Canadian Mineralogist,
Vol. 12, pp. 258-261 (1974)

AN EXPERIMENTAL STUDY OF IRON-MAGNESIUM EXCHANGE BETWEEN BIOTITE AND CLINOPYROXENE

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ABSTRACT

Three electrolyte solutions, 0.5 *M* $MgCl_2$, 0.7 *M* $FeCl_2$ and 1 *M* MgI_2, were tested for their ability to facilitate iron-magnesium exchange in synthetic biotites on the annite-phlogopite join. Synthesis and exchange experiments were carried out, at 1 kilobar of pressure, in standard cold seal pressure vessels with a graphite-methane external buffer. Solid silver-silver iodide was used as an internal buffer for iodide in experiments with magnesium iodide solution.

Chloride solutions proved unsuitable as exchange media because a solvus was produced in the annite-phlogopite series between 500° - 680°C at 1 kilobar.

Using 1 *M* MgI_2 with an Ag-AgI internal buffer to facilitate exchange, the reaction $\frac{1}{3}\,KFe_3^{2+}(AlSi_3O_{10})(OH)_2 + CaMgSi_2O_6 \rightleftharpoons \frac{1}{3}KMg_3(AlSi_3O_{10})(OH)_2 + CaFeSi_2O_6$ was calibrated at 500° and 600° at 1 kilobar. The range of distribution coefficients at 600°C and 500°C shows considerable overlap and the reaction is not greatly temperature-dependent.

Iodide solutions can be used to study a wide range of exchange reactions involving hydrous minerals (e.g. garnet-biotite, biotite-cordierite and biotite-amphibole.)

INTRODUCTION

Following the work of Kretz (1959) on the distribution of elements in coexisting garnet, biotite and hornblende in gneisses, many workers have concluded from regularities in element distribution that equilibrium has been approached in metamorphic rocks. Because many metamorphic minerals are of variable composition, experimental calibration of exchange reactions is of considerable significance in an understanding of metamorphic conditions. Many minerals important in metamorphic rocks are both ferromagnesian and hydrous and this study outlines the development of a method to study iron-magnesium exchange between hydrous minerals. Previous experimental work on iron-magnesium exchange (Medaris 1969) involved anhydrous phases only.

The hydrous minerals used in the study were synthetic biotites on the annite-phlogopite join and both chloride and iodide solutions were tested as suitable exchange media. The reaction

$$\tfrac{1}{3}KFe_3^{2+}\ (AlSi_3O_{10})(OH)_2 + CaMgSi_2O_6 \rightleftharpoons \tfrac{1}{3}KMg_3\ (AlSi_3O_{10})(OH)_2 + CaFeSi_2O_6$$

between synthetic biotites on the annite-phlogopite join and synthetic clinopyroxenes on the hedenbergite-diopside join was investigated at 500° and 600°C using 1 *M* MgI_2 solution as an exchange medium.

EXPERIMENTAL METHODS

Preparation of starting materials

Four biotites on the join annite-phlogopite with Fe/Fe + Mg of 0, 0.166, 0.5 and 1.0, and five clinopyroxenes on the join hedenbergite-diopside with Fe/Fe + Mg of 0, 0.25, 0.50, 0.75 and 1.0, were synthesized from oxide mixes. These oxide mixes were prepared using the 'gel' technique. All biotites and clinopyroxenes used in exchange experiments were synthesized for one week at 1 kilobar pressure, at temperatures between 600° - 730°C in the case of biotites and 600° - 800°C in the case of pyroxenes. The apparatus for synthesis was the same as for exchange experiments and is described below.

Synthesis and exchange apparatus

The experiments were carried out in 12-inch, externally-heated 'cold seal' pressure vessels. Temperature regulation of the furnace was by means of a potentiometer pyrometer. The temperature was measured using a chromel-alumel thermocouple inserted into a well which closely adjoined the sample chamber in the pressure vessel. Once the correct temperature had been reached the variability and uncertainty in temperature readings was always less than ± 5°C and in most cases was ± 2°C.

The pressure medium in all experiments was methane gas and was maintained at 1 kilobar ± 5%. This pressure was transmitted to the charges by the collapse of the silver-palladium (Ag70 Pd30) capsules containing them. The runs were quenched by directing a stream of compressed air on the pressure vessel walls until the temperature was below 200°C.

In order to avoid the formation of 'oxybiotite' (Wones & Eugster 1965) it was necessary to keep the oxygen fugacity at or below the quartz-fayalite-magnetite buffer and this was achieved by the use of the graphite-methane buffer for all experiments. This buffer, first suggested by Eugster & Skippen (1967), produces a fixed hydrogen fugacity which is transmitted through the capsule wall into an aqueous medium and produces an oxygen fugacity at or below that of the quartz-fayalite-magnetite buffer. The pressure of iodide or chloride in the fluid can only reduce oxygen fugacity.

Exchange media

Exchange media were 0.5 *M* $MgCl_2$, 0.70 *M* $FeCl_2$ and 1 *M* MgI_2 solutions. In the case of the first two solutions, about 30 mg of biotite were weighed into a silver-palladium capsule, 30 mg of either ferrous or magnesium chloride solution added, and the capsule welded shut. At the end of the runs (7 - 10 days) the Fe/Fe + Mg of the biotites was determined by *x*-ray diffraction and each run was examined optically. In experiments with 1 *M* MgI_2 solution, about 20 mg of biotite and pyroxene were weighed into separate crimped silver tubes. These were placed in a silver-palladium capsule, and solid AgI and approximately 40 mg 1 *M* MgI_2 solution added. The Ag-AgI was used as an internal buffer for iodide. The capsules were held at 500° or 600° and 1 kilobar for 4 to 5 weeks. The resulting biotites and clinopyroxenes were washed and analyzed by *x*-ray diffraction for Fe/Fe + Mg.

Determination of Fe/Fe + Mg in biotites and clinopyroxenes

Following the work of Wones (1963), Fe/Fe + Mg of the biotites was obtained by accurate determination of $d(060,\bar{3}31)$ using *x*-ray diffraction. There is a systematic increase in $d(060,\bar{3}31)$ with increase in Fe/Fe + Mg (Fig. 1). It is estimated that the maximum uncertainty in the Fe/Fe + Mg of unknown biotites is 0.03.

