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INFRARED SPECTRA OF PHOSPHATE MINERALS: SYMMETRY AND SUBSTITUTIONAL EFFECTS IN THE PYROMORPHITE SERIES

HANS H. ADLER, *U. S. Atomic Energy Commission, Washington, D. C.*

ABSTRACT

Molecular site and infrared-absorption data suggest that the normally tetrahedral XY_4^{3-} group in apatite- and pyromorphite-series minerals has C_{3v} or lower symmetry. Basic differences in the absorption patterns of pyromorphite, mimetite, and vanadinite are related to differences in mass and binding energy of the functional ions, inversion of the frequency of the v_3 and v_1 vibrations and substitution of non-periodic molecular components such as V for P and As. Complete replacement of Ca by Pb in the apatite structure causes a shift of the v_3 and v_1 vibrations to lower frequencies, as expected.

From inspection of absorption spectra, phosphate groups substituting in mimetite and vanadinite can be distinguished from intergrowths of pyromorphite with mimetite or vanadinite even at low PO_4^{3-} concentrations producing no detectable response in *x*-ray spectra obtained routinely. The PO_4^{3-} molecule is apparently slightly expanded when substituting for AsO_4^{3-} and VO_4^{3-} ions.

INTRODUCTION

The fundamental vibrations and, hence, corresponding absorptions, contributing to the infrared spectrum of a molecule are localized to a first approximation by the mass and internal binding energy of the functional group. In minerals, as in other solids, the vibrational and spectral characteristics of the molecule are further altered by the environment to which it is attached.

Because pyromorphite-series minerals enter into a wide range of substitutions involving the molecular ions, they are ideal for examining in an invariant structure the effects of solid-solution substitution on molecular absorption spectra. In this isomorphous series, which comprises the minerals pyromorphite, $Pb_5(PO_4)_3Cl$, mimetite, $Pb_5(AsO_4)_3Cl$, and vanadinite, $Pb_5(VO_4)_3Cl$, the functional ions and extramolecular cations are compositionally variant, with Ca frequently substituting for Pb and with P, As and V substituting mutually in the XY_4 position. Since substitution for Pb did not exceed one per cent in the specimens studied, the molecular environment remained essentially unaltered, thus permitting evaluation of the spectra in terms of molecular changes. For manifestations of the influence of the extramolecular environment the spectrum of apatite, $Ca_5(PO_4)_3(F, Cl, OH)$, was compared with pyromorphite. Experience already gained from studies of other mineral groups (Adler and Kerr, 1963) permitted interpretation of the Ca:Pb substitutional effect.

In this paper, the absorption spectra of apatite and the pyromorphite-series minerals are examined in relation to the site symmetry of the functional molecular group, change in mass and ionic radius of the participating atoms, and interaction between the functional ions and their external environment. Some potentially useful generalizations are offered regarding absorption trends, which provide a more complete foundation for the utilization of infrared spectra for interpretative purposes in mineralogical studies.

In addition to contributing to knowledge of the spectral changes that take place with chemical variations in mineral structures, a second gratifying aspect of this study has been the realization of an experimental result of direct mineralogical application. In investigating the pyromorphite system it was found that PO_4^{3-} ions substituting for the AsO_4^{3-} and VO_4^{3-} ions in mimetite and vanadinite can easily be distinguished on the basis of their spectral properties from phosphate ions present as intergrown pyromorphite even at concentration levels that did not produce apparent *x*-ray indications. The next obvious step would be to extend this application to other isomorphous systems not easily evaluated by *x*-ray or other means.

Infrared spectra shown here were obtained on a Perkin-Elmer spectrophotometer, Model 21, using finely ground sample material imbedded in KBr discs. The mineral specimens were obtained by permission of Dr. George Switzer from the collections at the U. S. National Museum. The writer is indebted to Dr. Irving Breger and the U. S. Geological Survey for the use of the recording spectrophotometer and to Dr. Howard Evans, Jr. for providing helpful comments on various aspects of this study.

SYMMETRY OF THE PO_4^{3-} ION IN APATITE

The free phosphate ion, PO_4^{3-}, is an example of a molecular ion belonging to point group T_d. In the ideal symmetry state only the triply degenerate vibration species, F_2, of tetrahedral molecules is infrared active and, therefore, among the fundamental bands only absorptions corresponding to the v_3 and v_4 vibrations should be observed. The two remaining fundamentals, v_1 and v_2, become apparent only when the configuration of the ion is modified to certain point groups of lower symmetry.

