

EVIDENCE FOR $[(\text{SiO}_3)_5]_\infty$ TYPE CHAINS IN INESITE
AS SHOWN BY X-RAY AND INFRARED
ABSORPTION STUDIES

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ABSTRACT

Examination of the infrared absorption spectra of the single chain silicates, augite, hedenbergite, pectolite, wollastonite, bustamite, rhodonite and pyroxmangite shows that the number of peaks in the $530\text{--}775\text{ cm}^{-1}$ region is an indicator of the number of tetrahedra in the repeat unit of the chains.

The infrared spectrum of inesite, a mineral having a formula close to $\text{Mn}_7\text{Ca}_2\text{Si}_{10}\text{O}_{28}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (as a result of this study now classified as a pyroxenoid), together with evidence from single crystal x-ray studies, indicates it to be made up of single chains with five silicon-oxygen tetrahedra per repeat unit.

INTRODUCTION

From an infrared absorption study of structurally characterised esters of orthosilicic acid, Lazarev (1960) derived an empirical method of determining the number of repeating units in a given single chain polymer. Lazarev and Tenisheva (1961a, b) successfully applied this method to the single chain silicates, the pyroxenes and pyroxenoids, that are known to contain differing numbers of silicon-oxygen tetrahedra in the repeat unit of the chain. In the infrared spectra of the single chain silicates Lazarev and Tenisheva (1961a, b) observed that the number of absorption peaks in the $550\text{--}750\text{ cm}^{-1}$ region is directly related to the number of Si-O tetrahedra in the repeat unit of the chain. The clinopyroxenes, typified by diopside, contain two tetrahedra per repeat unit (Warren and Bragg, 1928). The pyroxenoids wollastonite, bustamite and pectolite each have three tetrahedra in the repeat unit whereas rhodonite and pyroxmangite have five and seven tetrahedra respectively in the repeat unit.

Four years ago, one of us (I.M.T.) predicted that the rare mineral inesite, with a composition close to $\text{Mn}_7\text{Ca}_2\text{Si}_{10}\text{O}_{28}(\text{OH})_2 \cdot 5\text{H}_2\text{O}^1$ (Mn: Ca ratio of 3.7-3.4:1), would have a single chain structure with a five tetrahedra repeat along the length of the chain, similar to that found in rhodonite. The correlations reported by Lazarev and Tenisheva, from their infrared study, appeared to provide a promising means of testing this hypothesis.

Liebau (1956) proposed that inesite and babingtonite, though struc-

¹ See discussion of the chemical formula at the end of the paper.

turally related to rhodonite, differed from it in having double chains with a five tetrahedra repeat unit. The similarity of *b*-axis Weissenberg photographs of babingtonite to those of rhodonite led Prewitt and Peacor (1964) to suggest that babingtonite contains single chains with a five tetrahedra repeat and not double chains as suggested by Liebau.

In the present paper the infrared spectrum of inesite is presented and discussed in relation to the correlations proposed by Lazarev and Tenisheva.

EXPERIMENTAL

Preliminary investigations of the pyroxenoid spectra reported in the literature showed that several of these had been obtained from impure samples. For purposes of comparison it was necessary to prepare spectra of the minerals listed below.

Considerable difficulty was experienced in obtaining samples of wollastonite and pectolite that were carbonate free. All samples of pectolite used were found to contain carbonate as an impurity. This was removed by treating the mineral with acetic acid buffered with sodium acetate (Jackson, 1956). This did not affect the pectolite structure since, except for the absence of the carbonate features, the spectrum was identical to those obtained from untreated samples.

All minerals used to prepare the spectra in Fig. 1 were examined optically and by *x*-ray diffraction techniques and are believed to be free of detectable impurities. The spectra have been duplicated on minerals obtained from several different specimens.

Samples were ground in an agate mortar with KCl and from this mixture a 100 mg pellet containing 0.5 mg of the sample was pressed. Prior to pressing the sample was oven dried at 110° C. Pressed pellets were stored at 110° C. until required. All spectra were prepared using a KCl reference pellet and were calibrated against prominent absorption maxima of a polystyrene film.

The spectra were obtained on a Perkin-Elmer 337 grating infrared spectrophotometer.

Samples used in this study were derived from the following localities:

1. Augite, Lizard, Cornwall, U.K.
2. Hedenbergite, locality unknown.
3. Pectolite, Prospect, N.S.W.
4. Wollastonite, Marulan, N.S.W.
5. Bustamite, New Broken Hill Consolidated Ltd. Mine, Broken Hill, N.S.W.
6. Rhodonite, North Broken Hill Ltd. Mine, Broken Hill, N.S.W.
7. Pyroxmangite, North Broken Hill Ltd. Mine, Broken Hill, N.S.W.
8. Inesite, New Broken Hill Consolidated Ltd. Mine, Broken Hill, N.S.W.