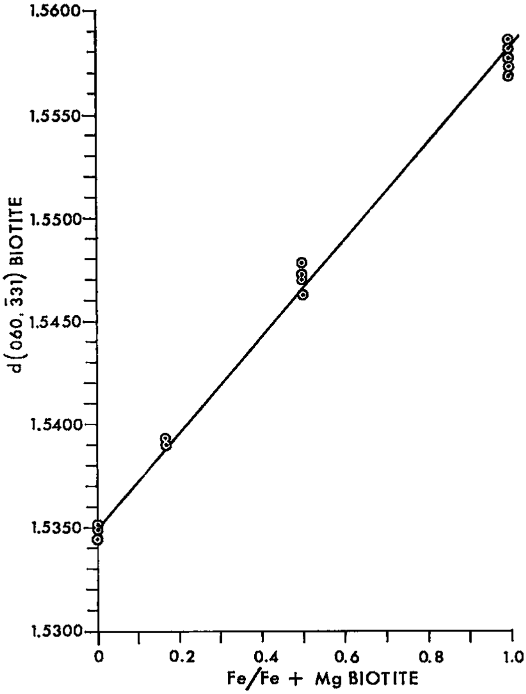

FIG. 1. Curve for the determination of Fe/Fe+Mg in biotites on the annite-phlogopite join.

X-ray films were made of five synthetic clinopyroxenes (Fig. 2) using cobalt radiation with an iron filter. The exposure times were 24 hours and silicon was used as a standard. The 531 line shows the maximum shift between magnesium and iron end members and when $d(531)$ of the pyroxene is plotted against Fe/Fe + Mg a linear relationship is observed (Fig. 2). The maximum uncertainty in Fe/Fe + Mg of the clinopyroxenes is estimated to be 0.02.

RESULTS

The results of runs using 0.5 *M* $MgCl_2$ and 0.07 $FeCl_2$ solutions are shown in Table 1. In all experiments, an iron-rich biotite and a magnesium-rich biotite were produced. The presence of two biotites in the run products was identified by two distinct 060 peaks in the *x*-ray diffraction patterns and by the appearance of two biotites of distinctly different refractive indices when run products were examined optically. No solid phases other than biotite were seen. The Fe/Mg ratios of the chloride solutions in equilibrium with biotite and pyroxene were analyzed by atomic absorption at the conclusion of three experiments (Table 1). These analyses consistently indicate a solution with a high iron content,

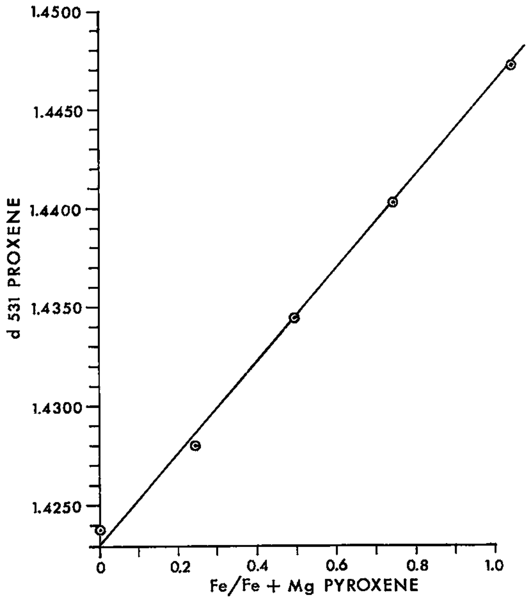

FIG. 2. Curve for the determination of Fe/Fe+Mg in clinopyroxenes on the hedenbergite-diopside join.

i.e. an Fe/Fe + Mg ratio between 0.954 and 0.930.

The Fe/Fe + Mg of the resultant biotites is plotted against temperature in Figure 3. The results suggest the presence of a solvus in the chlor-biotites produced by the use of chloride solutions.

The results of runs using 1 *M* MgI_2 solution as an exchange medium are shown in Table 2. In all runs there was an exchange of ferrous iron and magnesium between biotite and clinopyroxene. Ideal solution was assumed in both biotite and clinopyroxene solid solution series implying that the distribution coefficient,

$$K_D = \left(\frac{X_{Fe}^{Pyroxene}}{X_{Mg}^{Pyroxene}}\right)\left(\frac{X_{Mg}^{Biotite}}{X_{Fe}^{Biotite}}\right)$$

is constant over the entire range of compositions. The results of the runs plotted as log Fe/Mg pyroxene against Fe/Mg biotite are shown in Figures 4 and 5. The possible range of K_D *for* each temperature is indicated. The bracketing lines are not close, indicating that equilibrium is approached slowly in the experiments. K_D at 600°C is between 0.64 and 1.00 and K_D at 500°C is between 0.61 and 0.97. There is considerable overlap between the range of K_D values at 600°C

TABLE 1. RUN RESULTS: BIOTITE + (Mg,Fe)Cl_2 SOLUTION

Run Number	Length of run (days)	Temp. in °C	Starting Biotites Fe/Fe+Mg	Solution	Fe/Fe+Mg Starting System	Fe/Fe+Mg Final Biotites	Fe/Fe+Mg Solution at end of run
H_3Ex7	10	548±5	1.0	0.558$MgCl_2$	0.91	0.12 0.92	n.d.
H_3Ex8	8	653±5	1.0	0.558$MgCl_2$	0.85	0.9	n.d.
Rb9ExMg2	8	675±3	0.5	0.558$MgCl_2$	0.305	0.38 0.82	n.d.
H_1H_3ExMg2	9	555±2	0.0,1.0	0.558$MgCl_2$	0.275	***	0.954
RH1Ex6	10	548±5	0.0	0.7$FeCl_2$	0.1	0.00 0.95	n.d.
RH9ExFeMg	10	569±2	0.5	$MgCl_2$+$FeCl_2$		0.45 0.95	n.d.
RH9ExFe2	8	680±3	0.5	0.7$FeCl_2$	0.71	0.47 0.935	n.d.
H_3H_1ExFe1	9	660±2	0.0,1.0	0.7$FeCl_2$	0.82	0.34 0.896	0.937
H_1H_3ExFe2	9	568±2	0.0,1.0	0.7$FeCl_2$	0.78	***	0.930
RH1Ex9	8	650±5	0.0	0.3$FeCl_2$	0.45	0.10 0.81	

