INESITE, $Mn_7Ca_2Si_{10}O_{28}(OH)_2 \cdot 5H_2O$*

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ABSTRACT

A new orientation of inesite has been chosen with the elements: $a:b:c = 0.9700:1:1.3208$; $\alpha = 87°42'$, $\beta = 132°35\frac{1}{2}'$, $\gamma = 97°01'$ (Sheibe's elements transformed by the formula $\bar{1}0\bar{1}/0\bar{1}0/001$). *X*-ray measurements on a cleavage fragment gave $a_0 = 8.89$, $b_0 = 9.14$, $c_0 = 12.14$; $a_0:b_0:c_0 = 0.973:1:1.328$; $\alpha = 87°38\frac{1}{2}'$, $\beta = 132°30'$, $\gamma = 97°05\frac{1}{2}'$. This orientation has been selected to make the direction of elongation the *c*-axis and to retain the similarity inesite shows to members of the wollastonite group. Inesite is shown to be closely related to a high calcium rhodonite which theoretically may be considered as a dehydrated inesite. From published analyses and a new specific gravity determination, together with the lattice constants, the cell formula is calculated to be $Mn_7Ca_2Si_{10}O_{28}(OH)_2.5H_2O$.

INTRODUCTION

The chemical and optical data of inesite have been summarized and a new occurrence at Quinault, Washington, has been described by Miss J. J. Glass and W. T. Schaller.[1] They showed that neither of the two simple formulae generally given for inesite, with a 1:1 ratio of $RO:SiO_2$, are compatible with the analyses, and that MnO and CaO do not vary reciprocally. They were unable, however, to determine a simple formula for the mineral and proposed the complex one $15SiO_2 \cdot 3CaO \cdot 11MnO \cdot 10H_2O$. On the basis of *x*-ray studies, the more probable and simpler formula is $10SiO_2 \cdot 2CaO \cdot 7MnO \cdot 6H_2O$. This closely approximates two-thirds of the formula proposed by Glass and Schaller. Moreover, when this simpler formula is written $Mn_7Ca_2Si_{10}O_{28}(OH)_2 \cdot 5H_2O$, the chemical relation of inesite to rhodonite can be more clearly demonstrated.

During the course of an investigation of members of the wollastonite family composed of such minerals as wollastonite, pectolite, bustamite, and rhodonite, the writer was impressed by the outward similarity of inesite to these minerals.[2] An *x*-ray investigation of inesite was undertaken to determine whether this similarity was fortuitous. The first results obtained did not indicate any apparent structural relation to members of the wollastonite group. However, it will be shown that a close relation does exist between inesite and rhodonite, and the writer[3] has pointed out that there is a relation between rhodonite and wollastonite. This relation " . . . is confined to near equality of two of the principal lattice periods and the included axial angle; the remaining lattice parameters are quite dissimilar." Recent work by the writer, as yet unpublished,

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[1] Glass, J. J., and Schaller, W. T., Inesite: *Am. Mineral.*, **24**, 26–39 (1939).

[2] The inter-relationship of these and other minerals will be shown in a forthcoming paper.

[3] Richmond, W. E., On babingtonite: *Am. Mineral.*, **22**, 640 (1937).

indicates that "the remaining lattice parameters" of rhodonite are in simple rational relationship to the corresponding parameters of wollastonite. Without entering into details, which will be fully dealt with in a forthcoming paper, wollastonite and rhodonite may be considered as belonging to separate groups within the same family. As inesite and rhodonite are structurally related, they should belong to the same group and should be included in the family containing members of the wollastonite group. This group is composed of such minerals as wollastonite, pectolite, schizolite, and bustamite.

CRYSTALLOGRAPHY

The material used for the x-ray investigation was selected from the same specimen from Quinault, Washington, that was studied by Glass and Schaller. Single crystals were not found; a cleavage fragment, therefore, approximating $0.5\times0.25\times0.75$ mm. in size was used. The rotation axis was taken as the edge between the two perfect cleavages. This axis is the direction of greatest elongation. Rotation, zero, first, and second layer-line photographs were taken about the axis of elongation from which were calculated the six lattice parameters. The results are:

$$\begin{array}{ll} a_0=\ 8.89\ \text{Å} & a_0{:}b_0{:}c_0=0.973{:}1{:}1.328 \\ b_0=\ 9.14\ \text{Å} & \alpha=87°38\tfrac{1}{2}', \beta=132°30', \gamma=97°05\tfrac{1}{2}' \\ c_0=12.14\ \text{Å} & \end{array}$$

The unit cell, although its orientation does not conform to the normal triclinic setting, is a simple cell and has been selected to make the elongation the direction of the c-axis. The edge between the two perfect cleavages is also the direction of the elongation; the cleavages were taken as $\{100\}$ and $\{010\}$. This orientation likewise corresponds to that of most other members of the wollastonite family, in that the two cleavages are taken as the pinacoidal forms in the prism zone in second permutation. That is, triclinic wollastonite is reoriented so that the direction of elongation (corresponding to the b-axis of monoclinic parawollastonite) is taken as the c-axis.

