) |
| | | | Average | 2.675(2) | |
| Volume of the polyhedron (tetrahedron) | | | 2.241(4) Å$^3$ | | |

function of the order parameter $\sigma$. The orthorhombic form of ilvaite may thus be defined as a form of ilvaite whose order parameter $\sigma$ has an extreme value of zero. Ilvaites for which $\sigma \neq 0$ then comprise a series of monoclinic forms.

## *Symmetry of Techukhe ilvaite*

We give in Table 6 the interatomic distances and bond angles of Techukhe ilvaite. A closer examination of the structural data thus obtained suggests

**Table 6.** Bond lengths and edges (Å), and bond angles (°) of polyhedra about cations in the structure of Techukhe ilvaite. Symmetry code is given in Table 7

| Central cation | Neigh-bors | Bond lengths | Edges | Edge lengths | Angles subtended by the edges |
|---|---|---|---|---|---|
| Ca | O(21)p | 2.397(1) | O(21)p–O(22) | 3.113(2) | 80.91(4) |
| | O(22) | 2.401(1) | O(21)p–O(41)p | 3.493(2) | 92.29(4) |
| | O(3)q | 2.410(1) | O(21)p–O(5)q | 3.303(2) | 86.29(4) |
| | O(41)p | 2.447(1) | O(21)p–O(7) | 2.778(2) | 72.33(5) |
| | O(42) | 2.450(1) | O(22)–O(42) | 3.492(2) | 92.07(4) |
| | O(5)q | 2.433(1) | O(22)–O(5)q | 3.303(2) | 86.17(4) |
| | O(7) | 2.309(1) | O(22)–O(7) | 2.778(2) | 72.25(5) |
| Average | | 2.407(1) | O(3)q–O(41)p | 2.999(2) | 76.25(4) |
| | | | O(3)q–O(42) | 2.993(2) | 76.03(4) |
| | | | O(3)q–O(5)q | 2.506(2) | 62.33(4) |
| | | | O(41)p–O(42) | 3.133(2) | 79.55(4) |
| | | | O(41)p–O(7) | 2.996(2) | 78.04(4) |
| | | | O(42)–O(7) | 2.998(2) | 78.03(4) |
| | | | Average | 3.068(2) | |
| Fe(11) | O(1)r | 2.052(1) | O(1)r–O(1)w | 2.987(2) | 89.85(6) |
| | O(1)w | 2.176(1) | O(1)r–O(21) | 3.064(2) | 96.80(5) |
| | O(21) | 2.046(1) | O(1)r–O(3) | 3.027(2) | 93.40(5) |
| | O(3) | 2.107(1) | O(1)r–O(41)s | 2.910(2) | 88.70(5) |
| | O(41)s | 2.110(1) | O(1)w–O(21) | 2.827(2) | 84.00(5) |
| | O(7)n | 1.992(1) | O(1)w–O(41)s | 3.228(2) | 97.69(5) |
| Average | | 2.081(1) | O(1)w–O(7)n | 2.841(2) | 85.80(5) |
| | | | O(21)–O(3) | 2.871(2) | 87.42(5) |
| | | | O(21)–O(7)n | 2.778(2) | 86.91(5) |
| | | | O(3)–O(41)s | 2.999(2) | 90.63(5) |
| | | | O(3)–O(7)n | 2.938(2) | 91.51(5) |
| | | | O(41)s–O(7)n | 2.844(2) | 87.74(5) |
| | | | Average | 2.943(2) | |
| Volume of the polyhedron (octahedron) | | | 11.91(2) Å$^3$ | | |
| Fe(12) | O(1)r | 2.044(1) | O(1)r–O(1)u | 2.958(2) | 89.26(6) |
| | O(1)u | 2.165(1) | O(1)r–O(22) | 3.057(2) | 96.83(5) |
| | O(22) | 2.044(1) | O(1)r–O(3) | 3.027(2) | 93.78(5) |
| | O(3) | 2.102(1) | O(1)r–O(42)r | 2.901(2) | 88.63(5) |
| | O(42)r | 2.108(1) | O(1)u–O(22) | 2.822(2) | 84.15(5) |
| | O(7) | 1.990(1) | O(1)u–O(42)r | 3.216(2) | 97.66(5) |
| Average | | 2.075(1) | O(1)u–O(7) | 2.841(2) | 86.15(5) |
| | | | O(22)–O(3) | 2.863(2) | 87.33(5) |
| | | | O(22)–O(7) | 2.778(2) | 87.03(5) |
| | | | O(3)–O(42)r | 2.993(2) | 90.63(5) |
| | | | O(3)–O(7) | 2.930(2) | 91.39(5) |
| | | | O(42)r–O(7) | 2.840(2) | 87.68(5) |
| | | | Average | 2.936(2) | |
| Volume of the polyhedron (octahedron) | | | 11.82(2) Å$^3$ | | |