*** *x*-ray pattern diffuse

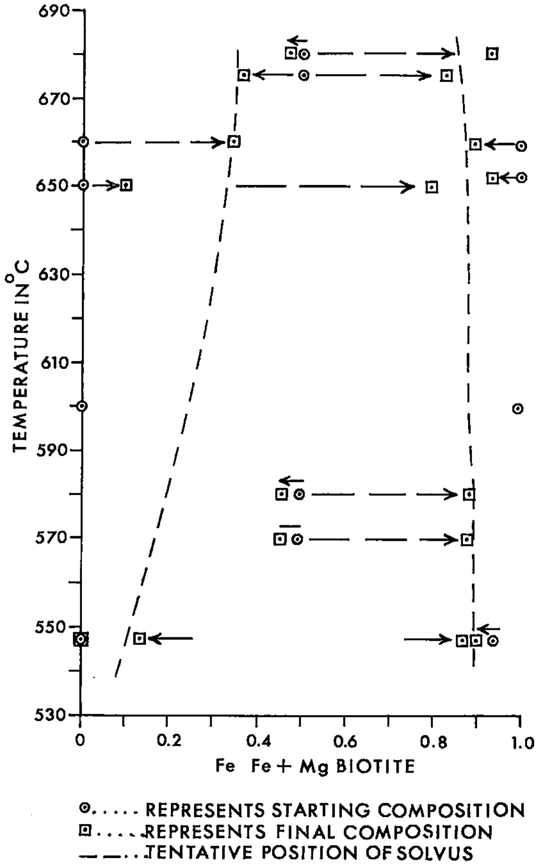

FIG. 3. Solvus produced in the annite-phlogopite series with 0·5 *M* $MgCl_2$ and 0·7 *M* $FeCl_2$.

TABLE 2. RUN RESULTS AT 600°C, 500°C, AND 1 KILOBAR. Ag/AgI INTERNAL BUFFER, 1M MgI_2 SOLUTION. EXTERNAL BUFFER C/CH_4

Run Number	Fe/Fe+Mg Initial Biotite	$d_{060,\bar{3}31}$ Final Biotite	Fe/Fe+Mg Final Biotite	Fe/Mg Final Biotite	Fe/Fe+Mg Initial Pyroxene	d_{531} Final Pyroxene	Fe/Fe+Mg Final Pyroxene	Fe/Mg Final Pyroxene
600°C								
6Ag1Mg	0.00	1.5375	0.11	0.125	0.25	1.4276	0.19	0.24
6Ag2Mg	0.50	1.5441	0.39	0.64	0.25	1.4290	0.265	0.36
6Ag3Mg	0.50	1.5441	0.39	0.64	0.75	1.4320	0.39	0.64
6Ag4Mg	1.00	1.5562	0.92	11.5	0.50	1.4441	0.88	7.34
6Ag5Mg	1.00	1.5572	0.96	24.0	0.75	1.4436	0.89	8.09
6Ag1MgR	0.167	1.5390	0.16	0.19	0.00	1.4247	0.065	0.07
6Ag2MgR	0.167	1.5396	0.195	0.24	0.25	1.4292	0.26	0.35
6Ag3MgR	0.167	1.5412	0.25	0.33	0.75	1.4416	0.54	1.17
6Ag4MgR	0.50	1.5440	0.40	0.66	0.75	1.4373	0.62	1.63
6Ag5MgR	0.50	1.5443	0.44	0.79	1.00	1.4439	0.86	6.14
500°C								
5Ag1Mg	0.00	1.5360	0.04	0.042	0.25	1.4269	0.165	0.20
5Ag2Mg	0.50	1.5460	0.47	0.89	0.25	1.4268	0.16	0.191
5Ag3Mg	0.50	1.5476	0.54	1.17	0.75	1.4395	0.69	2.22
5Ag4Mg	1.00	1.5511	0.695	2.28	0.50	1.4482	0.58	1.38
5Ag5Mg	1.00	1.5551	0.865	6.41	0.75	1.4412	0.77	3.34
5Ag1MgR	0.167	1.5387	0.155	0.185	0.00	1.4367	0.07	0.075
5Ag2MgR	0.167	1.5388	0.17	0.205	0.25	1.4268	0.165	0.20
5Ag3MgR	0.167	1.5397	0.2	0.25	0.75	1.4287	0.255	0.33
5Ag5MgR	0.50	1.5476	0.55	1.22	1.00	1.4424	0.90	9.0

and 500°C and the temperature dependence of the distribution coefficient is quite small.

CONCLUSIONS

The use of chloride solutions as exchange media has proved successful in facilitating exchange of iron and magnesium between synthetic olivines and pyroxenes (Medaris 1969) and in alkali exchange in plagioclase feldspars (Orville 1963, 1972), but appears unsuitable for hydrous minerals because of possible substitution of Cl^- for OH^-.

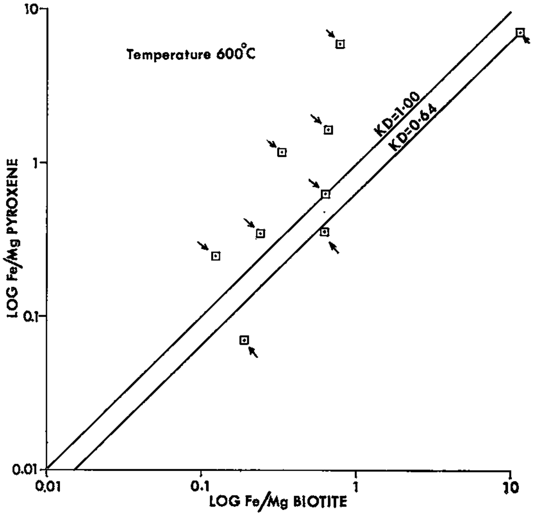

FIG. 4. Log Fe/Mg pyroxene versus log Fe/Mg biotite at 600°C and 1 kilobar.

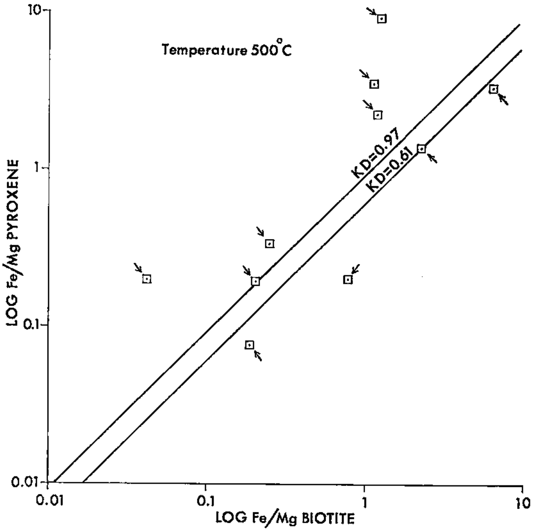

FIG. 5. Log Fe/Mg pyroxene versus log Fe/Mg biotite at 500°C and 1 kilobar.

This study has demonstrated that magnesium iodide solution can be used to facilitate exchange reactions in hydrous minerals. The presence of the Ag-AgI buffer for the iodide ion will eventually enable the composition of the fluid phase to be calculated although the lack of the dissociation constant for HI at the conditions of the experiments precludes such calculations at present. The temperature dependence of the end member exchange reaction between biotites on the annite-phlogopite join and clinopyroxenes on the hedenbergite-diopside join is apparently small.