The 2–15 μ infrared wavelength region scanned in this investigation includes only the v_3 and v_1 fundamentals of the phosphate ion. Herzberg (1945) places the v_3 and v_1 vibrations for the tetrahedral PO_4^{3-} ion at 1082 cm^{-1} (9.2 μ) and 980 cm^{-1} (10.2 μ), respectively; however, the frequencies can be expected to vary somewhat for different crystal structures. Since the v_1 mode is infrared active only for point groups compatible with a molecular dipole moment, *i.e.*, when centers of positive and negative charges of the molecule do not coincide, its appearence in phosphate mineral spectra is indicative of a lowering of the molecular symmetry from T_d to either C_{3v}, C_{2v}, C_2, C_s or C_1. For normally tetrahedral molecules having a modified symmetry, resolution of the latent v_1 mode is accompanied by removal of the degeneracies of v_3 so that either two or three absorption bands should be apparent for the latter mode. In some cases, however, the split bands may not be resolved, and only a single v_3 band will appear. In apatite, the symmetry of the phosphate ion, as deduced from its absorption spectrum (Fig. 1), has evidently been lowered from T_d to conform to a point group compatible with a v_1 dipole.

According to the site-group data for apatite (Strukturbericht II, 1928–1932), the P atom is on a C_s site, thereby restricting the PO_4^{3-} ion to point groups C_s, C_{2v}, C_{3v}, D_{2d} and T_d. T_d and D_{2d} symmetry are ruled out considering the molecular dipole indicated by the presence of v_1 at 10.35 μ (Table 1). Moreover, according to the character tables for symmetry species (Herzberg, 1945), the F_2 degeneracies characteristic of T_d molecules are completely removed for molecular point groups C_s and C_{2v}, and, therefore, three absorption maxima can be expected for v_3. The remaining point group, C_{3v}, has doubly degenerate and non-degenerate normal vibrations. Identification of the infrared-active modes and their state of degeneracy for a normally tetrahedral molecule modified to C_{3v} symmetry was accomplished with the aid of character tables (Herzberg, 1945). This analysis indicates that the v_3 vibration should consist of two infrared-active modes and that v_1 should yield a single band (Table 1).

TABLE 1. POSSIBLE MOLECULAR POINT GROUPS AND VIBRATION MODES FOR THE PO_4^{3-} ION WHERE P IS ON A C_s SITE

Molecular Point Group	Number of Infrared Active Vibrations			
	v_3	v_1	v_4	v_2
T_d	1	0	1	0
D_{2d}	2	0	2	0
C_{3v}[1]	2	1	2	1
C_{2v}[1]	3	1	3	1
C_s[1]	3	1	3	2

[1] Point groups to which a molecule with a dipole moment might belong.

The spectrum for apatite (Fig. 1) conforms to the vibrational requirements of C_{3v} symmetry for the phosphate ion (Table 1) and suggests that the PO_4^{3-} group in apatite has or approaches this symmetry; hence, the molecule apparently has higher symmetry than the surrounding crystal field. This interpretation is supported by the data of Fischer and Ring (1957) who found absorption bands at 16.6 and 17.5 μ. These correspond

