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DETERMINATION OF SULFUR AND CARBON COORDINATION IN SCAPOLITE BY INFRA-RED ABSORPTION SPECTROPHOTOMETRY

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ABSTRACT

An attempt has been made to identify the valence and coordination of sulfur and carbon in scapolite, by searching for infra-red absorption peaks whose intensity varies with the sulfur and carbon content of the sample. Because of interference by Si-O vibrational spectra it is impossible to decide whether SO_4^{2-} or HSO_4^- ions are present. Sulfite ions may be present in high-sulfur scapolites.

Carbon is present as the carbonate ion, probably strongly bound in a discrete structural site. A method of determining the CO_2 content of any scapolite has been developed. Recent analyses of scapolite suggest that carbon and sulfur may enter the scapolite structure loosely paired in some way.

INTRODUCTION

The use of infra-red absorption spectrophotometry to determine the coordination and structural position of complex ions in a crystal has been described by various workers (Hafner and Laves, 1961; Stubican and Roy, 1961). We have attempted in the present research to determine the coordination and location of sulfur and carbon in scapolite by use of infra-red spectra.

Chemical analyses of scapolite suggest that it may be represented by the formula (Shaw, 1960)

$$W_4Z_{12}O_{24}\cdot R$$

in which W = Ca, Na, K etc.; Z = Si and Al and R = an ionic group which may be one of the members of the following two classes

$$X = CO_3^{2-},\ SO_4^{2-},\ O_2H_2^{2-},\ Cl_2^{2-},\ F_2^{2-}$$
$$Y = Cl^-,\ F^-,\ HCO_3^-,\ HSO_4^-,\ OH^-$$

Any given scapolite is a solid solution of the two end members meionite (me) and marialite (Ma), these being the calcium and sodium end members respectively with appropriate Al-Si substitution to balance charge and with appropriate anionic groups attached. Any scapolite can therefore be written

$$r(\mathrm{Me}\cdot X)\cdot(1-r)(\mathrm{Ma}\cdot Y).$$

The components chosen by Shaw were selected merely for convenience in order to express the observed compositions according to a consistent formulation. There is no assurance that these components actually represent the structural state in which the chemical constituents are combined in scapolite. In particular, it is not known with certainty what is the valence or coordination of sulfur. Possible choices include those implied by the model formula given by Shaw, SO_4^{2-} or HSO_4^- ions plus other choices such as S^{2-}, SO_3^{2-}, SiS_4^{4-}, or $S_2O_3^{2-}$ ions. It was hoped at the outset of the present study to be able to distinguish between these possibilities by finding the characteristic group frequencies of complex ions in the infra-red absorption spectrum of scapolite.

The role of carbon is less uncertain, since it is almost always present as the 4-valent ion, that is, as CO_3^{2-}, HCO_3^- or CO_2. Infra-red spectroscopy has indeed been able to confirm the presence of the CO_3^{2-} ion in scapolite.

Experimental Method

Samples were ground in chloroform in an agate mortar for five minutes and then mixed with KBr in proportions 1:99 respectively. A 0.5″ disc weighing 100 mg. was pressed from the mixture in a cold die. The disc was analyzed on a Perkin-Elmer Model 21 spectrophotometer using NaCl optics. Some of the discs were analysed in the far infra-red on a Beckman Model 301. On both instruments a KBr blank disc was placed in the reference beam.

Low temperature measurements of two scapolites were made using a vacuum cell and cold-finger sample holder designed and loaned by A. Whitla. The end plates of the cell were KBr crystals. The sample was as usual dispersed at 1% concentration in a KBr pressed disc and cooled with liquid nitrogen. Measurements using this apparatus were made on a Perkin-Elmer Model 521 spectrophotometer.