Iodide solutions appear to offer a suitable medium for the study of a wide range of important exchange reactions among coexisting minerals, both hydrous and anhydrous. Possible examples are garnet-biotite, biotite-cordierite and biotite-amphibole.

ACKNOWLEDGMENTS

The author wishes to express her thanks to Dr. E. W. Reinhardt of the Geological Survey of Canada who developed the method for preparing biotite oxide mixes and provided three of the oxide mixes used in this study. Dr. G. B. Skippen of Carleton University and Dr. E. Froese of the Geological Survey of Canada gave much helpful advice and criticism. The research was financed by National Research Council grant, number A4253, to Dr. G. B. Skippen.

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Manuscript received October, 1973.

Canadian Mineralogist,
Vol. 12, pp. 262-268 (1974)

INFRARED SPECTROSCOPIC INVESTIGATION OF THE STRUCTURE OF SOME NATURAL ARSENATES AND THE NATURE OF H-BONDS IN THEIR STRUCTURES

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ABSTRACT

The IR-spectra of the arsenates durangite, mimetite, conichalcite, austinite, olivenite and adamite corroborate the character of the symmetry of the arsenate groups in these minerals. The changes in the symmetry of the point group of the anion $(AsO_4)^{3-}$ is the result of a coordinative bond with metal atoms. The hydroxyl group in conichalcite, austinite, olivenite and adamite is linked through H-bonds and coordinated with metal atoms. The frequencies of stretching vibrations of the hydroxyl group indicate that there are H-bonds with variable strengths between the OH groups and the oxygen in the O-AsO_3 groups. The strength of the H-bond falls in the following order: conichalcite > austinite > olivenite > adamite.

A band at 740 cm^{-1} in the spectra of Zn-bearing minerals such as adamite and austinite indicates that the oxygen atom of the arsenate group is partly protonated by the hydrogen atom of the OH group. This confirms that there is interaction between the anion and the cation (coordination) and that OAs (OH) groups may exist in the structure. The absence of bands in the 1500-1700 cm^{-1} region confirms the absence of water molecules in these minerals.

The following structural formulae are proposed: conichalcite, $Ca(CuOH)(AsO_4)$; austinite, $Ca(ZnOH)(AsO_4)$; olivenite, $Cu(CuOH)(AsO_4)$; and adamite, $Zn(ZnOH)(AsO_4)$.

INTRODUCTION

Durangite, $NaAl(AsO_4)F$, mimetite, $Pb_5(AsO_4)_3Cl$, adamite, $Zn_2(AsO_4)OH$, olivenite, $Cu_2(AsO_4)OH$, conichalcite, $CaCu(AsO_4)OH$ and austinite, $CaZn(AsO_4)OH$ have scarcely been studied by IR-spectroscopy. Adler (1961) and Moenke (1962) include the IR-spectra of some of these minerals, but they do not discuss them in detail and the spectra are used mainly for mineral identification. As *x*-ray data are available for this group of minerals, their IR-spectra, structures, and the nature of their chemical bonds may be correlated and analyzed.

All samples that were used were identified by optical methods and by *x*-ray analysis. The IR-spectra were registered with an IR-spectrophotometer (Zeiss, GDR) in the 400-3800 cm^{-1} region. The samples were prepared as emulsions in nujol. The spectra recorded were reproducible to ± 2 cm^{-1} in the 400-2000 cm^{-1} region and to ± 5 cm^{-1} in the 2000-3800 cm^{-1} region. Deuteration of the samples was carried out by means of a hermetic oven (Nasedkin 1962). Of the minerals studied, the only one completely deuterated was conichalcite and the substitution took about 20 hours.

All the minerals investigated are of the isolated tetrahedron type. Two, durangite and mimetite, have almost regular tetrahedrons and lack hydroxyl groups; the others (conichalcite, austinite, olivenite, and adamite) possess hydroxyl groups and their tetrahedral $(AsO_4)^{3-}$ structure is somewhat deformed. In the minerals investigated, three kinds of interactions are expected: 1) donor-acceptor, 2) H-bond and 3) electrostatic. The strongest type of interaction is probably the the donor-acceptor one, because most of the metallic cations are capable of forming strong complexes and because the anions are strong electrodonors. These interactions result in changes in the structure and in the chemical bonds and consequently the IR-spectra of these minerals are different from the spectra of free arsenates and free OH groups.

According to Mayantz (1960) and Siebert (1953, 1954, 1966), the tetrahedral symmetry, T_d, of the arsenate ion is indicated by four absorption bands of which only two appear in the IR-spectra and have the theoretical values $\nu_3(F_2) = 887$ cm^{-1} and $\nu_4(F_2) = 463$ cm^{-1}. The four bands appear in Raman spectra (Gupta 1948). When coordination of the arsenate ion with metals occurs, as in donor-acceptor bonds, then the symmetry of the arsenate group falls from $C_s(C_{3v})$ to C_{2v} (Fig. 1). A redistribution

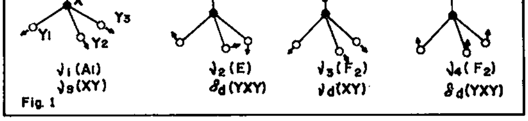

FIG. 1. Forms of vibration for the $(AsO_4)^{3-}$ tetrahedral group.

of the electronic cloud occurs which raises the strength of some of the As-O bonds, and decreases the strength of other bonds. This also results in the formation of new metal-oxygen bonds. The IR-spectra permit us to follow these changes and to interpret their nature. All the symmetry bands $\nu_1(A_1)$ and $\nu_2(E)$ are present. As the degeneracy of the $\nu_3(F_2)$ and $\nu_4(F_2)$ bands disappears, these split into two or three components and the band of valency vibrations of the Me-O(Me = metal) bond appears. Other bands related to the metal-arsenate system also appear. The coordination of the hydroxyl groups causes sharp changes in the IR-spectra. New bands related to deformation vibrations of the Me-OH bands appear in the 600-1200 cm^{-1} region and bands related to stretching vibrations appear in the 300-900 cm^{-1} region (Youxnevitch 1963, 1970).

MIMETITE

Mimetite, $Pb_5(AsO_4)_3Cl$, is an analogue of apatite and is hexagonal, bipyramidal, $6/m$. The unit cell has two $Pb_5(AsO_4)_3Cl$ units (Hendricks 1932; Machatski 1950). The As forms a regular tetrahedron with four oxygen atoms, in which the As-O distance is 1.82Å. The tetrahedra are interlinked by Pb atoms. The Pb atoms in the octahedra resemble empty cylinders on the walls of which are the Pb atoms, parallel to the c axis; the Cl atoms are distributed directly on the c axis. Pb forms a continuous column in which each Pb atom coordinates with 9 oxygens. These columns are linked together by the $(AsO_4)^{3-}$ tetrahedra.