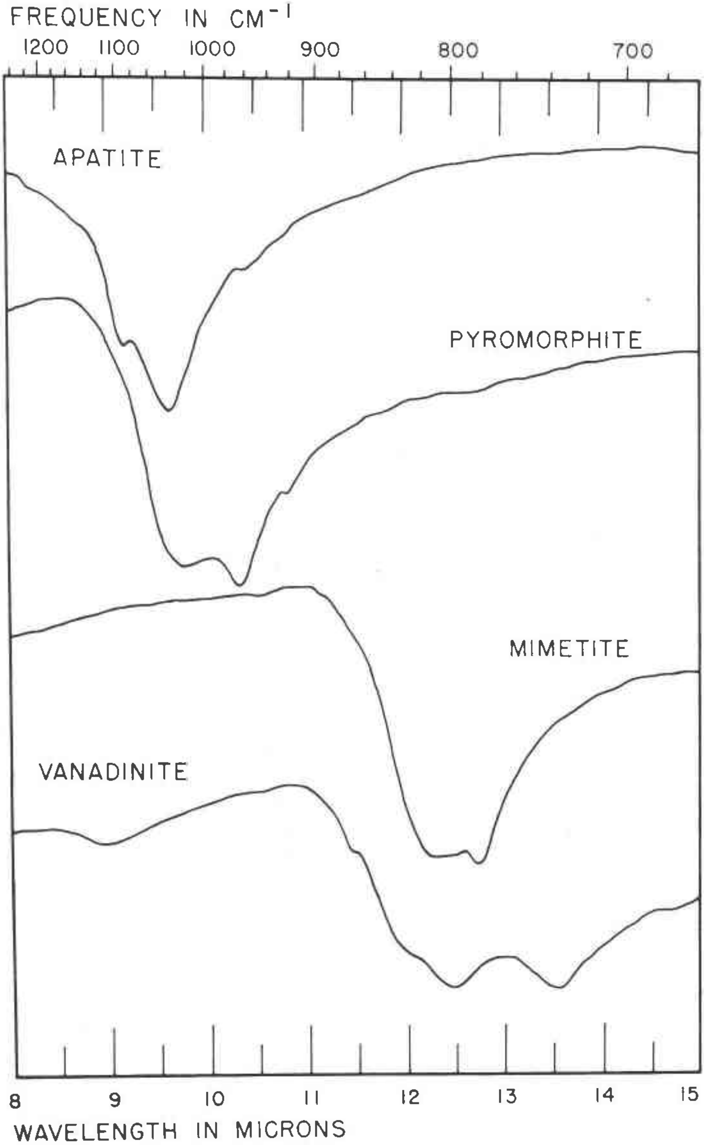

FIG. 1. Apatite, St. Lawrence Co. N. Y., R5224; pyromorphite, Phoenixville, Pa. 12572; mimetite, Tsumeb, S. W. Africa R12415; vanadinite, Chihuahua, Mex. R8741. Specimens are identified by U. S. National Museum numbers.

to the v_4 fundamental and are in accord with C_{3v} molecular symmetry. It presumes, however, that the observed bands correspond only to first-order fundamentals and that there are no accidental degeneracies. When consideration is given to the possibility of unrevealed degeneracies, it may be concluded that the molecule has C_{3v}, C_{2v} or C_s, but not higher, symmetry. Considering the bond-length data for the PO_4 group in apatite by Posner *et al.* (1958), C_s molecular symmetry appears most reasonable. It is possible, therefore, that one cannot unambigously draw a conclusion as to the exact molecular symmetry of the phosphate ion in apatite from the infrared data presented in this investigation. Nevertheless, it should be clear that the molecule would have no higher symmetry than C_{3v}.

TABLE 2. ABSORPTION WAVELENGTHS FOR MINERAL SPECTRA IN FIG. 1

Mineral		PO_4^{3-}		AsO_4^{3-}		VO_4^{3-}	
		v_3	v_1	v_3	v_1	v_3	v_1
Apatite	R5224[2]	9.16, 9.62	10.35				
Pyromorphite	12572	9.78, 10.34	10.8				
Mimetite	R12415			12.25–.5, 12.75	n.d.		
Vanadinite	R8741					12.48, 13.54	11.48[1]

n.d. Not detectable.

[1] Assignment based on Siebert's (1954) analysis of the Raman spectrum of Na_3VO_4, made certain by the polarization of the Raman line for Na_3VO_4 and confirmed by its intensity and sharpness.

[2] U. S. National Museum number.

SPECTRAL RELATIONS IN THE PYROMORPHITE SERIES

A knowledge of the site population in the apatite lattice is obtainable from structure data available in Strukturbericht II (1928–1932) which gives reference to the original data. As previously indicated, the P atoms are located on C_s sites, thus allowing considerable choice of molecular point groups. The apparent symmetry of the PO_4^{3-} ion, which in this case may only approximate the true symmetry, emerges from inspection of the infrared spectrum of the fundamental vibration modes.

The acceptable molecular sites for pyromorphite may be identified according to the method of Halford (1946) using data on space-group symmetry and the unit-cell content. However, this approach was unnecessary since the structures of pyromorphite and apatite are evidently analogous.

