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OH Groups and the Structure of Picropharmacolite by IR Spectroscopy

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Abstract

IR-spectra for picropharmacolite—proposed formula $Ca_2(MgOH)(HAsO_4)\cdot(AsO_4)\cdot 5\ H_2O$—show that its structure contains water molecules, hydroxl groups coordinated with Mg^{2+} atoms, and acid arsenate anions, $(HAsO_4)^{2-}$. The symmetry of the arsenate anions is lowered from T_d to C_{2v} or lower. The hydroxyls in the structure form H-bonds of different strength.

Introduction

The structure of picropharmacolite, especially the form and character of water in this structure, is important in the crystal chemistry and genesis of arsenates. However, the problems of water in minerals cannot be solved solely by X-ray methods and chemical analysis. Consequently we utilized IR-spectroscopy.

The natural arsenates are salts of the arsenic acid, an acid weaker than phosphoric acid. The arsenates, including picropharmacolite, form at very low pressures and temperatures in the oxidation zone of mineral deposits that contain arsenic. Depending upon the oxidation-reduction potential (Eh) and of the pH of the solutions, arsenic acid may dissociate to form $(AsO_4)^{3-}$, $(HAsO_4)^{2-}$, or $(H_2AsO_4)^{1-}$ groups. Indeed, any of these groups may occur in the structure of natural arsenates, depending on the conditions of formation. The knowledge of the type of group that is present in the arsenate is an important aid in determining the genesis of mineral deposits.

Picropharmacolite is a poorly known mineral, and the available data are not always reliable. The structure is not known. The unit cell parameters are given by Pierrot (1961, 1964) as $a_o = 6.74$ Å, $b_o = 21.0$ Å, $c_o = 13.5$ Å and $\beta = 140°$. The space group has not been established. One of the most difficult questions in the chemical constitution of this arsenate is the position of the Mg atoms. Furthermore, the placement of this mineral in the subclass of the arsenates with isolated polyhedra is uncertain.

Chemical analyses of picropharmacolite (Table 1) have been reported from four different deposits: Saxony, Hessen, Elzats, and Hovou-Aksi. Analyses 1 and 2 in Table 1 give the empirical formula: $4CaO\cdot MgO\cdot 2As_2O_5\cdot 13\ H_2O$, whereas Analysis 3 yields $5CaO\cdot MgO\cdot 2As_2O_5\cdot 12\ H_2O$. Analyses 4 and 5 are similar to Analyses 1 and 2 and give the formula: $4CaO\cdot MgO\cdot 2As_2O_5\cdot 12\ H_2O$. If we consider the formula that is commonly given for picropharmacolite—$(Ca,Mg)_3(AsO_4)\cdot 6\ H_2O$—then it is difficult to understand the recurrence of the proportion $4CaO\cdot MgO$ in analyses 1, 2, 4, and 5.

Experimental Method

The two samples of picropharmacolite studied here, respectively from Sante Marie aux Mines (France) and from Hovou-Aksi (USSR), were identified from their measured X-ray diffraction patterns and optical parameters, which were identical to those reported by Pierrot (1961, 1964) and Yahontova (1968).

The IR spectra were recorded with a Zeiss UR-20 (DDR) spectrophotometer in the 400 cm^{-1} —3800 cm^{-1} region. The samples for IR spectroscopy were prepared as emulsions in Nujol and fluorinated hydrocarbons or as pressed tablets with KBr. Dehydration of the samples and spectral recordings were carried out under vacuum. The samples deuterated for 20–40 hours in an hermetic autoclave at temperatures ranging from 120° to 180°C and pressures ~15 atm in order to define those bands in the IR spectra related to hydroxl groups.

TABLE. 1. Chemical Analysis of Picropharmacolite

Oxides	Weight Percent 1	2	3	4	5
CaO	24.65	25.77	27.90	24.49	24.65
MgO	3.22	3.73	4.45	4.43	3.17
As_2O_5	46.97	46.93	45.50	48.19	49.15
H_2O	23.98	24.01	21.36	22.42	23.65
Other	1.00 (Fe_2O_3)	--	0.48 (CoO)	0.75*	--
Total	99.82	100.44	99.69	100.28	100.62

1. Richelsdorf (Hessen) (Fisher, 1960).
2. Freiberg (Saxony)(Fisher, 1960).
3. Sante Marie aux Mines (France) (Pierrot, 1961, 1964).

4,5.Hovou-Aksi (Tuva, SSSR) (Yahontova, 1968).

* unidentified solid residues

Results

The IR spectra of acid arsenates differ from the spectra of ordinary arsenates. This is due to different bonding and to the difference in symmetry of the anion as well as to the presence of hydroxyl bonds.