The orientation of the chosen unit cell does not conform to the cell based on the morphology adopted by Scheibe as given in Dana,[4] but does confrm if the cell derived from Scheibe's orientation is rotated 180° about the c-axis. The forms and elements of Scheibe are transformed to the new orientation by the matrix $\bar{1}0\bar{1}/0\bar{1}0/001$. The axial ratios and angles so obtained, namely: $a{:}b{:}c=0.9700{:}1{:}1.3208$, $\alpha=87°42'$, $\beta=132°35\tfrac{1}{2}'$, $\gamma=97°01'$, agree closely with those obtained from the x-ray calculations. Therefore, the transformed elements of Scheibe were used in calculating the angle table (Table 1).

[4] Dana, E. S., *A System of Mineralogy*, 6th ed., 564 (**1892**).

TABLE 1. INESITE: ANGLE TABLE

Inesite—$Mn_7Ca_2Si_{10}O_{28}(OH)_2 \cdot 5H_2O$
Triclinic, pinacoidal—$\bar{1}$

$a:b:c=0.9700:1:1.3208$; $\alpha=87°42'$, $\beta=132°35\frac{1}{2}'$, $\gamma=97°01'$
$p_0:q_0:r_0=1.3709:0.9789:1$; $\lambda=86°40'$, $\mu=47°21'$, $\nu=82°35'$
$p_0'=1.8652$, $q_0'=1.3330$; $x_0'=0.9192$, $y_0'=0.0792$

Forms		φ	ρ	A	B	C
c	001	85°05½′	42°41½′	47°21′	86°40′	—
b	010	0 00	90 00	82 35	—	86°40′
a	100	82 35	90 00	—	82 35	47 21
M	$1\bar{1}0$	120 33½	90 00	37 58½	120 33½	56 28½
f	201	83 04½	77 52	12 08½	83 14	35 13
e	$\bar{1}01$	−99 51½	43 21½	133 18½	96 45	85 57½
l	$\bar{2}01$	−98 14½	70 24	160 23	97 45½	113 02
g	$\bar{3}01$	−97 55	77 55½	167 55	97 44½	119 41
d	$\bar{1}11$	−38 27	56 14½	115 23	49 23	84 23½

Rare forms {$3\bar{3}2$}, {$\bar{1}.0.12$}
Doubtful forms {$0\bar{4}7$}, {$3\bar{4}6$}

CONTENT OF THE UNIT CELL

The analysis of inesite from Quinault given by Glass and Schaller,[5] the determined specific gravity (3.03), together with the molecular weight of the unit cell (1322.6) were used in calculating the contents of the unit cell. The results are given in Table 2.

TABLE 2. INESITE: CONTENT OF THE UNIT CELL

	1	2	3		4	5	6
SiO_2	45.67	45.42	.7562		10.01	10	45.57
MnO	35.10	34.91	.4922	6.51			37.68
FeO	0.92	0.92	.0128	0.17	6.96	7	
MgO	0.86	0.86	.0213	0.28			
CaO	9.33	9.28	.1655		2.19	2	8.53
H_2O	8.66	8.61	.4783		6.33	6	8.22
	100.54	100.00					100.00

Specific gravity: determined = 3.03. Calculated from molecular weight of the unit cell and composition = 3.02. Calculated from the specific energies and indices of refraction = 2.94.

1. Analysis of inesite from Quinault, Washington; analyst, J. G. Fairchild.
2. Recalculated to 100%.
3. Molecular proportions.
4. Number of molecules in the unit cell.
5. Theoretical number of molecules in the unit cell.
6. Calculated analysis on the basis of the formula $Mn_7Ca_2Si_{10}O_{28}(OH)_2 \cdot 5H_2O$.

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[5] Glass and Schaller, *op. cit.*, p. 28.

The composition of inesite derived from column 5 is $Mn_7Ca_2Si_{10}O_{28}(OH)_2 \cdot 5H_2O$. Schaller has shown that the percentages of SiO_2, MnO, and CaO are remarkably constant in the seven listed analyses of inesite from various localities. The ratios SiO_2:MnO:CaO determined from column 4 of Table 2 closely approximate 10:7:2. The same ratios are apparent in the other listed analyses.