Although pyromorphite, mimetite and vanadinite are isomorphous, their spectra (Fig. 1) show certain basic differences. The absence of absorption corresponding to the v_1 vibration for arsenate ions in mimetite is caused by the proximity of the v_1 and v_3 modes so that v_1 cannot be resolved from the stronger v_3 absorption. This is in accord with Siebert's (1954) observation of the coincidence of Raman lines for v_3 and v_1 at 813 cm^{-1} (12.30 μ). For vanadinite, the v_1 vibration of vanadate ions occurs at a higher frequency than v_3, according to Siebert's (1954) assignment of the observed Raman line at 870 cm^{-1}; hence, the absorption at 11.48 μ for vanadinite specimen R8741 (Fig. 1) is presumably v_1. Because of its low amplitude, this band appears not to have been resolved sufficiently to be detectable in the spectrum of specimen R9320 (Fig. 3). The absorption patterns of mimetite and vanadinite are otherwise in accord with the molecular symmetry suggested for pyromorphite.

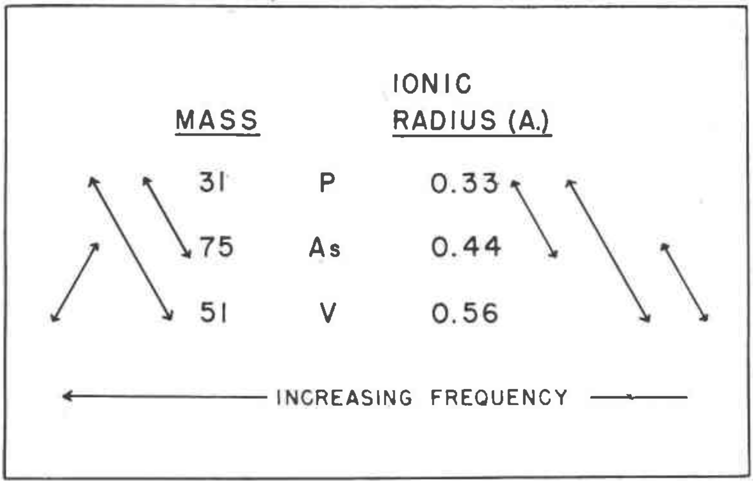

FIG. 2. Theoretical effects of change in mass and ionic radius on infrared vibration frequency of tetrahedral XO_4^{3-} molecules, where $X = P^{5+}$, As^{5+} or V^{5+}.

No detailed interpretation is offered to account for the apparent dissimilarity between the physical configurations of AsO_4^{3-} and VO_4^{3-} absorptions, which contrasts with the striking resemblance between the AsO_4^{3-} and PO_4^{3-} spectra (exclusive of v_1) of the pyromorphite series. There is, however, a suggestion of a dependency on atomic periodicity. Whereas the electronic arrangement is maintained for the P and As ions, it does not hold for the V ion which in its ground state has a different con-

