

The structure of bayldonite: chemical analysis, differential thermal analysis, and IR spectroscopy

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Abstract

Chemical analysis, differential thermal analysis, and IR spectroscopy show that the structure of bayldonite lacks water molecules and contains OH groups coordinated with Cu atoms, as well as acid arsenate anions $(\text{HOAsO}_3)^{2-}$. The H bonds formed by the hydroxyls of the $(\text{HOAsO}_3)^{2-}$ groups are very short and strong, with the possible appearance of a tunnel effect for the hydrogen atom. The formula $\text{Cu}_3\text{PbO}(\text{HOAsO}_3)_2(\text{OH})_2$ is proposed.

Introduction

Bayldonite is a Pb–Cu arsenate whose structure has not been established. Most samples come from Tsumeb in SW Africa, where it is found in the oxidation zone of this deposit (Guillemin, 1956; Frondel and Ito, 1957). Bayldonite has also been found in France: Verriere, Ardillats, Rôhe, Rebasse, Ceilhes, Herault (Guillemin, 1956); England: uranium mine, Grampound Road, Cornwall (Guillemin, 1956); and the USSR, Dzeskazghan (Satpaeva, 1961). This mineral was described by Church (1856) from St. Day, Cornwall.

Guillemin (1956) compared the chemical analysis of synthetic and natural bayldonite, and gave a Cu:Pb relation of 3:1 as reported previously by Church (Table 1). However, the agreement between the proposed formula and the analysis is unsatisfactory, especially the excess of water molecules from the analysis. The optical properties of bayldonite (Larsen, 1921, p. 45) showed that this mineral has monoclinic symmetry. This was confirmed by Guillemin (1956), using X-ray methods on a sample from Cap Garonne. The parameters of the unit cell are: $a = 5.03 \pm 0.02$, $b = 5.97 \pm 0.05$, $c = 6.93 \pm 0.02 \text{ \AA}$, $\beta =$

$77^\circ \pm 1$; $a:b:c = 0.843:1:1.161$. The crystal was optically positive with large $2V$. The refractive indices were: $\gamma = 1.99 \pm 0.01$, $\beta = 1.98$, $\alpha = 1.94$ (Guillemin, 1956). The calculated value $(-)\ 2V = 52^\circ$ shows that at least the value of β must be wrong. The results of Larsen: $\gamma = 1.99$, $\beta = 1.97$, $\alpha = 1.95$ give $-2V = 89^\circ$, which could be a tolerable error.

Bayldonite can be synthesized at 180°C and a pH between 5 and 8. At this temperature and at a pH of 7, bayldonite is formed from schultenite (HPbAsO_4) in the presence of $\text{Cu}(\text{NO}_3)_2$, or from a solution of H_3AsO_4 , malachite, and cerussite. When the pH is lowered to 3–4, duftite $[\text{CuPb}(\text{AsO}_4)(\text{OH})]$ is formed (Guillemin, 1956).

Mineralogical studies

Bayldonite used in this study occurs in the oxidation zone of a metasomatic Pb–Zn deposit in Kayrakty in central Kazakhstan. It was found in the upper layers of barite lenses of considerable size embedded in sandstone. Bayldonite is formed by pseudomorphic substitution of cerussite, resulting in irregular accumulations in fine-grained malachite and azurite. Concentric accumulations of pure bayldonite reach a diameter of ~ 7 cm. Occasionally bayl-

donite is found on thick spherulite-like crusts formed in fractures in the barite. Concretions of bayldonite (up to 3 cm in diameter) in clay layers interbedded with sandstone were also observed. In these concretions concentric color patterns occur due to alteration in the compactness of the material. Bayldonite has a characteristic apple-green color with a yellowish hue. Dense aggregations have an intense oily luster and show conchoidal fracture. The less dense type is dull with an irregular fracture. The dense bayldonite often shows cavities with small crystals of anglesite and azurite. Both types of bayldonite usually intergrow with beudantite, $\text{PbFe}_3(\text{SO}_4)(\text{AsO}_4)(\text{OH})_6$. Microscopic examination of grain immersion mounts and thin sections of bayldonite shows a microspherulitic structure of bayldonite aggregates. The dense type is homogeneous and sometimes small inclusions of anglesite growing on spherulites of bayldonite may be observed, while the less dense is more heterogeneous.