We studied two samples of mimetite, one from Tsumeb, S.W. Africa, with 1.93% P_2O_5 and another from Cumberland, England, with 11% P_2O_5. The IR-spectra of both samples (Fig. 2) show a slight splitting in the region of stretching vibrations of the AsO_4 groups, that is, the $\nu_3(F_2)$ band. This splitting gives rise to two bands at 790 cm^{-1} and 820 cm^{-1}. The $\nu_1(A_1)$ band appears as a weak shoulder at 735 cm^{-1}. In the region of deformation vibrations of the arsenate ion there is a weak splitting of the $\nu_4(F_2)$ band into two bands at 415 cm^{-1} and 430 cm^{-1}. From the IR-spectral data we conclude that there is a slight deformation of the $(AsO_4)^{3-}$ tetrahedron, giving this mineral a C_{3v} symmetry. This agrees with the correlation scheme (Table 1) and with the x-ray data. The arrangement in the correlation table enables one to find the symmetry of the ligand in the structure of the minerals (Nakamoto 1966). The interatomic distances are Pb-Cl = 3.16Å and Pb-O = 2.56Å, which are bigger than the sums of the ionic radii (2.65Å and 2.16Å), and this fact indicates that the Pb-O bond is mainly ionic. The ionic nature of the Pb-O and Pb-Cl bands is also confirmed by the absence of absorption bands in the 500-600 cm^{-1} region where the bands of stretching vibrations of the Me-O bonds usually appear.

TABLE 1. CORRELATION TABLE FOR GROUPS OF LOCAL SYMMETRY IN TETRAHEDRAL ANIONS (Nakamoto 1966)

		ν_1	ν_2	ν_3	ν_4
Td	infrared	-	-	F_2	F_2
	Raman spectra	A_1	E	F_2	F_2
C_{3v}	infrared	A_1	E	A_1+E	A_1+E
	Raman spectra	A_1	E	A_1+E	A_1+E
C_{2v}	infrared	A_1	A_1	$A_1+B_1+B_2$	$A_1+B_1+B_2$
	Raman spectra	A_1	A_1+A_2	$A_1+B_1+B_2$	$A_1+B_1+B_2$

The IR-spectra of mimetite from Tsumeb, which has only traces of phosphate, show four bands of medium intensity in the region of valency vibrations of the phosphate group, that is in the $\nu_3(F_2)$ region. These bands are ν_{3a} = 960 cm^{-1}, ν_{3b} = 990 cm^{-1}, ν_{3c} = 1010 cm^{-1} and a weak band $\nu_1(A_1)$ = 925 cm^{-1} (Table 2). In the region of deformational vibrations, the $\nu_4(F_2)$ band is split in three bands: ν = 545 cm^{-1}, ν_{4b} = 555 cm^{-1} and ν_{4c} = 570 cm^{-1}. This kind of splitting indicates that the site-symmetry of the $(PO_4)^{3-}$ group in the correlation scheme must correspond to C_{2v} symmetry, that is, to a symmetry lower than that of the $(AsO_4)^{3-}$ groups.

The IR-spectra of mimetite from Cumberland show an intense band $\nu_3(F_2)$ due to the phosphate anion. A weak band at 1320 cm^{-1} is probably due to an overtone 2 $\nu_4(PO_4)^{3-}$ and

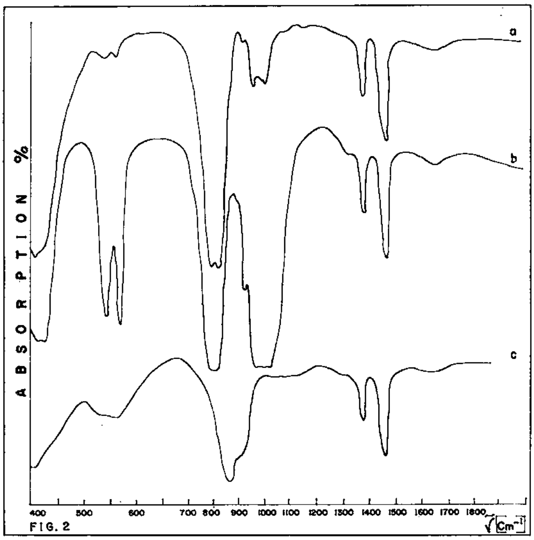

FIG. 2

FIG. 2. Infrared spectra of mimetite and durangite: (a) mimetite from Cumberland, England; (c) durangite from Durango, Mexico.

the 1650 cm^{-1} band may be related to the overtone 2 $\nu(AsO_4)^{3-}$.

DURANGITE

Durangite, $NaAl(AsO_4)F$, is a rare mineral. Its structure (Kokkoros 1938) is monoclinic, $2/m$, space group C_{2h}, Z = 4. The coordination number for Na is 7 and for Al, 6. The structure is of a sublayer type and is analogous to those of titanite and tilasite (Strunz 1938). In durangite, As forms a practically regular tetrahedron with As-O = 1.68Å in the $(AsO_4)^{3-}$ anion. The atoms of Al are surrounded by four oxygen atoms and by two F atoms that form an octahedral structure, AlO_4F_2, in which the interatomic distances are: Al-O = 1.81-1.90Å and Al-F = 1.81Å. In the vicinity of the Na atoms there are six O atoms and an F atom, with interatomic distances: Na-O = 2.40-2.47Å and Na-F = 2.35Å. These form NaO_6F polyhedra.

A fundamental difference between mimetite and durangite is the presence of Al atoms in durangite that are capable of forming strong covalent bonds. This is corroborated by the fact that the Al-O interatomic distances (1.81-1.90Å) are significantly lower than sum of the ionic radii (1.93Å). The coordination of the Al atoms with the arsenate groups in the structure of durangite decreases the As-O interatomic distance to 1.68Å as compared 1.82Å in mimetite, thus indicating that the As-O bond in durangite is the stronger.

The change in the energy of the valency bonds leads to changes in the IR-spectra. The frequencies of the As-O vibrations are 100 cm^{-1} higher than in mimetite (Table 2). The IR-spectra of durangite are considerably more complex than the spectra of mimetite (Fig. 2). In the region of valency frequencies $\nu_3(F_2)$, a very weak splitting is observed and it gives the bands ν_{3a} = 860 cm^{-1} and ν_{3b} = 915 cm^{-1}. In the $\nu_1(A_1)$ region there is a shoulder at 790 cm^{-1}. In the $\nu_4(F_2)$ region that corresponds to deformation vibrations, two bands are observed: ν_{4a} = 415 cm^{-1} and ν_{4b} = 450 cm^{-1}. This kind of splitting clearly points to a deformation in the $(AsO_4)^{3-}$ groups giving a C symmetry, which is in agreement with the correlation table and the *x*-ray data of Kokkoros (1938).