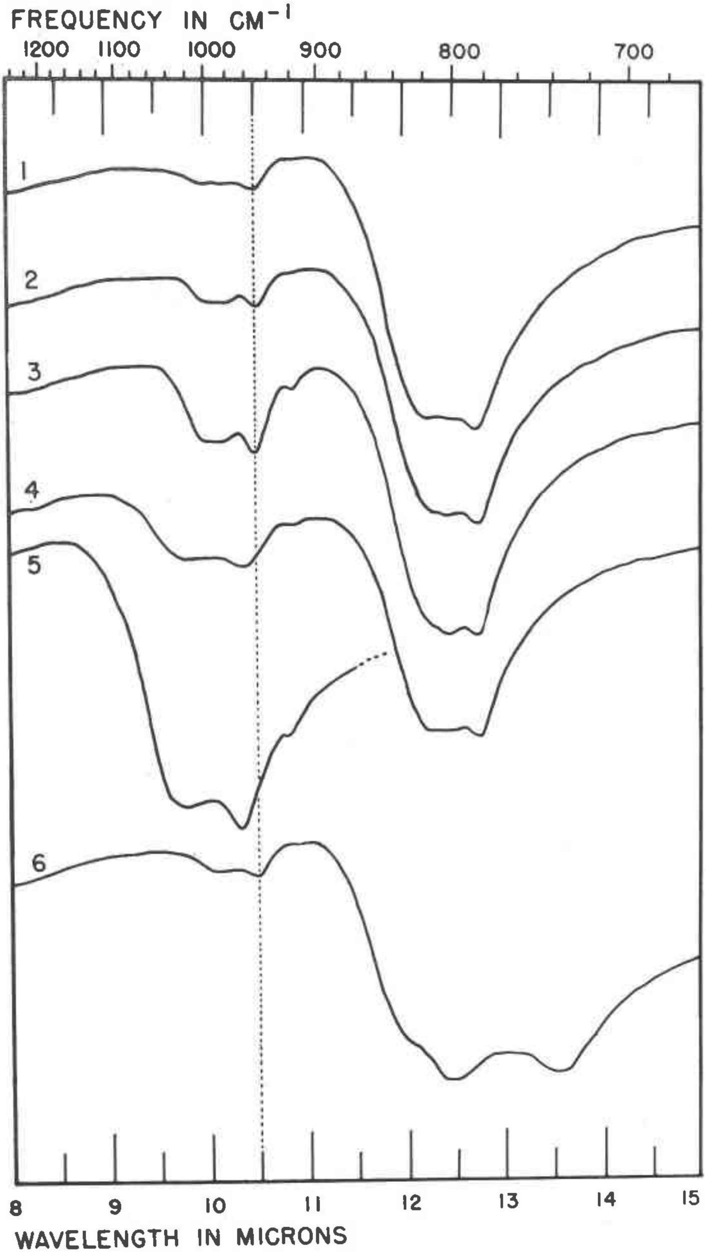

FIG. 3. 1. Mimetite, Durango, Mex. 95576; 2. mimetite, Zacatecas, Mex. R12470; 3. mimetite, Cumberland, Eng. C4130; 4. 80% mimetite, Chihuahua, Mex. C5879; 20% pyromorphite, Phoenixville, Pa. 12572; 5. pyromorphite, Phoenixville, Pa. 12572; 6. vanadinite, Durango, Mex. R9320. Specimens are identified by U. S. National Museum numbers.

figuration of valence electrons and a different orbital population. A somewhat similar though not strictly analogous relation has been observed for carbonate minerals (Adler and Kerr, 1963) which yield aberrant spectra on substitution of non-periodic cations adjoining vibrating CO_3^{2-} molecules, *e.g.*, Pb or Fe, Mn and Zn in place of Group II elements in the aragonite-type and calcite-type lattices.

At this point it seems desirable to comment concerning the implication of the alteration in pattern of the XO_4^{3-} absorption for the pyromorphite series when X ions have similar valence but different electron configurations. First, it might erroneously be concluded in the absence of knowledge of the structure of the minerals being examined, that such spectral difference denotes structural non-conformity. A number of recent papers could be cited in which similar conclusions have been drawn. Such a conclusion would have to be based on the assumption that isostructural minerals will yield absorptions that may differ in wavelength but are otherwise essentially alike. Accepting the evidence presented here as a contra-indication of this condition, we should be alert to a possible change in absorption pattern when functional components having similar chemical binding properties but different electronic structures are substituted in isomorphous systems.

VIBRATION FREQUENCY, MASS AND IONIC RADIUS DEPENDENCIES

The frequency of a molecular vibration is dependent first of all on the molecular parameters and to a lesser degree on the forces exerted on the molecule by the crystal field. For apatite and pyromorphite, the reduced masses of the molecular ions are identical, therefore the frequencies of the PO_4^{3-} oscillations are governed primarily by the molecular force constants, which for both minerals are dependent on the equilibrium internuclear distances between the P and O atoms in these structures. This distance is undoubtedly sensitive to variations in lattice characteristics that exert variable forces on the molecular ions. For example, it has been established for both calcite- and aragonite-type carbonates, in which divalent cations are coordinated to molecular oxygen atoms, that the frequencies of stretching and bending vibrations of the CO_3^{2-} ion are generally lowered with increasing cation size (Adler and Kerr, 1963). The relationship apparently is further dependent on the electronic arrangement of the cations, since frequency-cation-radius trends for series of cations belonging to different periodic groups have been found to be non-colinear. The displacement of the v_3 and v_1 fundamentals to lower frequencies (Fig. 1) on substitution of Pb for Ca in the apatite-type structure is consistent with these observations on carbonates.