The formula, $Mn_7Ca_2Si_{10}O_{28}(OH)_2 \cdot 5H_2O$, after all the water has been deducted, approximates closely that of a high-calcium rhodonite. Gossner and Brückl[6] have shown that the cell content of rhodonite is $(Mn, Fe, Ca)_{10}Si_{10}O_{30}$ or $10(RSiO_3)$. This has been verified by the writer. A high-calcium rhodonite with a ratio MnO:CaO of 7:2 would have the composition $Mn_{7.78}Ca_{2.22}Si_{10}O_{30}$, shown in column 1 of Table 3. This may be compared with the composition $Mn_{6.54}Ca_{2.46}Si_{10}O_{29}$ of inesite from Quinault, after deducting total water and recalculating to 100 per cent.

TABLE 3. COMPARISON OF THE COMPOSITION OF A HIGH-CALCIUM RHODONITE WITH THAT OF INESITE, WATER DEDUCTED

	Rhodonite $Mn_{7.78}Ca_{2.22}Si_{10}O_{30}$	Inesite, deducting H_2O and calculating to 100 per cent $Mn_{6.54} \cdot Ca_{2.46} \cdot Si_{10}O_{29}$
SiO_2	47.04	49.70
MnO	43.20	38.20
FeO	—	1.01
MgO	—	0.94
CaO	9.76	10.15
	100.00	100.00

A comparison of the two columns indicates that the composition of a high-calcium rhodonite and dehydrated inesite is approximately the same except that one of the manganese positions in inesite is unoccupied. The formulae for rhodonite and for a dehydrated inesite may also be written:

Rhodonite	$(Mn, Ca)_{10}Si_{10}O_{30}$
Dehydrated inesite	$(Mn, Ca)_9Si_{10}O_{29}$

If inesite is assumed to be a hydrated high-calcium rhodonite with rhodonite having a cell formula $R_{10}Si_{10}O_{30}$, then the sum of the RO group in inesite should be 10 if all the water were present as H_2O. The preponderance of evidence shows, however, that the sum of the RO

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[6] Gossner, B., and Brückl, K., Über strukturelle Beziehungen von Rhodonit zu anderen Silikaten: *Centralbl. Min.*, **A**, 320 (1928).

group in inesite is 9. This requires that two hydroxyl groups replace two oxygens, leaving one cation position unoccupied. The remaining water is present as H_2O. This may be expressed as follows, considering all the R as Mn, for brevity:

Rhodonite	$Mn_{10}Si_{10}O_{30}$
Inesite	$Mn_9Si_{10}O_{28}(OH)_2$.

When 2 O^{--} is replaced by $2(OH)^-$ the excess charge in the cation position is compensated by the removal from the structure of a cation with charge 2+. This structure may be termed unsaturated. The unsaturated structure may be seen also in babingtonite with the cell formula $Ca_4Fe_2''Fe'''_2Si_{10}O_{28}(OH)_2$. The structure contains two unoccupied cation positions, owing to the presence of ferric iron as well as the replacement of oxygen by hydroxyl.

A saturated structure, one in which all cation positions are occupied, may be illustrated by pectolite [$Na_2Ca_4Si_6O_{16}(OH)_2$]. If pectolite is assumed to be wollastonite ($Ca_6Si_6O_{18}$) with an additional hydroxyl and sodium, then the sodium with a valence of one, occupies positions in the wollastonite structure formerly occupied by Ca^{++}. Thus all cation positions are occupied and the structure is saturated. This may be seen more clearly by a comparison of the two formulae

Wollastonite	$Ca_6Si_6O_{18}$
Pectolite	$Na_2Ca_4Si_6O_{16}(OH)_2$

In wollastonite the six cation positions are occupied by $6Ca^{++}$. In pectolite the six cation positions are occupied by $4Ca^{++}$ plus $2Na^+$.

The assumption has been made that inesite may be considered as a hydrated calcium rhodonite. Conversely, high-calcium rhodonite may be considered as a dehydrated inesite. In order to test this assumption a specimen of powdered (100 mesh) inesite from Quinault was dehydrated by heating for seven hours at 800° C. in a stream of nitrogen. A powder photograph was taken of this material and compared with powder photographs of unheated inesite and of rhodonite. A reproduction of these photographs is shown in Fig. 1.

The powder photograph of the heated inesite is nearly identical with that of rhodonite and is dissimilar to that of the unheated inesite. Therefore, inesite may be assumed to bear a close structural relation to rhodonite and this relation should appear in a comparison of the lattice constants.

Comparison of x-ray powder photographs shows that the picture of dehydrated inesite is much closer to that of rhodonite than to that of pyroxmangite.