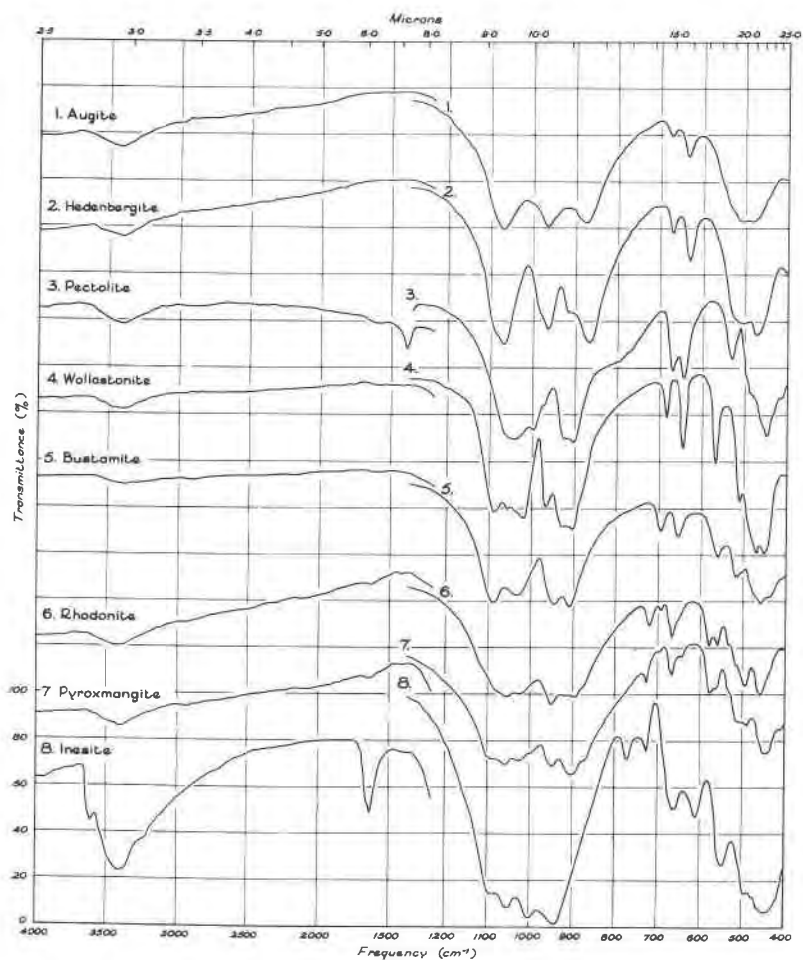


FIG. 1. Absorption spectra of some pyroxenes and pyroxenoids. Curves are displaced vertically 40%.

RESULTS

The infrared spectra of the eight single chain silicates examined are presented in Fig. 1. Absorption maxima are listed in Table 1.

In each of the spectra of Fig. 1 a strong absorption band containing from four to seven intense maxima of similar intensities occurs within the 850–1100 cm^{-1} region. This band contains the absorption peaks produced by Si-O asymmetric stretching frequencies within the tetrahedra (Saksena, 1961).

TABLE 1. FREQUENCIES OF ABSORPTION MAXIMA OF THE CHAIN SILICATES EXAMINED (CM⁻¹)