The IR-spectra of mimetite, which is a typical ionic compound, clearly differ from the spectra of durangite, which is a mineral with coordination bonds. For durangite, the two bands at 525 cm^{-1} and 560 cm^{-1} are probably due to antisymmetrical stretching vibrations of the Al-F and Al-O bonds in the octahedra. These two values are in the region of vibrational frequencies for the AlO_6 group (Nakamoto 1966). The observed spectral splitting may be explained as the result of a slight deformation in the symmetry of the octahedra. In durangite the 1030 cm^{-1} and 1098 cm^{-1} bands are probably due to the 2νAl-F and 2νAl-O overtones, and the 1650 cm^{-1} band is also probably due to an overtone $2\nu_3(AsO_4)^{3-}$.

It is concluded that the increase of the $\nu_3(F_2)$ value by 100 cm^{-1} and the appearance of a 560 cm^{-1} band related to Al-O bonds are a characteristic of coordination between arsenate groups and Al atoms. Therefore, it is possible to classify durangite as a compound with strong

TABLE 2. INFRARED ABSORPTION BAND FREQUENCIES.

Mineral	$[As(P)O_4]^{3-}$						*Me*-O	OH		OH..O	Overtone	
	$\nu_1(A_1)$		$\nu_3(F_2)$		$\nu_4(F_2)$		$\nu(Me\text{-}O)$	δOH	νOH	ν(OH..O)	2ν	cm^{-1}
	As-O	P-O	As-O	P-O	As-O	P-O						
Mimetite $Pb_5[AsO_4]_3Cl$		925	790 820	960 990 1010	415 430	545 555 570					$2\nu_4(PO_4)^-$ $2\nu_3(AsO_4)^-$	1320 1650
Durangite $NaAl[AsO_4]F$			830* 860 915*		415 450		525(Al-F) 560				2ν(Al-F) 2ν(Al-O) $2\nu_3(AsO_4)$	1030 1098 1650
Olivenite $Cu_2[AsO_4]OH$	750*		800 830 870	1040 1090	400 452 492		545	950	3440	3050		
Adamite $Zn_2[AsO_4]OH$	740		800 830 860		400 485		515 535	900	3580	2900		
Conichalcite $CaCu[AsO_4]OH$	740*		795 820 840 865		410 430 460		575	930 1020 1060 (815)	3480 (2600) 3170 (2360) 2380	2090 2700 2730	$2\nu(AsO_4)$	1650
Austinite $CaZn[AsO_4]OH$	750		800 845		410 430 465		525 570	915 980 1010	3550 3300	1940 2450		

* shoulder ( ) frequencies of absorption bands of deuterated samples

covalent bonds and mimetite as a compound with bonds of an ionic nature.

Conichalcite and Austinite

The structure of austinite is not known, but as austinite and conichalcite are isomorphous, their structures must be of the same type. Both minerals are basic arsenates with isolated $(AsO_4)^{3-}$ groups in their structures. Their unit cell is orthorhombic with $4[CaCu(AsO_4)OH]$ in conichalcite and $4[CaZn(AsO_4)OH]$ in austinite. The conichalcite structure has been investigated by Strunz (1939) and Qurashi *et al.* (1953, 1954, 1963). The lattice of these two minerals consists of deformed $(AsO_4)^{3-}$ tetrahedra. Each Cu (or Zn) atom is surrounded by an octahedron of oxygen atoms, two of which belong to -OH groups and four to the arsenate group. Each Ca atom has eight neighbouring atoms. Seven are oxygen atoms belonging to arsenate groups and the eighth is an oxygen atom or a hydroxyl group. The interatomic distances are given in Table 3.

The sample of conichalcite that we used is from the Lachin-Han deposits, Uzbekhistan, and was provided by the Mineralogical Museum of the Academy of Sciences of the USSR (No. 64923). The Lachin-Han deposits and conichalcite have been thoroughly described by Dunin (1962).

The IR-spectra of conichalcite (Fig. 3a, Table 2) show a band splitting in the $\nu_3(F_2)$ region of vibrational frequencies of arsenate groups. The splitting gives four bands: $\nu_{3a} = 795$ cm^{-1}, $\nu_{3b} = 820$ cm^{-1}, $\nu_{3c} = 840$ cm^{-1}, and $\nu_{3d} = 865$ cm^{-1}. The $\nu_1(A_1)$ band is observed as a weak shoulder at 740 cm^{-1}. The region of deformation vibrations, $\nu_4(F_2)$, has three well-resolved bands $\nu_{4a} = 410$ cm^{-1}, $\nu_{4b} = 430$ cm^{-1}, and $\nu_{4c} = 460$ cm^{-1}. According to the correlation table (Table 1), the arsenate anion has a C_{2v} symmetry, which agrees with the x-ray data

TABLE 3. *X*-RAY DATA OF SOME ARSENATES WITH ISOLATED TETRAHEDRA IN THEIR STRUCTURES

Mineral	Ion	$O_{(1)}$	$O_{(2)}$	$O_{(3)}$	$O_{(4)}$	$O_{(5)}$/OH	Symmetry
Conichalcite $CaCu[AsO_4]OH$	As	1.74	1.67	1.73	1.60		
	Cu	2.09		2.38	2.28	1.95	
		2.04				1.95	
	Ca	2.54	2.68	2.53	2.51	2.36	
			2.48	2.46	2.54		
	OH	2.74		2.96			
		2.90		3.18	2.97		
		2.97			3.04		
Olivenite $Cu_2[AsO_4]OH$	As	1.49	1.45	1.81	1.81		
	$Cu_{(1)}$	2.12		2.34	2.34	1.96	
						1.96	
	$Cu_{(2)}$		2.03			1.99	
			2.16	1.92	1.92		
	OH	2.97	2.78	2.85	2.85		
Adamite $Zn_2[AsO_4]OH$	As	1.59	1.59	1.81	1.81	3.01	Deformed tetrahedron
	$Zn_{(1)}$	1.99		1.84	1.84	1.91	Trigonal bipyramid
		2.19					
	$Zn_{(2)}$		2.08	2.29	2.29	2.08	
			2.08			2.08	
	OH	2.68	3.03	2.79	3.04	2.86	