Chemical analysis

The microchemical analyses were carried out in the Institute of Geology of Mineral Deposits, Mineralogy, Petrography, and Geochemistry of the Academy of Sciences of the USSR. Samples used for chemical analysis were apple-green and showed con-

choidal fractures. The separation of Pb and Cu was problematic due to the sensitivity to pH. The results of chemical analysis are given in Table 1.

IR spectroscopy

The IR spectra were recorded on a UR-20 Zeiss infrared spectrophotometer (DDR). The samples were prepared as emulsions in nujol on NaCl windows. Deuteration of the samples was carried out in an autoclave at pressure ~15 atm and at temperatures from 200° up to 500°C for a minimum of 48 hours. Two samples were used, one from Tsumeb and another from Kayrakty.

Differential thermal analysis

DTA was carried out in a Paulik Erdel JRED-58 DR analyzer. The samples weighed 0.4 g and the rate of heating was 5°C/min.

Results

The data of the chemical analysis reported in Table 1 were used to calculate two empirical formulas for bayldonite.

(1) Bayldonite from Kayrakty:



Table 1. Chemical analysis of bayldonite

Oxides	1	2	2	3	3	4	4
	Weight %	Weight	Relation of atomic Quantities	Weight %	Relation of atomic Quantities	Weight %	Relation of atomic Quantities
CuO	31.61	31.70	2.996	30.88	2.968	32.5	2.98
PbO	30.30	32.60	1.004	30.13	1.032	32.1	1.049
As ₂ O ₅	31.20	30.09	1.968	31.76	2.113	31.5	2
P ₂ O ₅	--	0.20	0.021	--	--	--	--
H ₃ O ⁺	4.89	4.20	3.504	4.58	3.887	3.7	3.00
SO ₃	--	1.00	--	--	--	--	--
CaO	--	--	--	--	--	--	--
Fe ₂ O ₃	--	--	--	2.65	--	--	--
	100.00	99.79		100.00		99.8	
Sp.gr.	--	5.24		5.35		5.42	

1.- $\text{Cu}_3\text{PbO}(\text{HAsO}_4)_2$ (Calculated)

2.- Kayrakty, Central Kazakhstan, USSR

3.- St. Day, Cornwall (Church, 1865) Cit, after Dana's System of Min., 7th ed.

4.- Synthetic Bayldonite (Guillemin, 1956).

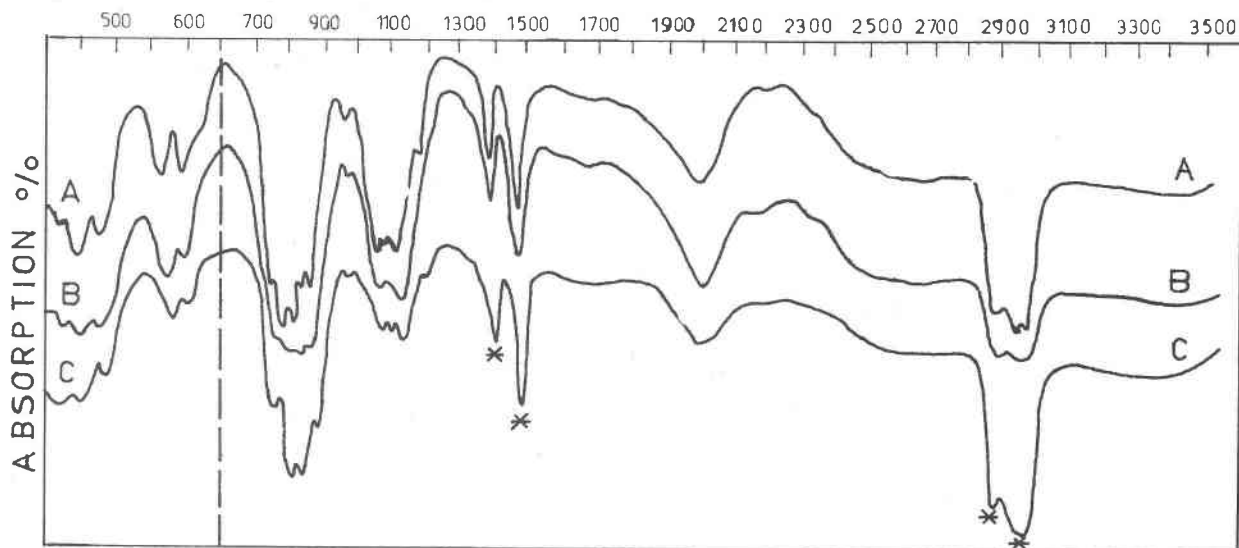
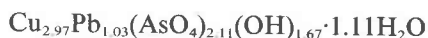
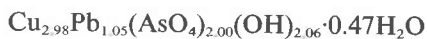


Fig. 1. IR spectra of bayldonite (in nujol): (a) Tsumeb; (b, c) Kayraky. * = bands of nujol.