Lowering the symmetry from T_d to $C_{2v}(C_s)$ produces (Fig. 1) a splitting of the $\nu_3(T_2)$ and $\nu_4(T_2)$ bands and also the appearance of bands $\nu_1(A_1)$ and $\nu_2(A_1)$. Finally the presence of OH groups in the structure of the mineral gives new stretching vibration bands in the 2400–3500 cm^{-1} region and of deformation vibration bands in the 800–1350 cm^{-1} region. The vibrations of the As(P)–OH bond are characterized by four absorption bands: 1265 cm^{-1}, 1680 cm^{-1}, 2400 cm^{-1}, and 2730 cm^{-1} (Blinc and Hadzi, 1958, 1960; Hadzi, 1965). The last two bands are related to the stretching vibrations of the hydroxyl group; the first two, to the deformation vibrations. Four analogous bands have been described for acid silicates (Ryiskin and Stavitskaya, 1960; Ryiskin, Stavitskaya, and Toropov, 1960) and for germanates (Stavitskaya and Ryiskin, 1961).

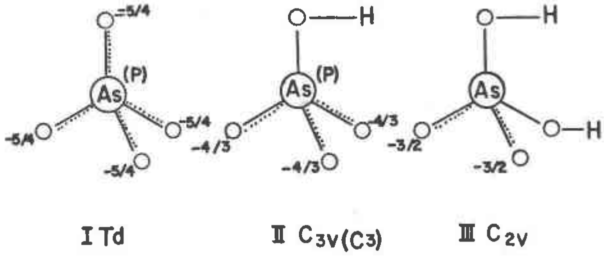

Fig. 1

FIG. 1. Distribution of electron density in the $(AsO_4)^{3-}$ anion.

In many spectra the hydroxyl bands lie in the same region as the stretching vibrations of water. For this reason it is difficult to use this region for identifying hydroxyl groups. On the other hand, the region of deformation vibrations of water is very specific. Theoretical analysis (Youhnevitch, 1963, 1970) shows that the formation of H-bonds between water molecules should not bring about a lowering of the deformation band frequencies. In comparison, hydrogen bonding to the H atom in the OH group, strongly varies the frequency of the deformation vibration δOH. Consequently the deformation vibrations of the X-OH groups (where X = any atom) are found in the 700 cm^{-1} to 1300 cm^{-1} region and are not obscured by the bands of the deformation vibrations of H–OH which are in the 1580 cm^{-1} to 1670 cm^{-1} region. Therefore, the presence of generally broad bands in the 1580 cm^{-1} to 1680 cm^{-1} region can be used as a criterion for the presence of water molecules.

The IR spectra for picropharmacolite are shown in Figure 2, and the values of the frequencies are given in Table 2. The $\nu_3(T_2)$ stretching vibrations of the As–O bond produce a wide band, well resolved in three doublets: 800 cm^{-1}/815 cm^{-1}, 850 cm^{-1}/865 cm^{-1}, and 890 cm^{-1}/905 cm^{-1}. In the $\nu_1(A_1)$ region there is also an intensive doublet

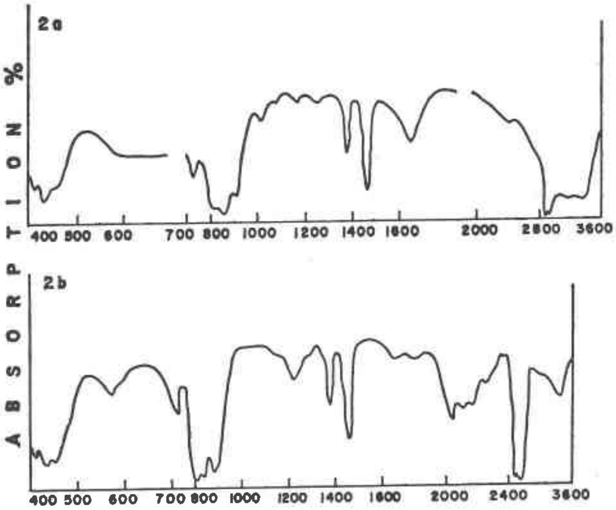

FIG. 2. IR spectra of picropharmacolite (a) picropharmacolite from Hovou-Aksi; (b) deuterated sample.

TABLE 2. Frequencies of Absorption Bands in the IR Spectra of Picropharmacolite and Tentative Explanation of the Absorption Bands

	As - O			As - O				Me - OH			H_2O	
	$\nu_1(A_1)$	$\nu_3(T_2)$	$\nu_4(T_2)$	A	B	C	D	δ	ν	γ	δ	ν
PICROPHAR-MACOLITE	710/725	810/815 850/865 890/905	425 438 465	2700-2800 (2050)	2350 (1740)	1600 (1160)	1290 (850)	1025 (740)	3490 (2500) 3600 (2600)	630 (430)	1660 (1220)	3350 (2360)