**Table 6.** (Continued)

| Central cation | Neigh-bors | Bond lengths | Edges | Edge lengths | Angles subtended by the edges |
|---|---|---|---|---|---|
| Fe(2) | O(1) | 2.152(1) | O(1)–O(21)v | 2.827(2) | 80.22(5) |
| | O(21)v | 2.235(1) | O(1)–O(22)t | 2.822(2) | 79.91(5) |
| | O(22)t | 2.241(1) | O(1)–O(41)p | 2.910(2) | 82.18(5) |
| | O(41)p | 2.273(1) | O(1)–O(42) | 2.901(2) | 81.77(5) |
| | O(42) | 2.278(1) | O(21)v–O(22)t | 3.113(2) | 88.14(4) |
| | O(6) | 1.979(1) | O(21)v–O(41)p | 3.180(2) | 89.71(4) |
| Average | | 2.193(1) | O(21)v–O(6) | 3.209(2) | 98.99(5) |
| | | | O(22)t–O(42) | 3.182(2) | 89.53(4) |
| | | | O(22)t–O(6) | 3.209(2) | 98.79(5) |
| | | | O(41)p–O(42) | 3.133(2) | 87.02(4) |
| | | | O(41)p–O(6) | 3.242(2) | 99.13(5) |
| | | | O(42)–O(6) | 3.243(2) | 99.03(5) |
| | | | Average | 3.081(2) | |
| Volume of the polyhedron (octahedron) | | | 13.68(2) Å$^3$ | | |
| Si(1) | O(21) | 1.634(1) | O(21)–O(22) | 2.729(2) | 113.18(7) |
| | O(22) | 1.636(1) | O(21)–O(5)u | 2.615(2) | 105.37(7) |
| | O(5)u | 1.654(1) | O(21)–O(6)q | 2.658(2) | 111.16(8) |
| | O(6)q | 1.589(1) | O(22)–O(5)u | 2.614(2) | 105.22(7) |
| Average | | 1.628(1) | O(22)–O(6)q | 2.652(2) | 110.69(8) |
| | | | O(5)u–O(6)q | 2.672(2) | 110.93(7) |
| | | | Average | 2.657(2) | |
| Volume of the polyhedron (tetrahedron) | | | 2.206(4) Å$^3$ | | |
| Si(2) | O(3) | 1.644(1) | O(3)–O(41) | 2.747(2) | 113.83(7) |
| | O(41) | 1.634(1) | O(3)–O(42) | 2.748(2) | 113.97(7) |
| | O(42) | 1.633(1) | O(3)–O(5) | 2.506(2) | 98.66(6) |
| | O(5) | 1.660(1) | O(41)–O(42) | 2.709(2) | 112.06(7) |
| Average | | 1.643(1) | O(41)–O(5) | 2.676(2) | 108.64(7) |
| | | | O(42)–O(5) | 2.675(2) | 108.62(7) |
| | | | Average | 2.677(2) | |
| Volume of the polyhedron (tetrahedron) | | | 2.246(4) Å$^3$ | | |

that the structure of Techukhe ilvaite is probably not exactly orthorhombic. Pieces of evidence that support this view include:

(1) So far the average values are concerned, Ca–O and Si–O lengths of Techukhe ilvaite and of Tsumo ilvaite are the same within the tolerance of estimated error (Table 5 and Table 6). The difference, however, in average bond length between Fe(11)–O and Fe(12)–O amounts to a value which is six times the estimated error; this difference is probably significant.