(2) Bayldonite from Cornwall:



For the synthetic compound we obtained the formula:



From these results we conclude that the formula $\text{Cu}_3\text{Pb}(\text{AsO}_4)_2 \cdot (\text{OH})_2$ cannot be correct. The two empiric formulas suggest that bayldonite contains a water molecule: $\text{Cu}_3\text{Pb}(\text{AsO}_4)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$.

The IR spectra of the samples of bayldonite from Tsumeb and Kayraky both show an intense band

(Fig. 1, Table 2) in the $\nu_3(\text{T}_2)$ region of the arsenate anion. This band is split into four components: 780 cm^{-1} , 815 cm^{-1} , 840 cm^{-1} , and 870 cm^{-1} . In the deformation vibrations region $\nu_4(\text{T}_2)$, the same kind of splitting appears with three maxima: 400 cm^{-1} , 440 cm^{-1} , and 475 cm^{-1} . The $\nu_1(\text{A}_2)$ band is very sharp and intense. The 1060 cm^{-1} , 1090 cm^{-1} , and 1120 cm^{-1} do not shift after deuteration (Fig. 2) and are probably due to $\nu_3(\text{T}_2)$ vibration of the phosphate anion which is present in bayldonite. The $\nu_1(\text{A}_1)$ band of the phosphate anion also appears at 970 cm^{-1} as a weakly defined shoulder. In the Me-O (Me = metal) stretching vibration region only Cu-O vibrations are

Table 2. Frequencies of absorption bands in the IR spectra of bayldonite and tentative explanation of the absorption bands

	$[\text{AsO}_4]^{3-}$				$[\text{PO}_4]^{-3}$			Cu-OH	$\nu\text{OH} \dots \text{O}$	2ν	Other bands
	$\nu_1(\text{A}_1)$	$\nu_3(\text{T}_2)$	$\nu_4(\text{T}_2)$	$\nu_1(\text{A}_1)$	$\nu_3(\text{T}_2)$	$\nu_4(\text{T}_2)$	δOH				
Byaldonite from Tsumeb and Kayraky									A B C D		
	750	780	400	970	1060	562	700-	3200			615
		815	440		1090	185	800				1650
Frequencies, cm^{-1}		840	475		1120						1190
		870					(540)				2000
											1500

() Numbers in parentheses represent frequencies of absorption bands of deuterated samples.

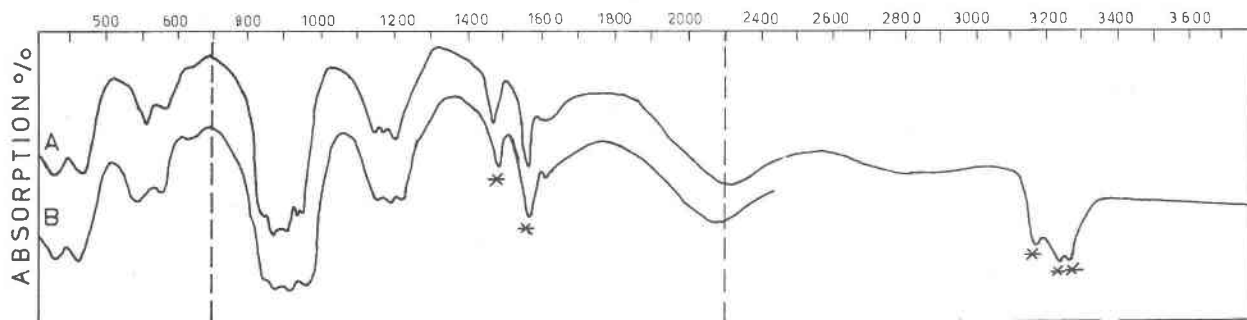


Fig. 2. IR spectra of deuterated sample of bayldonite from Kayraky (a, b different concentration of bayldonite in nujol). * = bands of nujol.

expected, due to the covalent nature of this bond. The vibrations of the Pb–O bond do not appear in the IR spectra because of its predominantly ionic character. Two sharp bands at 562 cm^{-1} and 585 cm^{-1} occur in the IR spectra of bayldonite. Analogous bands are present in the spectra of olivenite and conicalcite (Sumín de Portilla, 1974), and euchroite and lironite (Sumín de Portilla, unpublished results). These bands are related to vibrations of the Cu–O bonds. The $\nu_4(T_2)$ band for the phosphate anion does not appear in the spectrum. A band with very low intensity occurs at 1650 cm^{-1} in the deformation vibration region of water. However, this band does not shift after deuteration, which makes it highly improbable that this band should be associated with the presence of water molecules.