Nine chemically analyzed scapolites were obtained from D. M. Shaw. Peaks due to sulfur or carbon-bearing complexes were searched for by arranging the charts obtained from the nine samples in order of sulfur or carbon content and visually scanning them. It is assumed in using such a method that the various complex ions vary in abundance independently of one another. However, it was discovered in the course of this research that this condition is violated for sulfur and carbon, therefore, casting doubt on the utility of such a procedure for identifying diagnostic absorption peaks.

Sulfur in Scapolite

Although sulfur is usually reported in chemical analyses as SO_3, giving the impression that the sulfur may be present initially as the S^{6+} ion, the chemical analysis procedure is generally such that considerable oxidation of sulfur of lower oxidation states could occur, especially during initial dissolution of the scapolite. Lovering and White (1964) have proposed that sulfur in high-sulfur scapolites such as described by von Knorring and Kennedy (1961) from Mampong, Ghana, occurs structurally as S^{2-} ions in the same site as Cl^- ions. If sulfur were present as an S^{2-} ion no infra-red identification would be possible since the lone S^{2-} ion would not have a characteristic vibrational spectrum (assuming one sulfur ion per anion site). The other principal possibilities for the occurrence of sulfur are as an oxy-anion, either SO_4^{2-}, HSO_4^- or SO_3^{2-}.

The tetrahedral SO_4^{2-} ion has four principal modes of vibration, identified as ν_1, ν_2, ν_3 and ν_4. Of these modes only ν_3 and ν_4 are active in the infra-red. All four modes are active in the Raman. It is likely, however, that in a crystalline host the symmetry at the site of the SO_4^{2-} ion will be less than the symmetry of the free ion (T_d) in which case some or all of the Raman-only modes may become infra-red active. This is analogous to the effects on the CO_3^{2-} ion spectrum described by Adler and Kerr (1963).

If sulfur were present as SO_4^{2-} ions in scapolite one should hope to observe absorption maxima at frequencies corresponding to one or more of the normal modes of the free ion and varying in intensity with sulfur content of the scapolite. The normal modes are given in Table 1. Spectrum *a* of Fig. 1 is of a scapolite containing only a trace of sulfur. It is seen that at each of the diagnostic frequencies for SO_4^{2-} there is an absorption maximum present. The frequencies of normal modes ν_1 and ν_3 for SO_4^{2-} lie within a broad absorption maximum attributed to distorted SiO_4^{4-} ionic vibrations (Launer, 1952). Frequencies ν_2 and ν_4 lie coincident with maxima attributed to Si-O bond bending frequencies (Stubican and Roy, 1961). Thus it can be seen from the outset that it is unlikely that SO_4^{2-} normal modes could be detected in scapolite.

TABLE 1. NORMAL MODE FREQUENCIES OF SULFUR-BEARING OXY-ANIONS (CM^{-1})

	ν_1	ν_2	ν_3	ν_4	Ref.
SO_4^{-2}	983	450	1105	611	Nakamoto, 1963, p. 110
SO_3^{-2}	1010	633	961	496	Evans and Bernstein, 1955

In the hope of reducing the breadth of the SiO_4^{4-} maximum centered at 1100 cm^{-1} and thus revealing the presence of SO_4^{2-} ion modes on the flank of that peak, measurements were performed at liquid nitrogen temperatures. No qualitative change in the peak shape was observed. Two samples, one containing no sulfur, the other containing 0.9 per cent SO_3 were analyzed. As can be seen in Fig. 1, no significant change aside from increase in some peak heights was observed. In conclusion, therefore, the infra-red data do not serve to decide whether or not sulfur is present as SO_4^{2-} ions.