**Table 7.** Symmetry code

| | | |
|---|---|---|
| n, $x, y, 1+z$ | r, $\frac{1}{2}-x, -\frac{1}{2}+y, 1-z$ | u, $-\frac{1}{2}+x, \frac{1}{2}-y, z$ |
| p, $x, y, -1+z$ | s, $\frac{1}{2}-x, -\frac{1}{2}+y, 2-z$ | v, $\frac{1}{2}+x, \frac{1}{2}-y, -1+z$ |
| q, $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$ | t, $\frac{1}{2}+x, \frac{1}{2}-y, z$ | w, $-\frac{1}{2}+x, \frac{1}{2}-y, 1+z$ |

(2) Among Fe(11)–O and Fe(12)–O bonds of Tsumo ilvaite which are mutually related by pseudo mirrors as seen in Figure 1(ii), Fe(11)–O(1)*w* and Fe(12)–O(1)*u* show a maximum difference of 0.141(1) Å in bond length. This situation suggests that the positional parameters of O(1) vary sensibly depending on the contents in the Fe(11) or Fe(12) sites. The corresponding pair of bonds in Techukhe ilvaite likewise shows a maximum difference of 0.011(1) Å among pairs of bonds related by pseudo mirrors.

(3) The edges O(1)*r*–O(1)*w* of the octahedron about Fe(11) and O(1)*r*–O(1)*u* of that about Fe(12) in the structure of Tsumo ilvaite show a maximum difference of 0.379(2) Å (Table 5) among pairs of edges each related by a pseudomirror. In the case of Techukhe ilvaite, the corresponding pair of edges likewise shows a maximum difference of 0.029(2) Å (Table 6); differences shown by other pairs do not exceed 0.009(2) Å. The small difference in the Fe content between Fe(11) and Fe(12) of Techukhe ilvaite is probably significant.

(4) Trials of redetermining cell parameters with single-crystal diffractometry unexceptionally showed a relatively large deviation of the $\beta$ angle from 90°. The deviation amounts to 0.030 ∼ 0.034° whereas those of $\alpha$ and $\gamma$ to 0.014° at most. The value of $\beta$ given in Table 1 is thus thought to be significant.

The Fe(11)–O and Fe(12)–O bond lengths of Techukhe ilvaite give an over-all average of 2.078 Å which is close enough to 2.080 Å, the average of $Fe^{2+}$–O and $Fe^{3+}$–O lengths given by Ghose (1969). Then the mean lengths of Fe(11)–O and that of Fe(12)–O found for Techukhe ilvaite were normalized by the factor 2.080/2.078 in order to estimate atomic occupancy. The order parameter of the structure was then found to be 6%.

## *Octahedra about Fe(2)*

The octahedra about Fe(2) in both Tsumo and Techukhe ilvaites are considerably distorted. The variance $\varepsilon$ of bond lengths which is as a measure of octahedral distortion, yields a value of 133.7 ($\times 10^4$ Å$^2$) for the Fe(2) octahedra of Tsumo ilvaite, for example, which is to be compared with 49.3 and 27.1 for the Fe(11) and Fe(12) octahedra, respectively. This large value of $\varepsilon$ is comparable with those of the M(2) octahedra in synthetic

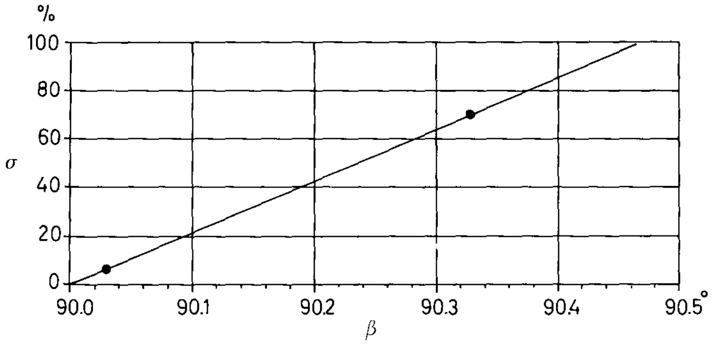

**Fig. 2.** A plot of order parameter, σ, versus monoclinic angle, β.

fayalite, $Fe_2SiO_4$ (Fujino et al., 1981) and of the M(2) octahedra in synthetic clinoferrosilite $FeSiO_3$ (Burnham, 1967), the values being 100.7 and 133.4 respectively. In the former case the mean $Fe^{2+}-O$ length is 2.177 Å while in the latter it is as large as 2.224 Å.