For the pyromorphite series, the equilibrium internuclear X–Y distance in XY_4 molecules such as PO_4^{3-}, AsO_4^{3-} and VO_4^{3-} is primarily a function of the ionic radius of the variable X atom. Since Pb, in this case, is always the dominant externally coordinated cation, there is for the various members no significant change in the interaction between the molecular vibrations and the external environment. Badger's (1934) equation,

$$k_0 = 1.86 \times 10^5/(R - d_{ij})^3,$$

although specifically applicable to diatomic molecules, reflects generally the inverse relationship between the force constant, k_0, and the internuclear distance, R. The molecular vibration frequency, v, is dependent on the restoring forces, measured in terms of k_0, between the participating atoms as well as the masses of these atoms. The relationship may be expressed approximately by

$$v = \tfrac{1}{2}\pi c\sqrt{\frac{k}{u}}$$

where the vibration frequency, v, is a function of the force constant, k, and the reduced mass, u, of the vibrating atoms, all other terms being invariant.

The spectral frequency differences between pyromorphite, mimetite and vanadinite are explicable and to a considerable degree predictable in terms of these parameters. On complete substitution of As or V for P the effect of diminished force constants is reinforced by the increases in mass, thereby shifting v_3 and v_1 to lower frequencies. Because of opposing mass and force-constant effects and perhaps also because of dissimilarities in orbital configuration, the relative positions of absorption bands are less predictable for mimetite and vanadinite than for pyromorphite and mimetite. The theoretical frequency trends are depicted in Fig. 2, and the actual displacements are shown in the mineral spectra (Fig. 1).

EFFECTS OF LIMITED MOLECULAR SUBSTITUTION

Phosphate was detected in the spectra of several specimens of mimetite and vanadinite, and its presence in concentration of the order of 1 to 10 per cent P was confirmed by spectrographic analysis. The positions of the phosphate bands suggest that the ion is not present as an admixture, *i.e.*, in intergrown pyromorphite, nor are sufficient amounts of other cations present (none exceeds 1 per cent) to suggest the presence of another phosphate component. It is also very unlikely that the bands are contributed by another lead-phosphate mineral inasmuch as the few known natural compounds of this kind are fairly rare and ordinarily contain additional cationic components which would reveal the presence of such compounds. It may reasonably be concluded, therefore, that the phosphate in these specimens is a substitutional component replacing arsenate and vanadate ions in the mimetite and vanadinite lattices.

The spectra of the specimens under discussion are shown in Fig. 3 and the absorption data appear in Table 3. Pyromorphite (curve 5) characteristically has its two v_3 absorptions at about 9.78 and 10.34 μ and its single v_1 band at about 10.8 μ. These values are also observed for pyromorphite in an artificial mixture of 20% pyromorphite and 80% mimetite by weight (curve 4). For natural phosphatian mimetite (curves 1, 2 and 3) and phosphatian vanadinite (curve 6) the corresponding phosphate absorptions are shifted to about 10.0 and 10.50 μ (v_3) and 10.9μ (v_1). This displacement to lower frequencies appears to be diagnostic of substituted phosphate groups. It indicates an expansion of unknown but probably very low magnitude of the P to O distance when PO_4^{3-} groups occur on AsO_4^{3-} or VO_4^{3-} sites in the mimetite and vanadinite lattices. No conspicuous changes were observed in the arsenate- and vanadate-band positions for phosphatian and non-phosphatian mimetite and vanadinite.

Table 3. Absorption Wavelengths for Mineral Spectra in Fig. 3

Mineral	PO_4^{3-}		AsO_4^{3-}		VO_4^{3-}	
	v_3	v_1	v_3	v_1	v_3	v_1
Mimetite 95576[1]	10.0, 10.48	n.d.	12.2–.4, 12.73	n.d.		
Mimetite R12470	10.0, 10.50	v.w.	12.4, 12.74	n.d.		
Mimetite C4130	10.05, 10.50	10.9	12.45, 12.74	n.d.		
80:20 mixture Mi/Py	9.8, 10.34	10.8	12.4, 12.75	n.d.		
Pyromorphite 12572	9.78, 10.34	10.8				
Vanadinite R9320	10.05, 10.50	v.w.			12.50, 13.50	n.d.

n.d. not detectable.
v.w. very weak.
[1] U. S. National Museum number.

Of three specimens identified by museum label as endlichite (arsenian vanadinite) only one showed evidence of phosphate substitution (curve 6, Fig. 3). Emission spectrographic analyses indicated less than 1 per cent As in each of the three, and the P content exceeded 1 per cent only in the specimen represented by curve 6. The phosphate bands for vanadinite in curve 6 are identical in frequency to those for phosphate-substituted mimetite and are, also, indicative of solid-solution substitution.