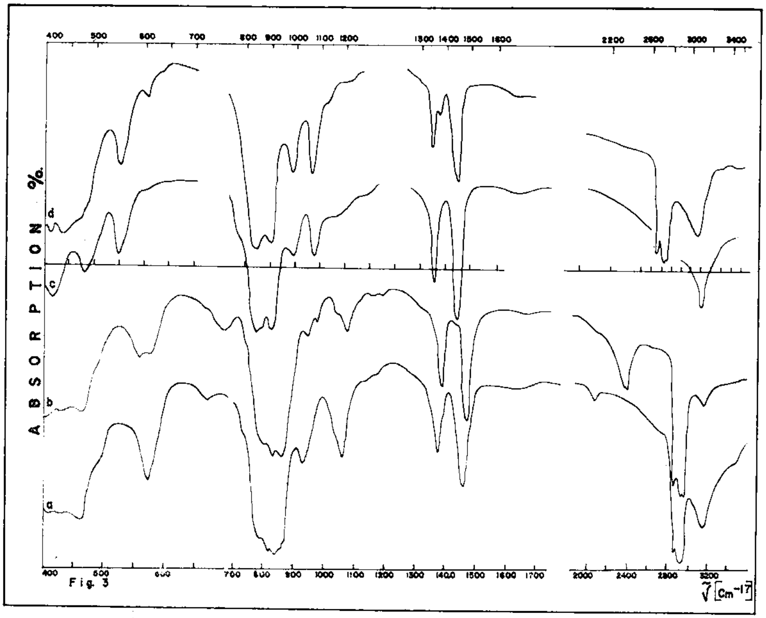

Fig. 3. Infrared spectra of conichalcite and austinite: (a) conichalcite from Lachin-han, USSR; (b) deuterated conichalcite from Lachin-han; (c) austinite from Hovon-aksi, USSR; (d) austinite from Ojue'a, Mexico. For cm^{-17} read cm^{-1}.

(Qurashi *et al.* 1963). A band of high intensity at 575 cm^{-1} is attributed to the stretching vibrations of the Cu-O bonds because the band does not change after deuteration of the mineral. The presence of Cu-O bonds is corroborated by *x*-ray data on the coordination of arsenate groups with Cu atoms. The interatomic distances of 2.04-2.28Å for the Cu-O bond are significantly less than the sum of the ionic radii, which is about 2.34Å (Qurashi *et al.* 1963). The 3480 cm^{-1} band is due to vibrations of the hydroxyl groups, which also give absorption bands at 3170 cm^{-1}, 1060 cm^{-1}, and 930 cm^{-1}. The relation of these bands with the hydroxyl groups is based on their shift after deuteration with D_2O (Fig. 3b). The spectra of deuterated conichalcite has the following features:

1. The 3170 cm^{-1} band is displaced to a lower frequency region and appears as two sharp, strong bands at 2360 cm^{-1} and 2380 cm^{-1}. The coefficient of isotopical shift is given by: OH 3170/OD 2370 $\simeq$ 1.33.
2. The intensity of the 930 cm^{-1} band is lowered and the band shifts to a lower frequency (695 cm^{-1}). The shift also reveals a previously hidden band at 960 cm^{-1}. The coefficient of isotopical shift is given by: νOH 930/νOD 695 $\simeq$ 1.33
3. The intensity of the 1060 cm^{-1} band is also lowered and its displacement reveals another band at 1020 cm^{-1}. Taking into consideration the coefficient of isotopical shift, the 1060 cm^{-1} band should be displaced to 750 cm^{-1}. Observation of the displaced band is obscured in this region by the stretching vibrations band $\nu_1(A_1)$ of arsenate groups.
4. The 3480 cm^{-1} band is probably shifted to 2600 cm^{-1} where a wide absorption band appears in the spectra of the deuterated samples.

The 3170 cm^{-1} band in the IR-spectra of conichalcite is related to the stretching vibrations of the OH groups in arsenates. These hydroxyl groups are linked, through strong H-bonds, with the oxygen of arsenate groups. In fact the oxygen atoms of the arsenate groups the strongest acceptors for H-bonds in the mineral. The *x*-ray data (Qurashi *et al.* 1963) show that the lowest value for the $O_{(5)} \ldots (HO)$ distance is 2.74Å, in agreement with the interatomic distance in a strong H-bond. The wide band at 3480 cm^{-1} is probably due to weaker H-bonds as is indicated by the higher interatomic distances (2.90-296Å) between oxygen atoms.

Two samples of austinite were used, one from Mapimi, Mexico and the other from Hovon-aski, Touva, USSR. The latter contains Mg (2.5%), Mn (1.6%) and Co and Ni (less than 1%) (Yahontova 1968). The Mapimi austinite has not been chemically analyzed.

The IR-spectra of both samples are very similar. In the $\nu_3(F_2)$ region, two bands were observed at 845 cm^{-1} and 800 cm^{-1}. The $\nu_1(A_1)$ band is poorly resolved and appears as a shoulder at 750 cm^{-1}. In the $\nu_4(F_2)$ region bands appear at 410 cm^{-1}, 430 cm^{-1} and a sharp shoulder at 465 cm^{-1}. This splitting (Fig. 3), according to the correlation table (Table 1), is probably linked to the site-symmetry of the arsenate ion. The arsenate group in austinite is probably less deformed than in conichalcite. This may be due to the specific crystallochemical properties of Zn that takes, in austinite, the place that Cu has in conichalcite.

The 525 cm^{-1} band is related to stretching vibrations of the Zn-O bonds. The Mapimi austinite shows a weak band at 570 cm^{-1} which is analogous to the band of stretching vibrations of Cu-O bonds in conichalcite; this band is probably due to the presence of traces of Cu in the austinite from Mapimi. The 915 cm^{-1} and 980 cm^{-1} bands are due to deformation vibrations *Me*O-H.

In the spectra of samples from Hovon-aksi (Fig. 3c), the region of valency vibrations of OH groups shows a sharp symmetrical band at 3300 cm^{-1} and a poorly-resolved wide band which appears as a shoulder at 3350 cm^{-1}. The IR-spectra of austinite from Mapimi show an asymmetrical band at 3270 cm^{-1} and a shoulder at 3520 cm^{-1}, which are due to the presence of H-bonds of different strength. This difference in strength of the H-bonds is probably linked to differences in the cationic composition of the two samples. (The 1400 cm^{-1} band in the IR-spectra of austinite from Mapimi indicates the presence of carbonate that is probably a mechanical contamination).