In the particular case of the Fe(2) octahedra of the ilvaite structure, a reliable relation between mean bond length and atomic occupancy has been provided by Haga and Takéuchi (1976). By means of occupancy refinement using a set of neutron diffraction data of an ilvaite crystal, they showed that the Fe(2) octahedra, having mean bond-length of 2.187 Å, contain 0.185 $Mn^{2+}$ and 0.815 $Fe^{2+}$. From these values we obtain a value of 2.177 Å for $Fe^{2+}-O$ on the assumption that $Mn^{2+}-O$ has a value of 2.23 Å (Shannon, 1970). The set of these two values may be used to estimate the Mn content, as a close approximation, in the Fe(2) site of the ilvaite structure. For Techukhe ilvaite, we found 0.30 Mn which is to be compared with 0.29 Mn obtained for this specimen by electron microprobe analysis (Bunno, 1980). While, for Tsumo ilvaite, we found 0.20 Mn which is considerably higher than 0.05 Mn given by Bunno. This discrepancy might probably be ascribed to the fact that the distribution of Mn in an ilvaite crystal tends to be spacially inhomogeneous (Bunno, 1980).

## Order-disorder of $Fe^{2+}$ and $Fe^{3+}$ in ilvaite

The order parameter found for Tsumo and Techukhe ilvaites are plotted in a σ versus β diagram as shown in Figure 2. A straight line defined by the two entries passes through the origin of the diagram defined by $\sigma = 0$ and $\beta = 90°$, suggesting that the line would closely represent the true correlation between σ and β. From this diagram we can then predict a β angle of about 90.45° for the ilvaite structure in which $Fe^{2+}$ and $Fe^{3+}$ are perfectly ordered.

Among the ilvaite specimens from 36 localities, which Bunno (1980) examined, those from 21 localities have $\beta$ in the range from 90.20 to 90.30°. The $\beta$ angles of reported monoclinic ilvaites (Bartholomé and Duchesne, 1968; Dietrich, 1971) also fall in this range. This range of $\beta$ corresponds to that of $\sigma$ from about 40 to 65 % (Fig. 2). The interpretation on the abundance of ilvaite having that range of $\sigma$ should be reserved for further study.

Regarding types of disorder in ilvaite, we point out the following two cases in which an ilvaite crystal, having a low value of $\sigma$, is generated from a structural unit having $\sigma = 100\,\%$:

(1) Suppose that an ilvaite crystal is growing in which $Fe^{2+}$ and $Fe^{3+}$ are perfectly ordered. If a mistake occurrs, during crystal growth, in the ordered array along $c$, a twin is generated with the twinning plane parallel to (001). Therefore, the order parameter of the resulting crystal structure as a whole may vary depending upon the frequency of twinning even if the 'twin individuals' themselves have an order parameter of 100 %. Ramdohr (1960) mentioned in his book that 'typical polysynthetic twinning' rarely occurs in ilvaite. The nature of this twinning, however, is quite unknown because no details of the twinning is described in his book.

(2) In each double chain of octahedra, Figure 1 (ii), there is a lateral pair of the Fe(11) sites, related to each other by a center of symmetry, and a similar pair of Fe(12). A one-dimensional cation array defined by an alternative arrangement, parallel to $c$, of such two kinds of pairs has a pseudotranslation of $c/2$. A displacement of $c/2$ of the cation array in a double chain, therefore, would not impose a significant effect on the surrounding polyhedra about nonmagnetic cations by which the double chain is linked to others. If such a displacement of the cation array occurs in a double chain of an ilvaite structure, it evidently gives an effect of lowering the order parameter of the structure even if $Fe^{2+}$ and $Fe^{3+}$ are perfectly ordered, in the same fashion, in every double chain of the structure.

## Addendum

Through a letter, dated 14 May 1982, from Dr. Larry W. Finger, Geophysical Laboratory at Washington, D. C., we learned that he was also working on the crystal structure of monoclinic ilvaites having beta angles smaller than that of Tsumo ilvaite. His sets of the atomic parameters were well in line with our results which had been available at that time.