| Band Assignment | Augite | Hedenbergite | Pectolite | Wollastonite | Bustamite | Rhodonite | Pyroxmangite | Inesite |
|------------------------------------|-----------|--------------|------------|--------------|-----------|------------|--------------|------------|
| (M-O) stretching (Si-O) bending | 480 s | 475 s | 448 vs | 452 vs | 435 sh, w | 458 s | 447 s | 450 s |
| | 511 s | 500 w | 460 sh, w | 470 vs | 460 s | 495 s | 492 m | 462 sh, w |
| | 528 sh, w | 511 w | 484 sh, w | 478 sh, w | 517 m | 514 sh, w | 511 sh, w | 475 sh, w |
| | | | | 509 m | | 530 sh, w | 530 sh, w | 495 w |
| (Si-O-Si) stretching | 635 m | 627 m | 532 m | 567 m | 562 m | 559 m | 563 sh, w | 549 m |
| | 675 m | 668 m | 644 m | 644 m | 656 m | 579 m | 576 m | 611 m |
| | | | 671 m | 680 m | 695 m | 667 m | 645 w | 663 m |
| | | | | | | 694 m | 668 m | 727 m |
| | | | | | 720 m | 673 sh, w | 773 m | |
| | | | | | | 695 w | 695 w | |
| | | | | | | 726 m | 726 m | |
| (Si-O) stretching | 875 s | 863 vs | 903 vs | 905 vs | 908 vs | 870 sh, w | 870 sh, w | 937 vs |
| | 965 s | 913 sh, w | 925 s | 930 vs | 945 vs | 895 s | 900 vs | 999 s |
| | 1070 s | 962 s | 972 sh, w | 968 s | 1035 s | 915 sh, w | 948 vs | 1050 s |
| | | 1067 vs | 998 s | 1020 vs | 1090 vs | 950 vs | 1002 sh, m | 1087 s |
| | | | 1030 sh, w | 1038 sh, s | | 1025 s | 1026 s | |
| | | | 1044 vs | 1058 s | | 1058 s | 1060 s | |
| | | | 1395 m | 1090 vs | | 1075 sh, w | 1085 sh, s | |
| (OH) bending and stretching | 1620 w | 1620 w | 1610 w | 1610 w | 1605 w | 1628 w | 1620 w | 1640 s |
| | 3420 w | 3420 w | 3400 m | 3400 m | 3380 w | 3420 w | 3400 w | 3250 sh, w |
| | | | | | | | | 3420 s |
| | | | | | | | | 3620 m |

Band intensity: vs-very strong; s-strong; m-medium; w-weak; sh-shoulder on a stronger band.

Absorption peaks between 550 and 750 cm^{-1} occur near the region generally attributed to the frequency associated with the totally symmetrical stretching vibration of the SiO_4 tetrahedron. As the Si-O tetrahedra are coupled to form a single chain, splitting of symmetrical vibration of the SiO_4 group takes place resulting in the peaks observed at about 550–750 cm^{-1} (Lazarev and Tenisheva, 1961a).

Strong absorption bands occurring below about 500 cm^{-1} may be due to bending (deformation) vibrations of the chains (Si-O) and to metal-oxygen stretching vibrations (M-O) (Lazarev and Tenisheva, 1961a, b).

The broad, shallow absorption band near 3400 cm^{-1} is due either to hydrogen bonded hydroxyl or adsorbed water. The peak near 1620 cm^{-1} is due to the deformation vibration of either adsorbed or zeolitic water. The inosite spectrum shows strong absorption bands at 3620, 3420 and 1640 cm^{-1} corresponding to positions generally believed to indicate the presence of free OH, bonded OH and zeolitic or interlayer water respectively (Kalousek and Roy, 1957). As the spectra were all obtained from desiccated samples, and the peaks of the inosite spectrum are so strong in comparison with the corresponding peaks of the spectra Nos. 1–7, it is apparent that in the inosite structure there occurs free OH together with zeolitic water.

In pectolite, hydrogen bonding is reported to occur between two oxygens, O_3 – O_4 , which are 2.44 Å apart (Buerger, 1956; Prewitt and Peacor, 1964). With such a close O_3 – O_4 distance we would expect the hydrogen to be symmetrically placed and result in a peak at about 1800 cm^{-1} (Nakamoto *et al.*, 1955). However, no such peak is observed in any of our pectolite spectra. The closest peak is at 1610 cm^{-1} and is due to the presence of adsorbed water that contributes in part to the broad, shallow peak at about 3400 cm^{-1} . The 1395 cm^{-1} peak was also recorded by Lazarev and Tenisheva (1962) who assigned it to a carbonate impurity. This peak, however, does not correspond to any recorded carbonate peak. The absence of the other strong carbonate peaks and the persistence of this peak after treatment with acetic acid buffered with sodium acetate leads us to believe that it is characteristic of the pectolite spectrum and may be due to an OH bending mode.

The simple spectra of augite and hedenbergite, Nos. 1 and 2 respectively, agree with the published data (Lazarev and Tenisheva, 1961a; Lyon, 1962). Consistent with the occurrence of two Si-O tetrahedra in the repeating unit of the single chain, two prominent absorption maxima are observed within the 550–750 cm^{-1} range.¹

¹ The writers have, however, noted exceptions in this region of the spectra of the acmitic and orthopyroxenes. In these, from two to six peaks have been observed in spectra reported in the literature (Lyon, 1962).