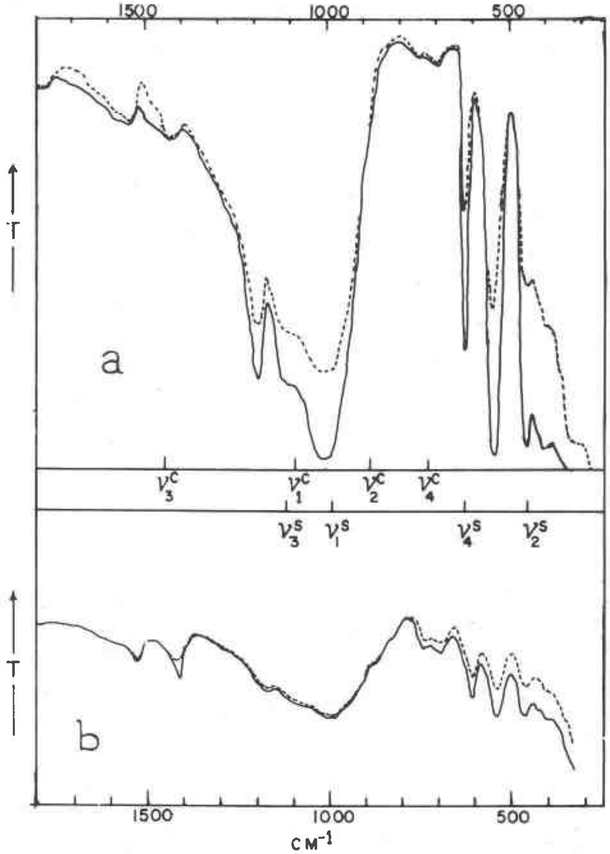

FIG. 1. Infra-red absorption spectra of scapolite at 25° C. (dashed line) and −190° C. (solid line). a—ON 8, containing 0.03% SO_3, 1.11% CO_2. b—M 730, containing 0.94% SO_3 and 2.86% CO_2. $\nu_{1,2,3,4}{}^S$ are frequencies of normal modes of sulfate ion expected in crystalline sulfates. $\nu_{1,2,3,4}{}^c$ are frequencies of carbonate ion expected in crystalline carbonates.

A third possible coordination state for sulfur is as the bisulfate ion, HSO_4^-. Infra-red spectra of $NaHSO_4$, $KHSO_4$ and NH_4SO_4 (Miller and Wilkins, 1952) have common absorption maxima at approximately 1170, 1050 and 860 cm^{-1}. The first two of these modes are obscured by Si-O vibrational modes. The last mode coincides with a normal mode of the CO_3^{2-} ion. This precludes determining if the bisulfate ion is present by the method of comparing scapolites of varying sulfur content since the carbon and sulfur contents of scapolite are apparently correlated (see below).

A fourth possible state in which sulfur might occur in scapolite is as the SO_3^{2-} (sulfite) ion. Although it has not been reported to occur in any

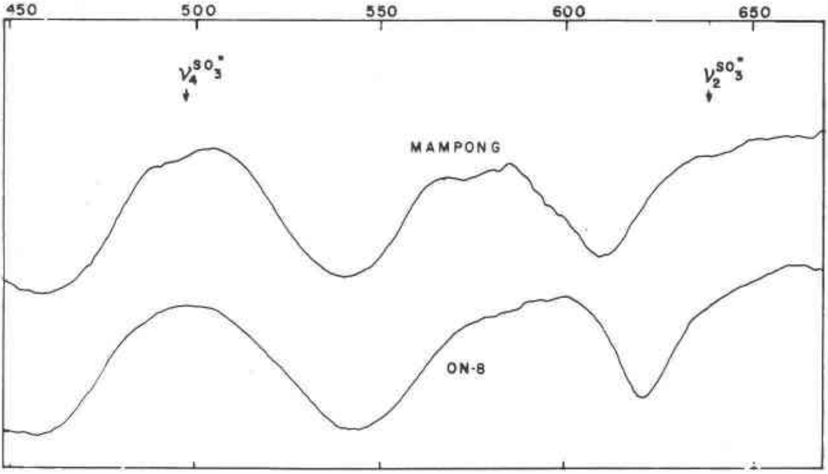

FIG. 2. Far infra-red absorption spectra of sulfur-free (ON8) and sulfur-rich (Mampong; 4.17% SO_3) scapolites at 25° C. $\nu_{2,4}SO_3^=$ are frequencies of normal modes of sulfite ion as observed in Na_2SO_3.