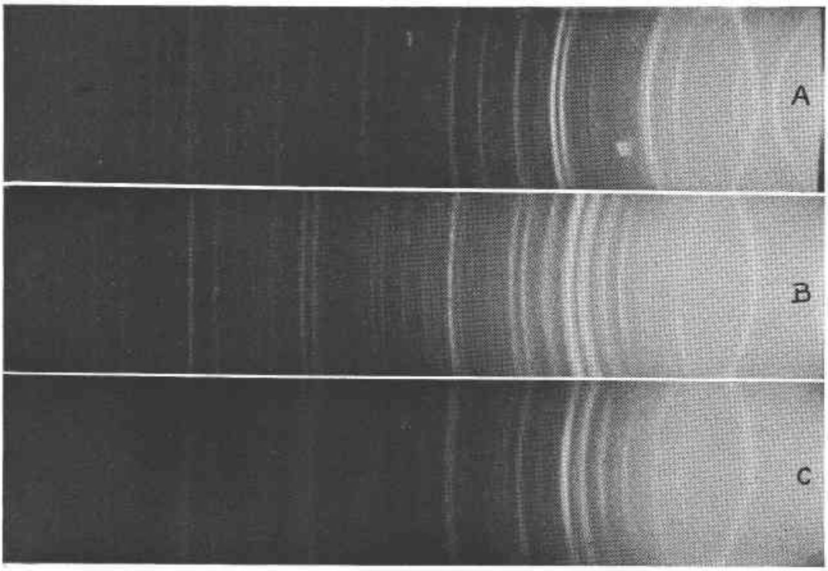

FIG. 1. Powder photographs of (A), inesite; (B), rhodonite; and (C), inesite after dehydration at 800° C.

The lattice constants of rhodonite in the orientation of inesite together with those of inesite are given below.

	Rhodonite[a]	*Inesite*
a_0	6.65	8.89
b_0	7.85	9.14
c_0	12.16	12.14
V_0*	571.37	720.41
α	91°38′	87°38½′
β	114°53½′	132°30′
γ	96°38′	97°05½′

[a] These figures are derived from *x*-ray data by the writer, as yet unpublished.

* = Volume of the unit cell.

If inesite is to be considered as basic hydrated rhodonite, the increase in the volume of inesite over that of rhodonite is due to the introduction of H_2O into the rhodonite lattice. A comparison of the cell edge lengths shows that this introduction has probably taken place along the *b*-axis in such a manner as to increase the length of c_0 (34 per cent increase) approximately twice as much as that of a_0 (16 per cent increase). This differential increase in the lengths of a_0 and c_0 is reflected in a distortion of the rhodonite lattice by a large increase in the β angle.

The dehydrated inesite which had previously been crushed to 100 mesh, when placed in immersion oils and examined under the microscope, is seen to have undergone only a slight shrinkage. The individual fragments, when observed under low magnifications, extinguish almost as a unit. Under high magnification, the extinction is seen to be slightly undulatory, but no more so, according to W. T. Schaller,[7] than the massive rhodonite which has replaced johannsenite in specimens of these minerals from Mexico. The birefringence is low, most of the fragments showing only gray of the first order with but occasional patches of red and very occasionally small areas of blue of the second order. The birefringence does not exceed 0.015 and hence agrees with the birefringence of rhodonite (0.013) and is considerably different from the much higher birefringence of inesite (0.035).

When first placed in immersion oils, the extreme indices of the dehydrated inesite, as observed, are about 1.67 and 1.685. Miss J. J. Glass obtained an average index of about 1.68 with apparent extremes of about 1.67 and 1.69, after soaking in the index oils for three days. After immersion for several months, the average index seemed to drop about 0.01.

These values of the indices of refraction of the dehydrated inesite are much higher than the γ value of inesite (1.651), but appreciably lower than the indices of high-calcium rhodonite (with about 10 per cent of CaO) which are approximately $\alpha=1.715$, $\beta=1.72$, $\gamma=1.73$.

The lower values of the indices of the dehydrated inesite as compared with those of a high-calcium rhodonite, may be a reflection of the unsaturated structure in which one cation position is unoccupied.

No satisfactory observations on the size or sign of the axial angle could be made.

In conclusion, it is well to point out that the expressed relations between rhodonite and dehydrated inesite are not to be taken as implying an actual genesis in nature of one of these minerals from the other. There is no evidence that any inesite has actually been derived from rhodonite. It is pertinent, however, to note that in the Harstig mine, Wermland, Pajsberg, Sweden, inesite occurs with rhodonite and from the same mine, another hydrated manganese aluminum silicate, ganophyllite, is reported to surround crystals of rhodonite. It is possible, however, that under proper conditions either one of the two minerals, inesite or rhodonite, may be converted to the other. Therefore, it is well to bear in mind, when examining suites of minerals containing either of these minerals, that there is a possibility of finding one of these minerals being replaced by the other.

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[7] W. T. Schaller examined the dehydrated inesite under the microscope and prepared the description of his observations.