Several bands lie in the region of stretching vibrations of the hydroxyl groups: an intense band occurring as a shoulder at 1190 cm^{-1} , a sharp and intense band at 2000 cm^{-1} , and two wide and intense bands at 2600 cm^{-1} and 3200 cm^{-1} . Comparison of these bands with those for phosphates, arsenates, and silicates indicate that they are the A, B, C, and D bands of OH groups coordinated with the As atoms of the arsenate anion (Blinic and Hadzi, 1958; Hadzi, 1965; Ryskin *et al.*, 1960; Ryskin and Stavitskaya, 1960).

The DTA and DTG curves (Fig. 3) show a double endothermic effect at 525° and 599°C . The decomposition of the mineral begins at 470°C , as can be seen from the DTG curve. Guillemin (1956) states that this decomposition occurs between 450° and 510°C . The observed weight loss in the 470° to 620°C interval is 2.75%, a value slightly higher than that of a single water molecule in the empirical formula $3\text{CuO}\cdot\text{PbO}\cdot\text{As}_2\text{O}_5\cdot 2\text{H}_2\text{O}$. The endothermic effect at 780°C is due to the melting of bayldonite. The overall loss from 470° to 780°C is 4.12%, which is slightly less than the weight of water in the empirical formula.

Discussion

The structure of bayldonite is unknown. From the chemical analysis of bayldonite from Kayraky we conclude that the empirical formula $\text{Cu}_3\text{Pb}(\text{AsO}_4)_2(\text{OH})_2$ given by Guillemin (1956) lacks two hydrogen atoms and an oxygen atom. The search for a possible water molecule in the structure of bayldonite is important in order to establish the correct chemical formula. The IR data were mainly used to answer this question. The splitting of the $\nu_3(T_2)$ and $\nu_4(T_2)$ bands in three components and the appearance of a $\nu_1(A_1)$ band in the spectra of bayldonite clearly indicate that the arsenate anion tetrahedra are strongly deformed and show the presence of a low symmetry, C_{2v} , or lower (Mayantz, 1960). The same type of splitting is observed in the phosphate anion bands. The $\nu_1(A_1)$ band is probably related to the coordination of the arsenate anion with an atom of Cu or to the presence of an acid arsenate in the struc-

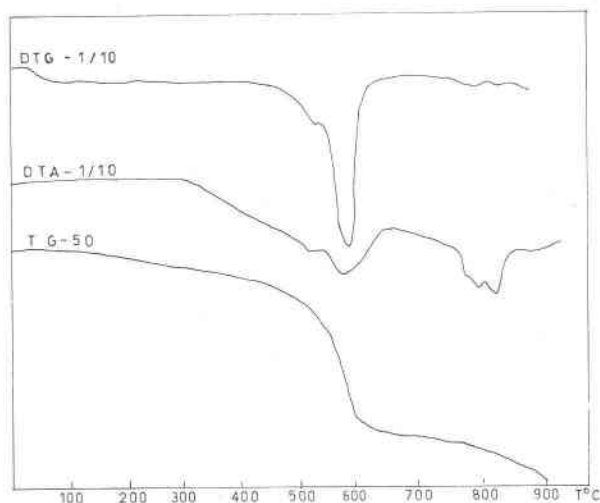


Fig. 3. Thermogravimetric (TG), differential thermal (DTA), and differential thermogravimetric (DTG) curves of bayldonite from Kayraky.

ture (or both). The 562 cm^{-1} and 585 cm^{-1} bands are due to stretching vibrations of the CuO bond. The same bands appear in the spectra of other arsenates which contain a Cu-O bond: olivenite (545 cm^{-1}), conichalcite (573 cm^{-1}) (Sumín de Portilla, 1974), euchroite (535 cm^{-1}), and lironite (520 cm^{-1}) (Sumín de Portilla, unpublished results). Note that in olivenite, euchroite, and lironite, where the vibration bands of Cu-O bonds occur between 520 cm^{-1} and 545 cm^{-1} , the Cu atom is in octahedral coordination whereas in conichalcite this band occurs at 575 cm^{-1} , with Cu in tetrahedral coordination (Qurashi and Barnes, 1963). We therefore conclude that Cu in bayldonite has a low symmetry coordination since the frequencies of these bands are very high, $565\text{--}595\text{ cm}^{-1}$. It could be a tetragonal bipyramid as in conichalcite.