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# Refinement of the structure of Ikaite, $CaCO_3 \cdot 6\,H_2O$

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*Crystal structure* / $CaCO_3 \cdot 6\,H_2O$

**Abstract.** Ikaite, $CaCO_3 \cdot 6\ H_2O$, is monoclinic, $C2/c$, with $a = 8.792(2)$, $b = 8.310(2)$, $c = 11.021(2)$ Å, $\beta = 110.53(5)°$, $Z = 4$. With 2205 independent reflections taken at −25 °C of a naturally grown crystal specimen the structure was refined to a weighted $R_w = 0.028$. The $CO_3$ group is planar with C–O distances 1.279(2) and 1.290(1) (2 ×) Å. The hydrogen bond network is determined. The optical behaviour is explained by structural characteristics.

## Introduction

Synthetic hydrates of $CaCO_3$ were first described by Daniell (1819). Pelouze (1831) was the first to synthesize the hexahydrate. Conditions of formation and stability have been studied by Krauss and Schriever (1930), Brooks et al. (1951), and Marland (1975). — Several claims of natural occurences, partially questionalbe though, are listed by Krauss and Schriever (1930). Pauly (1963) discovered euhedral crystals in the waters of the Ika Fjord in Greenland, and named the mineral "Ikaite" after this locality (Fleischer, 1964). — Crystallographic properties of $CaCO_3 \cdot 6\,H_2O$ were described by Bütschli (1908), Vetter (1911) and Johnston et al. (1916). A crystal structure analysis at −122° using a synthetic crystal specimen was performed by Dickens and Brown (1970): refinement from photographically collected data, with isotropic temperature factors and without hydrogen atoms, led to $R = 0.10$. It seemed desirable, therefore, to refine the structure to a higher degree of accuracy. Contrary to the investigation of Dickens and Brown, a natural crystal specimen was used in the present study.

## Experimental and results

A sediment core retrieved from a water depth of 1950 meters and sub-zero temperatures in a shelf basin of the Bransfield Strait (Antarctica) (Suess et al., 1982) contained $CaCO_3 \cdot 6\,H_2O$ single crystals. Since decomposition occurs rapidly at room temperature the crystals were kept below 0 °C in a freezer during transport. A specimen of approximately isometric shape and a mean diameter of 0.2 mm was chosen for intensity data collection on a Philips PW 1100 diffractometer with Mo$K\alpha$ radiation and was cooled in a stream of evaporated liquid nitrogen to $-25\,^{\circ}$C. The lattice parameters, as listed in the abstract, were obtained by a least-squares fit to diffractometrically determined Bragg angles of a single crystal. Intensities of 2404 reflections were collected in the range $2^{\circ} < \vartheta < 40^{\circ}$. Corrections for absorption were made assuming spherical shape ($\mu = 8.2\,\mathrm{cm}^{-1}$). The specimen partially decomposed to calcite during the measurement. At the end of the measurement, the reference reflections yielded only about 60% of the counting rates at the beginning of the measuring process. This effect was taken into account in the refinement procedure: since the data were collected successively with increasing Miller index $l$, a separate scale factor was assigned to each "layer" with constant $l$. Calculations were performed using the SHELX-76 system (Sheldrick, 1976).

Atomic parameters of Dickens and Brown (1970) were chosen as starting values for the refinement process. Hydrogen atoms were detected by difference Fourier synthesis. Refinement, using 2205 independent reflections [$I > \sigma(I)$], with anisotropic temperature parameters for the non-hydrogen atoms led to a weighted $R_w = 0.028$ (unweighted $R = 0.034$). Extinction was considered: $g = 1.1 \cdot 10^{-6}$. $F_o/F_c$ lists can be obtained from the authors. Final atomic parameters are summarized in Table 1. Bond lenghts within the Ca coordination polyhedron and the geometry of the $CO_3$ group are listed in Table 2.