minerals the sulfite ion is a possible constituent of sulfur-rich hydrotermal solutions at moderately high P_{O_2} values, being formed by the hydrolysis of SO_2 which is in turn formed by the oxidation of sulfide ions. The net equilibrium is

$$2S^{2-} + 3O_2 \rightleftharpoons 2SO_3^{2-}$$

In solid Na_2SO_3 the SO_3^{2-} ion has infra-red-active absorption bands at 1011, 961, 633 and 496 cm^{-1} (Evans and Bernstein, 1955). The first two bands are obscured by SiO_4^{4-} bands as was the case for the SO_4^{2-} bands. The last two should be detectable in far infra-red spectra. Figure 2 shows a comparison between the far infra-red spectrum of a sulfur free scapolite (ON 8) and the sulfur-rich scapolite from Mampong. Note shoulders at 643 and 498 cm^{-1} in the sulfur-rich sample. It is possible that these peaks, which were not observed in any other sample, are due to SO_3^{2-} ions. However, it is hazardous at this time to generalize on the basis of this evidence that all sulfur is bound in scapolite as SO_3^{2-} ions.

The structure of scapolite has been studied by Papike (1964) who has essentially confirmed the existence of the silicate framework proposed by Pauling. The anion site is found to lie in the center of a cavity of equant shape, coordinated with four Na or Ca. In carbonate-bearing scapolite the carbon atom presumably is situated on this site, the oxygens of the CO_3^{2-} ion being randomly oriented through the structure to preserve the four-fold rotational symmetry at that point as averaged over all sites.

If the sulfite ion were present in the scapolite structure it would presumably be similarly situated, the sulfur atom being located at the site determined for Cl atoms by Papike. There is, however, room sufficient to fit an SO_4^{2-} tetrahedron in this site and on the basis of size considerations alone SO_4^{2-} cannot be ruled out.

A further clue to the role of sulfur in scapolite may lie in the relation between sulfur and carbon content. Plotting analyses listed by Shaw (1960) as of "Satisfactory quality" one finds no correlation between SO_3 and CO_2. However, using only the recently obtained analyses quoted for eight of the scapolites used in the present study a strong correlation between carbonate and sulfate content is observed (Fig. 3). Assuming that the present set of scapolites is typical of scapolites in general, it would appear that earlier analyses for SO_3 and CO_2 were generally unreliable. Carbonate analyses may easily be high due to admixed traces of dolomite or calcite. They may be low due to the difficulty in releasing CO_2 from scapolite by roasting or acid treatment (J. Muysson, pers. comm.). Sulfate determinations may be in error simply because the level of concentration is so low. Most of the present analyses were done in a single laboratory, which may aid in bringing out the correlation between these