**Me = metal; numbers in parentheses represent frequencies of absorption bands of deuterated samples.*

710 cm^{-1}/725 cm^{-1}. The $\nu_4(T_2)$ region for the arsenate group shows a broad intense band well resolved into three components: 425 cm^{-1}, 438 cm^{-1}, and 465 cm^{-1}. The appearance of doublets in the $\nu_1(A_1)$ and $\nu_3(T_2)$ region is due to the presence of two types of site-symmetry for the $(AsO_4)^{3-}$ group. According to the correlation table of Mayantz (1960), the nature of the splitting of the $\nu_3(T_2)$ and $\nu_4(T_2)$ bands and the presence of the $\nu_1(A_1)$ band indicate that the symmetry of the arsenate ion is C_{2v} or lower. The presence of the $\nu_1(A_1)$ band is due to the presence of acid $(HAsO_4)^{2-}$ arsenate groups. The 630 cm^{-1}, 1025 cm^{-1}, 1290 cm^{-1}, 1600 cm^{-1}, 1660 cm^{-1}, 2350 cm^{-1}, 2700 cm^{-1}, 3350 cm^{-1}, 3490 cm^{-1} and 3600 cm^{-1} absorption bands are shifted or change their intensity after deuteration of the sample, so we relate these bands to the OH groups in the mineral.

The presence of four bands due to vibrations of As–OH groups in the IR-spectra of picropharmacolite at 1290 cm^{-1}, 1600 cm^{-1}, 2350 cm^{-1}, and 2700 cm^{-1} indicate that As–OH groups are present in the structure of the mineral. Similar bands have been reported by Blinc and Hadzi (1958, 1960) and by Hadzi (1965) for acid arsenates and phosphates (artificial compounds). The band in the region of the deformation vibrations of water molecules has an asymmetrical structure with two maxima: 1600 cm^{-1} and 1660 cm^{-1}. The 1660 cm^{-1} is probably due to vibrations of As–OH groups, and the 1660 cm^{-1} band is due to deformation vibrations of the water molecules. The 630 cm^{-1} $\nu_3(T_2)$ band is probably also related to a deformation of water molecules (translation vibration).

Considering the chemical composition of this mineral, the presence of $(HAsO_4)^{2-}$ groups must be accompanied by the presence of OH groups. The IR spectra show that, in fact, there is a band in the region of deformation vibrations of Me–OH groups (where Me = any metal) at 1025 cm^{-1} and also three intense bands: 3350 cm^{-1}, 3490 cm^{-1}, and 3600 cm^{-1} in the region of the stretching vibrations. These bands may be related to the stretching vibrations of hydroxyl groups in water molecules or to the vibrations of hydroxyls linked with metallic atoms.

The 1025 cm^{-1} band is due to deformation vibrations of the metal hydroxyl bond, but in picropharmacolite two different kinds of metallic atoms, Ca and Mg, occur. The vibrations of the Ca–OH bond are inactive in the IR spectra and are active only in the Raman spectra or at very low frequencies in the IR spectra. The 1025 cm^{-1} band consequently can only be due to the Mg–OH groups; this indicates that the hydroxyl is coordinated with Mg atoms.

Conclusions

Therefore, the IR spectra of picropharmacolite permit us to conclude that there are acid arsenate groups, OH^- groups, and water molecules in the structure of this mineral. The differential thermal analysis of picropharmacolite (Pierrot, 1964) is in agreement.

Considering the picropharmacolite formula to be $Ca(MgOH)(HOAsO_3)(AsO_4) \cdot 5H_2O$, then the data from DTA completely agree with the interpretation of the IR spectra. The DTA curve has two closely adjacent maxima at $t_{1,2} = 140°C$ which are probably due to two different types of water molecules linked by H-bonds of slightly different strength. The $t_3 = 330°C$ maximum is probably related to the loss of OH groups coordinated with Mg. The low intensity of this peak may indicate that there is only a small quantity of OH groups coordinated with Mg. The Mg–OH band in the IR spectra is also of low intensity so both methods completely agree on this point. The $t_4 = 650°C$ peak in the DTA curve indicates destruction of the crystalline structure, perhaps through loss of hydroxyl groups belonging to the $(HAsO_4)^{2-}$ anions. These OH groups are strongly bonded. The exothermic effect at $t_4 = 650°C$ and attendant destruction of the structure may be explained by the fact that the hydrogen atom of the hydroxyl group is very near the oxygen atom of the AsO–H group. The position and high intensity of the $\nu_1(A_1) = 710\ cm^{-1}/725\ cm^{-1}$ band of the AsO_4 tetrahedron is also a clear indication of the character of these hydroxyl groups.

DTA data indicate the presence of water molecules, hydroxyl groups coordinated with Mg atoms, and acid arsenate groups in the structure of picropharmacolite. Furthermore, from the frequencies of the OH stretching vibrations we may conclude that they form weak H-bonds, and this can explain the loose crystalline structure of picropharmacolite. The formula $Ca(MgOH)(HOAsO_3)(AsO_4)\cdot 5H_2O$ that we propose for picropharmacolite agrees with the chain-like character of the structure of this mineral.

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