There is more to be learned about substitutional effects. For instance, if Ca were to substitute partially for Pb in the phosphatian mimetite or vanadinite lattice, the vibrations of the phosphate ion would probably be shifted to higher frequencies. This shift could possibly cause coincidence with the frequencies for pyromorphite. In this circumstance, the spectrum could be misinterpreted. However, inasmuch as the vibration frequencies of arsenate and vanadate ions should also increase with Ca substitution, this problem may be circumvented by a close inspection of the position of arsenate and vanadate bands. Moreover, a spectrographic analysis will readily confirm the presence of significant amounts of Ca if there is any doubt concerning the interpretation.

X-RAY SPECTRA

X-ray spectra were obtained on all samples for which infrared patterns are shown. End members can be identified readily on the basis of distinct 2θ values.

The three phosphatian mimetite and one phosphatian vanadinite specimens studied show no obvious indication in their *x*-ray spectrograms of the presence of phosphate. No peak deviation greater than 0.2 2θ was observed. Since these minor shifts were not unidirectional, they do not appear to be structurally significant. The *x*-ray spectrum of a mixture comprising 10% pyromorphite and 90% mimetite by weight yielded no obvious indication of the presence of pyromorphite; however, phosphate as pyromorphite was readily detectable in the infrared spectrum. When the ratio is increased to 20:80, however, the three most intense *x*-ray "lines" of pyromorphite are observed (Fig. 4). Hence, routine *x*-ray determination does not seem to provide an indication of phosphate in these specimens. Since substitution of PO_4 for AsO_4 may possibly be detected by careful and rigorous *x*-ray determination of axis dimensions as a function of composition, infrared spectra do not provide a unique manifestation of this phenomenon. However, it may be concluded as a result of this study that infrared spectroscopy is much more sensitive and rapid than *x*-ray diffraction, used routinely, in recognizing pyromorphite mimetite and pyromorphite-vanadinite intergrowths and in distinguishing such aggregates from phosphate-substituted mimetite and vanadinite. It seems less likely, however, because of overlapping absorptions, that arsenate substitution or mimetite intergrowth in vanadinite will be discernible by this method. These results appear to provide some justification for