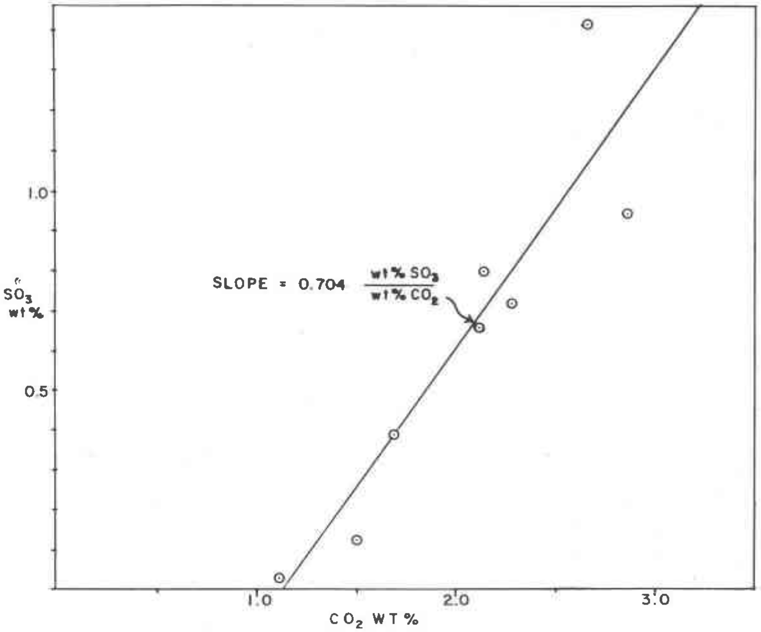

FIG. 3. Relation between SO_3 content and CO_2 content (weight per cent) in eight scapolites, based on analyses in a single laboratory.

two components since constant additive errors would not affect the correlation. However, errors arising out of admixture of carbonate minerals in the analyzed material would not be eliminated in this way.

The interpretation of this correlation is not clear. Note that the SO_3 content falls to zero at about 1.1 per cent CO_2. No scapolites with less than this content of CO_2 were studied by us. The slope of the line in figure 3 implies that about 0.91 S atoms enter the scapolite structure for each carbon atom. Considering the scatter of the data this value is not significantly different from unity, suggesting that sulfur and carbon may enter the structure paired in some fashion. Finally, the Mampong scapolite does not lie on this curve at all, containing only 2.16% CO_2 suggesting that very high-sulfur scapolites may contain sulfur in more than one coordination site. It may be that SO_3^{2-} ions occur only in such very high-sulfur scapolites.

CARBONATE IN SCAPOLITE

The carbonate ion which is trigonal planar when free (in solution or vapour) has four normal modes of vibration of which ν_2, ν_3 and ν_4 are infra-red active. The activity of any of these modes is dependent on the site symmetry of the point at which the ion is located in the crystal structure. The effect of site symmetry on the infra-red spectrum of the CO_3^{2-} ion in calcite and aragonite has been discussed by Bhagavantum and Venkatarayudu (1939), Davydov (1961) and subsequently by Adler and Kerr (1963).

Besides determining whether a mode may be infra-red or Raman-active, environmental changes about the CO_3^{2-} ions induce the splitting of the degenerate modes into doublets (Adler and Kerr, 1963). This may occur when the point-group symmetry of the structural site differs from the ideal symmetry of the ionic group. The CO_3^{2-} ion has two triply degenerate modes active in the infra-red, ν_3 (asymmetric stretch) and ν_4 (planar bending). In aragonite each of these modes is split into two frequencies separated by about 10 cm^{-1}.

Absorption maxima which correlated in intensity with carbonate content were found at the frequencies listed in Table 2. In Table 2 are also shown for comparison the normal mode frequencies for the carbonate ion in calcite and aragonite. The two frequencies 1420 and 1527 cm^{-1} may correspond to the triply degenerate mode ν_3, strongly split by the influence of adjacent ions on the vibrational motion of the CO_3^{2-} group. The splitting is much larger than that observed in aragonite and therefore suggests that the CO_3^{2-} ion is relatively strongly influenced by neighboring ions.

The normal mode ν_3 of the CO_3^{2-} ion corresponds to a symmetric in-plane stretching of C-O bonds, the degeneracy arising out of loss of the

TABLE 2. NORMAL MODE FREQUENCIES OF CARBONATE ION (cm^{-1})

		ν_1	ν_2	ν_3	ν_4	Ref.
calcite	IR	—	879	1429–1492	706	1.
	R	1087	—	1432	714	
aragonite	IR	1080	866	1492 1504	706 714	1.
	R	1084	852	1460	704	
scapolite		obs.	847[1]	1420 1527	—	2.

obs. = obscured by SiO_4^{-4} group vibrations.

[1] Present as shoulder on flank of Si-O absorption maximum centered at 1000 cm^{-1}.