## Discussion

Since the general outline of the structure has been given already by Dickens and Brown (1970) only some additional and complementary remarks concerning the higher accuracy and the incorporation of the hydrogen atoms will be given. Ca ions as well as $CO_3$ groups [C and O(1)] lie on twofold axes. The oxygen atoms O(1), O(2), and O(2)′ form an almost equilateral triangle (cf. Table 2). The mean C–O distance of 1.286(1) Å practically equals the reported mean value of 1.284(4) Å for the average C–O bond lengths in 34 carbonate groups (Zemann, 1981). Some recent accurate structure analyses of crystals containing carbonate groups in a position allowing aplanarity displayed significant displacement of the carbon atom from the plane of the three oxygen atoms. In the present structure, the $CO_3$ group should be planar by space group symmetry requirements. But even then deviations from

**Table 1.** Fractional atomic coordinates and thermal parameters $U_{ij}$ (all $\times 10^4$). The temperature factor is of the form $\exp\left[-2\pi^2 \left(U_{11}\, h^2 a^{*2} + \ldots 2\, U_{12}\, hka^* b^* + \ldots\right)\right]$

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ca | 5000 | 6472(0) | 2500 | 148(1) | 101(1) | 127(2) | 0 | 51(1) | 0 |
| C | 5000 | 3055(2) | 2500 | 109(4) | 120(4) | 171(6) | 0 | 31(4) | 0 |
| O(1) | 5000 | 1515(1) | 2500 | 213(4) | 96(3) | 325(5) | 0 | 48(4) | 0 |
| O(2) | 5262(1) | 3852(1) | 1588(1) | 197(3) | 160(2) | 162(3) | −10(2) | 87(2) | −11(2) |
| O(3) | 6146(1) | 7222(1) | 913(1) | 278(3) | 196(3) | 172(3) | −10(2) | 102(3) | −44(2) |
| O(4) | 7872(1) | 5581(1) | 3829(1) | 202(3) | 179(3) | 172(3) | −8(2) | 63(2) | −9(2) |
| O(5) | 6707(1) | 8849(1) | 3589(1) | 177(3) | 140(3) | 204(3) | 10(2) | 74(2) | 1(2) |
| H(1) | 5795(20) | 6897(19) | 158(16) | 404(43) | | | | | |
| H(2) | 6374(23) | 8063(23) | 905(18) | 566(55) | | | | | |
| H(3) | 8530(20) | 5959(18) | 3574(18) | 392(43) | | | | | |
| H(4) | 8105(19) | 5848(17) | 4580(16) | 330(40) | | | | | |
| H(5) | 7628(19) | 8838(16) | 3567(15) | 304(38) | | | | | |
| H(6) | 6324(19) | 9668(19) | 3422(16) | 411(44) | | | | | |

**Table 2.** Bond lengths (Å) around the Ca ion and bond lengths and angles (°) of the $CO_3$ group

| | | | | |
|---|---|---|---|---|
| | Ca−O(2) | 2.442(1) (2×) | C−O(1) | 1.279(2) |
| | Ca−O(3) | 2.387(1) (2×) | C−O(2) | 1.290(1) (2×) |
| | Ca−O(4) | 2.544(1) (2×) | O(1)−C−O(2) | 120.9(1) (2×) |
| | Ca−O(5) | 2.516(1) (2×) | O(2)−C−O(2)′ | 118.2(1) |
| all other | Ca−O | >4.1 | Ca−C | 2.839(1) |

planarity are possible if two (or more) non-planar groups are statistically distributed. The thermal motion perpendicular to the plane then possibly indicates asymmetry. In the present case, however, the rms displacements of C, O(1) and O(2) are 0.098(2), 0.135(1), and 0.134(1) Å, respectively. The lower value for C and the comparable values for the oxygen atoms are consistent with a librational motion of the $CO_3$ group, and yield no indication of an aplanarity.

The O−H distances within the water molecules scatter between 0.73 and 0.83 Å, the H−O−H angles between 107.3 and 111.4°. The hydrogen bonding scheme proposed by Dickens and Brown (1970) was verified. The configuration of the hydrogen bonds is listed in Table 3.

The knowledge of the structure allows an estimate of the refractive behaviour of Ikaite. Dickens and Brown (1970) report that $n_\beta$ is parallel to $b$ and that $n_\gamma$ extinguishes at 17° from $c$ in the acute angle $\beta$ (cf. Fig. 1). Contrary, Johnston et al. (1916) report $n_\gamma$ to be inclined by 17° in the obtuse angle $\beta$. They refer, however, to the setting of Vetter (1911) which differs from the setting used in the more recent papers. Refractive indices were measured by different authors and are listed in Table 4.