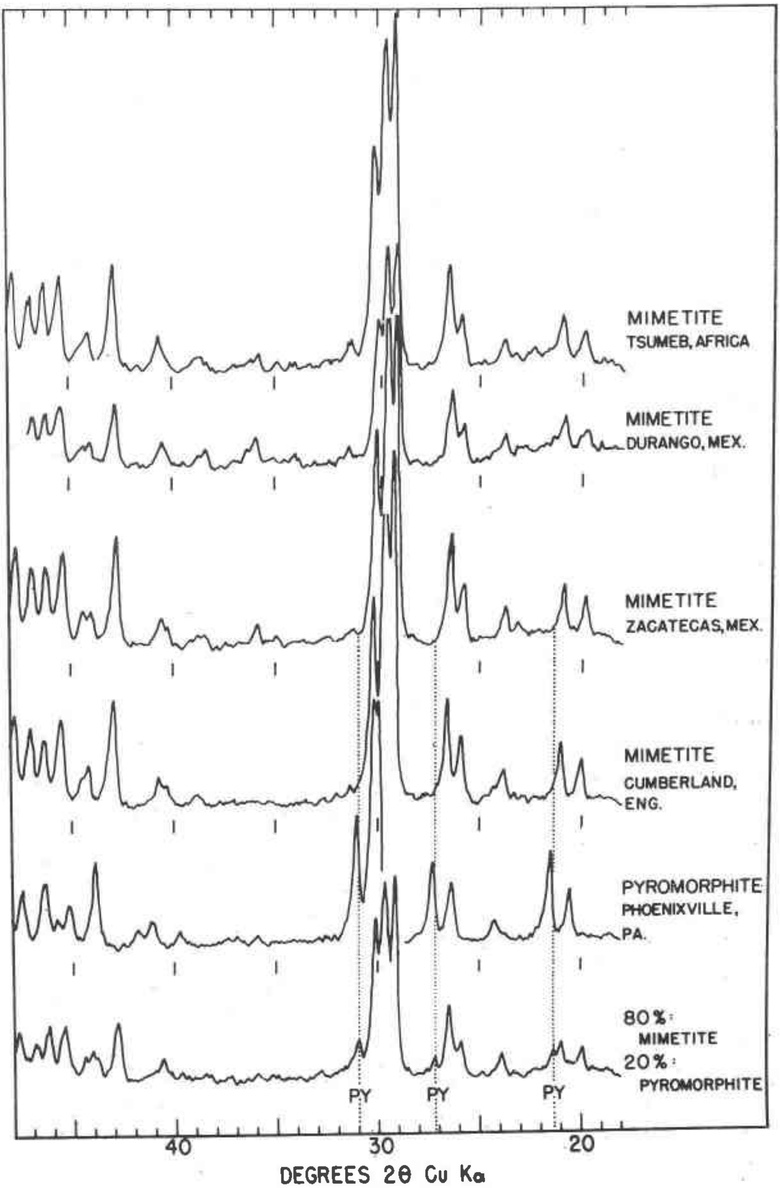

FIG. 4. *X*-ray diffractometer powder patterns of pyromorphite and mimetite. Mimetite from Tsumeb yields an infrared spectrum containing no phosphate bands; mimetites from Durango, Zacatecas and Cumberland yield infrared spectra that contain phosphate bands.

making greater use of infrared spectroscopy in investigating molecular substitution in mineral structures.

V_3-V_1 INVERSION

It is of some interest that v_3 is at a lower frequency than v_1 for the vanadate ion, whereas for the phosphate and arsenate ions v_3 is higher than v_1. Woodward and Roberts (1956) have pointed out that according to the simple valence force field, v_3 should always be greater than v_1 in tetrahedral molecules, the two approaching equality as m_x/m_y increases, *i.e.*, as the mass of X in XY_4 increases with respect to Y. In a number of cases with high values of m_x/m_y, v_3 is observed to be slightly less than v_1 so that one is apt to infer that this reversal of position can be correlated with a high value of m_x/m_y. However, examination of m_x/m_y relationships for the pyromorphite series indicates no such dependency, inasmuch as the v_3-v_1 reversal is prominent for VO_4^{3-} but not for AsO_4^{3-} in spite of the much larger mass of As.

This frequency inversion might also be examined from the standpoint of a possible relationship to the repulsion forces between nearest oxygen atoms in contiguous tetrahedra. One is encouraged to believe that the repulsion between oxygen atoms linked through a mutual Pb atom has a real effect on the molecular vibration frequencies, for if Ca substitutes for the larger Pb ion, the oxygen atoms in adjoining tetrahedra are brought closer together resulting in a shortening of the P–O distances and a corresponding increase in the vibration frequencies of the PO_4^{3-} ion. However, for all pyromorphite-series minerals, the distance between nearest oxygen atoms in adjacent tetrahedra should be relatively constant since the size of the extramolecular cation is invariant and the increase in size of the X ion, when, for example, As substitutes for P, is compensated structurally by expansion of the lattice. It appears, therefore, that the v_1-v_3 frequency inversion may be more closely related to an internal, non-mass-dependent property of the XY_4 ion, such as its possible distortion and expansion along certain symmetry directions. It is interesting to note in this connection that tetrahedrally coordinated ions with v_1 higher than v_3, namely ReO_4^-, VO_4^{3-}, MoO_4^{2-}, and WO_4^{2-}, also have large four-fold radii, whereas those with v_3 higher than v_1, such as SO_4^{2-}, SeO_4^{2-}, PO_4^{3-}, SiO_4^{4-}, CrO_4^{2-}, MnO_4^-, ClO_4^- and IO_4^-, have relatively small four-fold radii.

CONCLUSIONS

As far as its application to mineralogy is concerned, the present work has demonstrated that infrared spectra can distinguish phosphatian mimetite and vanadinite rapidly and easily from pyromorphite-mimetite and pyromorphite-vanadinite intergrowths at phosphate concentrations producing no readily detectable response in routine *x*-ray spectra. It is likely that other mineral systems will also lend themselves to this approach.

The results obtained here also lead to the conclusion that dissimilarities in the spectra of isostructural minerals may result from substitutions of electronically dissimilar components and from v_3-v_1 inversions. This consideration becomes especially important when using infrared spectra as a basis for demonstrating or confirming the structural equivalence or non-equivalence of two mineral substances. There is also sufficient grounds for suggesting that absorption spectra obtained on powdered samples may not always reflect the true symmetry of the functional molecule because of insufficient spectral resolution; nevertheless, they are useful in restricting consideration to specific point groups.

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