The pyroxenoids with three tetrahedra in the repeat unit, wollastonite (No. 4) and bustamite (No. 5), have three prominent absorption maxima within the 550–750 cm^{-1} range. Pectolite (No. 3) has, however, near this region one of the three prominent absorption maxima situated at 532 cm^{-1} , slightly below the arbitrary lower limit selected by Lazarev and Tenisheva (1961b). However, since pectolite is known to possess a wollastonite-type structure (Buerger, 1956), it is highly probable that the absorption peak at 532 cm^{-1} is also of the (Si-O-Si) type, indicating that the limits chosen by these authors need to be extended to include the pectolite structure.

Rhodonite, a pyroxenoid known to have a five Si-O tetrahedra repeat unit, shows within the 550–750 cm^{-1} region five well resolved absorption maxima as well as a slight inflexion at about 640 cm^{-1} . A similar inflexion, at 638 cm^{-1} , was also noted by Lazarev and Tenisheva. The writers have observed this same feature at 642 cm^{-1} in the spectrum of a zincian rhodonite (fowlerite) from Franklin Furance, N.J.

Consistent with a seven tetrahedra repeat, the spectrum of pyroxman-gite (No. 7) shows seven absorption maxima in the 550–750 cm^{-1} range. Some peaks are poorly resolved, particularly the one at 673 cm^{-1} which is almost superimposed on the stronger peak at 668 cm^{-1} .

The above observations help to substantiate the claim of Lazarev and Tenisheva that the region from 550–750 cm^{-1} can, in general, provide significant information as to the number of tetrahedra in the repeat unit of a single chain silicate.

The details of the crystal structure of inesite are as yet unknown.¹ However, there are certain features of silicate infrared spectra that characterise the various groups (Launer, 1952; Saksena, 1961). The similarity of the inesite spectrum (No. 8) to those of the pyroxenes and pyroxenoids indicates that inesite probably also has a single chain structure. The inesite spectrum shows five very prominent absorption peaks between 550 and 775 cm^{-1} . In the spectra Nos. 1–7, the first prominent peak on the low frequency side of the intense absorption band between 1100–850 cm^{-1} is one of the peaks indicative of the number of tetrahedra in the repeat unit. It is noteworthy that the two hydrogen-bearing minerals, pectolite and inesite, show well developed absorption maxima beyond the arbitrarily selected limits of Lazarev and Tenisheva.

It is to be expected that in hydrogen-bearing compounds such as pectolite or inesite differences will occur in the position of the absorption maxima when they are compared to structurally related nonhydrogen-bearing compounds, *e.g.* pectolite-wollastonite. Therefore, it is not incon-

¹ A three dimensional x-ray structural analysis of inesite is at present being carried out by one of us (W.R.R.) and will be reported elsewhere.

ceivable that the 773 cm^{-1} peak of inesite is of the same type as those that occur in the $550\text{--}750\text{ cm}^{-1}$ range, suggesting that inesite is, like rhodonite, a pyroxenoid with an $[(\text{SiO}_3)_5]_\infty$ type chain.

The presence of a 12 \AA repeat along the morphological c axis of inesite, measured on single crystal x -ray photographs, indicates that the chain is oriented parallel to this axis and contains five tetrahedra in the repeat unit. Consistent with this is the 12.2 \AA repeat distance measured along the five-membered rhodonite chain (Hilmer *et al.*, 1956).

DISCUSSION OF THE INESITE FORMULA

In 1942 Richmond, using the chemical data presented by Glass and Schaller (1939), ascribed to inesite the generally accepted formula of $\text{Mn}_7\text{Ca}_2\text{Si}_{10}\text{O}_{28}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. Such a formula is in agreement with that derived from analytical work on inesite from Broken Hill, N.S.W., recently completed by the authors and to be presented at a later date.

Richmond's formula requires that within each five-membered Si-O tetrahedral unit of the chain, one of the fifteen oxygen positions is occupied by a hydroxyl ion. Buerger (1956) and Prewitt and Peacor (1964) inferred that in pectolite, $\text{Ca}_2\text{NaHSi}_3\text{O}_9$, the hydrogen ion enters into bonding between two near oxygens. By analogy with pectolite the formula for inesite can be expressed as $\text{Mn}_7\text{Ca}_2\text{H}_2\text{Si}_{10}\text{O}_{30} \cdot 5\text{H}_2\text{O}$. However, the infrared trace of inesite, No. 8, Fig. 1, clearly shows that there exists in inesite free hydroxyl ions in contradistinction to the situation in pectolite, No. 3, Fig. 1.

From the evidence presented above the present writers believe that the formula for inesite should be expressed as $\text{Mn}_7\text{Ca}_2\text{Si}_{10}\text{O}_{28}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and thus demonstrate the tetrahedral co-ordination of a hydroxyl ion within one of the five tetrahedra of the repeat unit of the chain.

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