The considerable double refraction and the negative character is caused by the $CO_3$ groups which are arranged paralled to each other. Their plane

**Table 3.** Bond lengths (Å) and angles (°) of the hydrogen bonds

| | O...O | O−H | H...O | ∢(O−H...O) |
|---|---|---|---|---|
| O(3)−H(1)...O(2) | 2.744(1) | 0.825(17) | 1.923(16) | 173.6(1.9) |
| O(3)−H(2)...O(4) | 2.906(1) | 0.728(19) | 2.184(19) | 172.0(2.1) |
| O(4)−H(3)...O(1) | 2.859(1) | 0.791(20) | 2.088(21) | 164.6(1.6) |
| O(4)−H(4)...O(5) | 2.778(1) | 0.811(17) | 1.982(19) | 167.1(1.6) |
| O(5)−H(5)...O(2) | 2.740(1) | 0.818(18) | 1.922(18) | 176.7(1.5) |
| O(5)−H(6)...O(1) | 2.709(1) | 0.753(15) | 1.979(15) | 163.6(1.6) |

**Table 4.** Refractive indices and extinction angle $\sigma$

| $n_\alpha$ | $n_\beta$ | $n_\gamma$ | $\sigma$ | Authors |
|---|---|---|---|---|
| 1.460 | 1.535 | 1.545 | – | Johnston et al. (1916) |
| 1.455 | 1.538 | 1.545 | – | Pauly (1963) |
| 1.482 | 1.530 | 1.542 | – | Suess et al. (1982) |
| – | – | – | 17° | Dickens and Brown (1970) |
| 1.480 | 1.545 | 1.535 | 15.8° | present theoretical estimation |

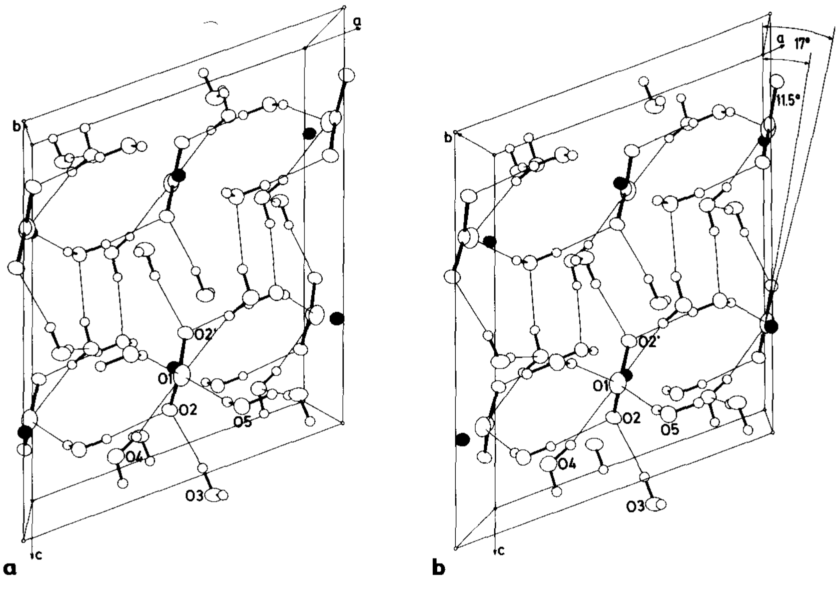

**Fig. 1.** Stereoscopic view as seen down the *b*-axis. Hydrogen atoms are drawn with a uniform fixed radius. Hydrogen bonds are denoted by lines. Ca ions are black. The planar $CO_3$ groups form angles of 11.5° with the *c*-axis. Extinction is at 17° from the *c*-axis

forms an angle of 11.5° with the *c*-axis (Fig. 1) which is in rough agreement with the extinction angle of 17°. The deviation will be caused by the water molecules which contribute to the mutual polarization within the structure. This interaction can be considered using the computer program DIPSUM of Pohl (1978). For that purpose, the C-atom is assumed to be non-polarizable, and the polarizabilities of Ca and oxygen atoms of the carbonate group are assumed to be 0.42 and 1.43 $Å^3$, respectively (Pohl, 1979), and the polarizability of the water molecules is estimated to be 1.47 $Å^3$ (by means of the Lorentz-Lorenz formula applied to water (Pohl, 1982). The calculated values are listed in Table 4. The angle of extinction amounts to 15.8°, which agrees fairly well with the experimentally determined angle of 17°.

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