1. Bhagavantam and Venkatarayudu (1939).
2. This work.

3-fold rotational symmetry about the carbon atom. Papike (1964) has shown that the anionic site is surrounded by a square-planar array of Na^+ or Ca^{2+} ions. If the plane of the CO_3^{2-} ion were parallel to the plane of the (Na^+, Ca^{2+}) square, then the effect of the Na^+ and Ca^{2+} ions in disturbing the ν_3 vibrations would be maximized, since the plane of vibration would coincide with the plane of the (Na^+, Ca^{2+}) ions. However, the space available inside the square cation array does not appear to be large enough to hold a CO_3^{2-} in the same plane as the (Na^+, Ca^{2+}) ions. Rather it would seem likely from space considerations alone that the CO_3^{2-} group is oriented in a plane perpendicular to (001) and parallel to one edge of the (Na^+, Ca^{2+}) square.

Normal mode ν_4 which is infra-red active in calcite and aragonite does not appear in the spectrum of carbonate rich scapolites probably because it is of too low intensity to be observed.

A procedure for determining the carbonate content of any scapolite

TABLE 3. SULFUR AND CARBONATE CONTENT (WT. %) OF SCAPOLITES

Sample No.	SO_3	CO_2	X/Y
M730	0.94	2.86	0.337
ON6A	0.39	1.69	0.127
ON8	<0.03	1.11	0.027
Q87	0.87	2.14	0.212
Q19-D	0.72	2.28	0.257
Q85	1.42	2.66	0.257
JG1	0.66	2.12	0.075
ON7	0.13	1.50	0.137
Mampong	4.17	2.16	0.249

has been devised using the absorption intensity of the 1420 cm^{-1} absorption maximum. Samples were prepared and analyzed as described above. The height of the principal SiO_4^{4-} absorption peak at 1000 cm^{-1} was taken as a reference, assuming silica content to be essentially constant. Actually SiO_2 content varies by up to ±17% of the amount present but AlO_4^{5-} ions which replace SiO_4^{4-} ions appear to absorb at about the same frequency (Lecomte, 1958). The shape of the peak is observed to be independent of the Me:Ma ratio, over a range from 20 to 75% Me. Assuming that the transition probabilities for the corresponding normal modes of the AlO_4^{5-} ion are about the same as those for the SiO_4^{4-} ion, then the intensity of the main peak should remain almost constant with changing Me:Ma ratio. Peak to valley absorption amplitude measurements are taken as shown on Fig. 4, and the ratio X/Y was used as the index of CO_2 content. A graph of measurements on the 9 analyzed specimens is shown in Fig. 5.

The peak at 1525–1530 cm^{-1} may also be used as a measure of CO_2 content. Its intensity is shown as X′ on Fig. 4. A graph of CO_2 content versus X′/Y yields a working curve with essentially the same dispersion as that using X/Y.

It was found that day-to-day variations in the sensitivity of the recorder made significant changes in the position of the working curve but not on its linearity.

Owing to the correlation between SO_3 and CO_2 content discussed above, these absorption measurements may also be used as an estimate

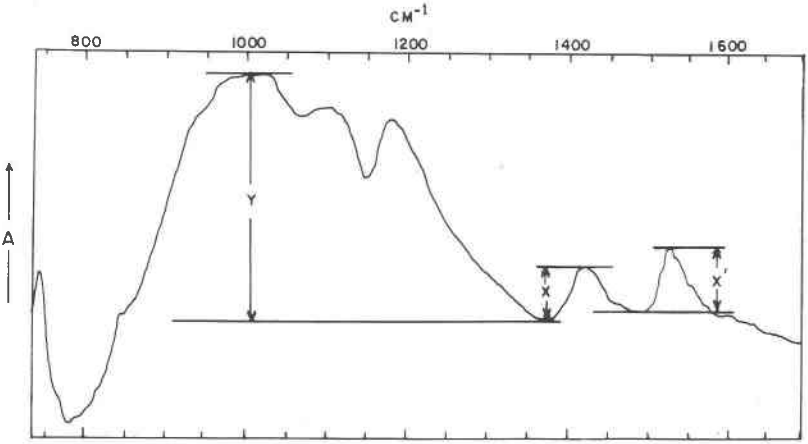

FIG. 4. Absorption spectrum of typical carbonate-rich scapolite (Q19D) showing peaks used to determine carbonate content. X′ = height of 1527 cm^{-1} peak; X = height of 1420 cm^{-1} peak. Y = height of SiO_4^{4-}–$A10_4^{5-}$ absorption maximum, used as internal standard. A = absorbance in arbitrary units.