The $\nu_4(\text{T}_2)$ band of the phosphate anion, which should lie in the same region as the Cu-O vibration bands and does not appear in the spectrum, has probably a very low intensity and could be hidden by the intense Cu-O vibration bands. The low intensity of the $\nu_3(\text{T}_2)$ band of the phosphate anion seems to support this hypothesis.

The δOH bands of Cu-OH probably overlap with the very intense $\nu_3(\text{T}_2)$ bands of the arsenate and phosphate anions. However, a 540 cm^{-1} band appears in the spectra of deuterated bayldonite, which shifts from the 700 cm^{-1} to the 800 cm^{-1} region (taking the coefficient of shift as 1.35). This band is probably due to δOH vibrations of Cu-OH.

Four wide intense absorption bands in the IR spectrum of bayldonite, *i.e.*, the 3200 cm^{-1} , 2600 cm^{-1} , 2000 cm^{-1} , and 1190 cm^{-1} bands, indicate the presence of acidic $(\text{HOAsO}_3)^{2-}$ groups in the crystal lattice. Analogous bands are characteristic in the spectra of $\text{O} = \text{XOH}$ groups ($\text{X} = \text{P}, \text{As}, \text{Se}$ or S). These bands occur in the $2800\text{--}2400\text{ cm}^{-1}$ (A), $2850\text{--}1900\text{ cm}^{-1}$ (B), $1720\text{--}1500\text{ cm}^{-1}$ (C), and $1300\text{--}1000\text{ cm}^{-1}$ (D) regions (Blinc and Hadzi, 1958; Hadzi, 1965). These bands could be due to the presence of OH groups, and they shift after deuteration (Blinc and Hadzi, 1958). The IR spectra of acid germanates, phosphates, silicates, and carbonates also show these four characteristic bands (Stavitskaya and Ryskin, 1961; Ryskin *et al.*, 1960; Ryskin and Stavitskaya, 1960). The available data seem to indicate that these four bands are characteristic of compounds that have OH groups bonded to electronegative atoms and linked by strong hydrogen bonds. If these bands are absent acidic anions such as $(\text{HOAsO}_3)^{2-}$, $(\text{HOPO}_3)^{2-}$, and $(\text{HOSO}_3)^{2-}$ occur in the crystal lat-

tice. The 1650 cm^{-1} band has a very low intensity and could be an overtone of the $\nu_3(\text{T}_2)$ band, *i.e.*, 2ν (AsO_4). The spectra of anhydrous arsenates, *i.e.*, olivenite, adamite, durangite, and mimetite show this low-intensity band (Sumín de Portilla, 1974), which confirms the absence of water molecules in the structure of bayldonite. The two stages in the weight loss seen in the DTA curves may be understood if there are two types of Cu groups, Cu-OH and HO-AsO₃, with different attachment energies. This agrees with the results obtained from IR spectra, which suggest the presence of both types of groups.

The 2000 cm^{-1} band is very intense and sharp in the IR spectra of bayldonite. Analogous bands have not been observed in the IR spectra of other natural arsenates. Blinc and Hadzi (1958) observed sharp, intense bands in the 2000 cm^{-1} region in the IR spectra of acidic phosphates and arsenates with very short H-bonds, and concluded that these bands are due to a tunnel effect of the hydrogen atom in hydrogen bonds when the length of the hydrogen bond is less than 2.4 \AA . We consider that the hydrogen bonds in bayldonite could be short enough to present this tunnel effect and that the 2000 cm^{-1} in the IR spectra could be due to this effect.

Conclusions

The IR and DTA data indicate that the structure of bayldonite lacks water molecules, and that there are OH groups attached to Cu as well as As atoms. The crystal lattice has acidic arsenate groups that form very strong H-bonds, which could be accompanied by a tunnel effect of hydrogen atoms in these bonds. Based on the chemical analyses and the IR and DTA data, we propose the formula $\text{Cu}_3\text{PbO}(\text{HOAsO}_3)_2(\text{OH})_2$ for bayldonite.

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