As the frequencies of the stretching vibrations of the hydroxyl groups in conichalcite (3170 cm^{-1}) are lower than in austinite (3270 cm^{-1} and 3300 cm^{-1}), the H-bonds are stronger and shorter in conichalcite than in austinite. From the comparison of IR-spectra and *x*-ray data the arsenate and hydroxyl groups are coordinated with Zn and Cu. We can thus consider conichalcite and austinite as minerals with coordination bonds and we propose the formulae $Ca(CuOH)(AsO_4)$ for conichalcite and $Ca(ZnOH)(AsO_4)$ for austinite.

OLIVENITE AND ADAMITE

These minerals were included because they are typical arsenates of the isolated (AsO_4) group type and contain hydroxyl.

The adamite sample is from the Ojuela deposits, Mapimi, Mexico. The mineralogical, optical and chemical properties of adamite have been studied in detail by Mrose (1948). The sample of olivenite is from Tsumeb, Africa, and was obtained from the Mineralogical Museum of the Academy of Sciences of the USSR. This mineral has also been thoroughly described (Richmond 1940; Berry 1951).

Adamite, $Zn_2(AsO_4)OH$, and olivenite, $Cu_2(AsO_4)OH$, are orthorhombic and isostructural. The structure of adamite has been described by Kokkoros (1937) and that of olivenite by Heritsch (1938). Both minerals have a deeply deformed tetrahedron $(AsO_4)^{3-}$ as the basis of their structure. The tetrahedra have interatomic As-O distances of 1.49-1.81Å in olivenite and 1.59-1.81Å in adamite. Half of the Cu atoms in olivenite have an octahedral coordination typical of Cu^{2+}; two oxygen atoms and two hydroxyl groups surround the Cu ion, forming a square with Cu-O interatomic distances of 2.03Å for the hydroxyl (Cu-OH), and 2.12-2.34 for the oxygen in the arsenate ($Cu\text{-}OAsO_3$). The two remaining oxygen atoms are at a larger distance from the Cu atom (2.39Å). Their coordination polyhedra have the geometry of a deformed trigonal bipyramid which has five oxygen atoms and one hydroxyl group on the apices. The Cu atom is slightly shifted from the center of this bipyramid and has a medium Cu-O distance of 2.03Å for the hydroxyl (Cu-OH). The oxygen octahedra around the Cu atom are linked by a common edge. The chains are interlinked by the Cu bipyramids and the $(AsO_4)^{3-}$ tetrahedra.

The structure of adamite is analogous to the structure of olivenite except that the Zn atoms occupy Cu positions. Interatomic distances for these two minerals are given in Table 3.

The IR-spectra of our samples showed a band $\nu_3(F_2)$ split into four components (Fig. 4). The $\nu_1(A_1)$ band is not completely resolved and has the form of a shoulder at 740-750 cm^{-1}. Two intense bands appear in the $\nu_4(F_2)$ region. It is probable that the third component of the $\nu_4(F_2)$ band is located in a lower frequency region, beyond the 400 cm^{-1} limit that we could register. From these data we conclude that the symmetry of the $(AsO_4)^{3-}$ group is lowered to C_3 or C_{2v} and this concurs with the x-ray data. The deformation of the tetrahedron may be explained by the linking of the arsenate group with an atom of Cu or Zn through coordination bonds. This supposition is confirmed by the presence, in olivenite, of a stretching vibration band of Cu-O at 545 cm^{-1}, which can be observed after deuteration. The splitting of this band in adamite, which gives two components at 515 cm^{-1} and at 535 cm^{-1} for the valency vibration band of Zn-O, indicates that its octahedra have a lower symmetry.

The presence of deformation vibration bands *Me*-OH in the 900-950 cm^{-1} region confirms the coordination of the hydroxyl group with the

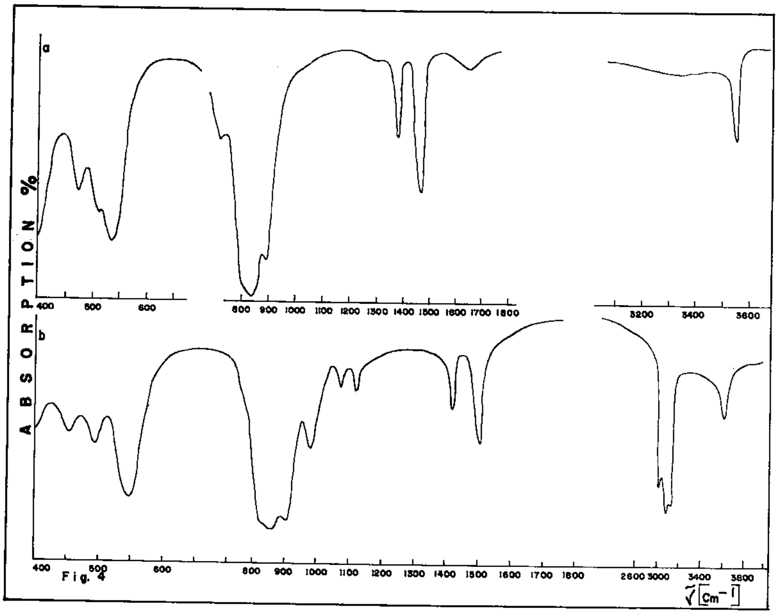

FIG. 4. Infrared spectra of (a) olivenite from Tsumeb, Africa, and (b) adamite from Ojuela, Mexico.

atom of metal. This agrees with the shift of the 950 cm^{-1} band after deuteration of conichalcite. Two sharp bands of equal intensity at 1040 cm^{-1} and at 1090^{-1} may be due to the $\nu_3(F_2)$ vibrations of the phosphate anion. Chemical analysis of the Tsumeb olivenite gave 1.5% phosphorous.

The absence of absorption bands in the 1500-1700 cm^{-1} region shows that neither olivenite nor adamite contains water. The 3440 cm^{-1} band in olivenite corresponds to the stretching vibrations of the hydroxyl groups. The high value of the band at 3580 cm^{-1} in the spectra of adamite shows that its hydroxyl groups show less indication of hydrogen bonding than those in olivenite and therefore interatomic distances between oxygen atoms O-----H-O should be larger (Table 3). X-ray data corroborate this.

From the combination of x-ray and infrared data, it is concluded that the arsenate and hydroxyl groups are coordinated with the Zn or Cu atoms. The hydroxyl groups form H-bonds with a varying degree of strength and when coordination occurs, they bind through H-bonds. It is considered that the formulae of adamite and olivenite should be represented as $Cu(CuOH)(AsO_4)$ and $Zn(ZnOH)(AsO_4)$ respectively.

ACKNOWLEDGMENTS

The author is grateful to Professor G. P. Barzanov and Dr. B. E. Zaitsev for their help in this study, which formed part of a Ph.D. Thesis at Moscow University.

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Manuscript received August 1973, emended November 1973.