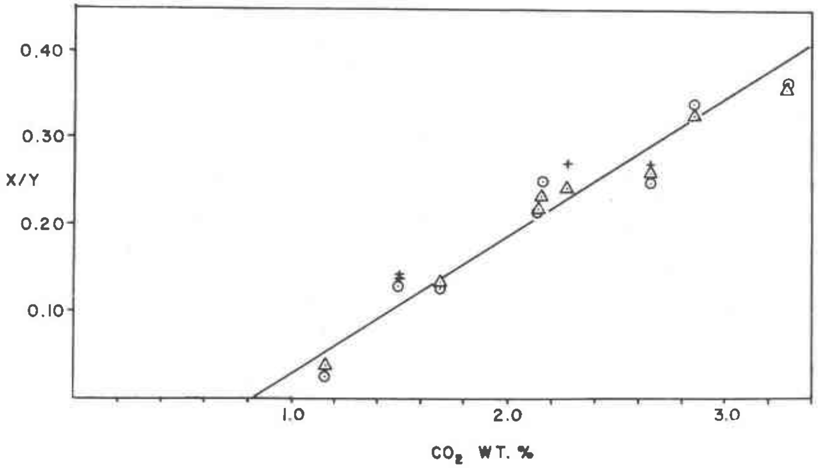

FIG. 5. Working curve for determination of carbonate content of scapolites.

of sulfur content converting by means of the equation of the line on Fig. 3,

$$SO_3(\text{wt. }\%) = 0.704\ CO_2\ (\text{wt. }\%) - 0.800$$

The uncertainty of such a sulfur determination is very large, approximately ±0.3%. The scapolite from Mampong, with an exceptionally high sulfur content (4.2% SO_3), does not have a correspondingly high CO_2 content and fails to conform to the proposed relation.

CONCLUSIONS

Sulfur in scapolite. The infra-red absorption data is inconclusive as to the role of sulfur in scapolite. Because of interference by absorption bands attributed to SiO_4^{4-} it is impossible to see the relatively weak (if present) SO_4^{2-} absorption bands in the near infra-red. Lattice vibrations block the far infra-red bands. Therefore, the I-R data is at the best not in contradiction with sulfur being present as sulfate. The possibility of sulfur occurring as sulfite (SO_3^{2-}) ions is supported by two weak absorption peaks in the most sulfur-rich sample. A correlation between sulfur and carbon may indicate a chemical linkage with carbon necessary for sulfur to enter scapolite.

Carbon in scapolite. An absorption band corresponding to the CO_3^{2-} ion, split into two subpeaks can be recognized in all scapolites studied. The frequency of the two peaks is constant and they are quite sharp, suggesting that the CO_3^{2-} ions are strongly bound in a well determined position, not randomly distributed in the rather large hole provided for anionic species in the Pauling structure. Using a pseudo-internal standard procedure a method of determining carbonate (and indirectly, sulfate) content has been developed.

The possible role of the sulfite ion in other sulfur-containing silicates should be investigated. Since the pyramidal SO_3^{2-} ion is more similar in shape to the CO_3^{2-} than is the tetrahedral SO_4^{2-} ion, it is probably able to substitute for CO_3^{2-} more freely than is SO_4^{2-}. In particular the minerals hauyne and cancrinite both of which contain CO_2 and SO_3, should be investigated with this possibility in mind. The infra-red method should be useful in dealing with this problem.

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