

# INFRARED SPECTRA OF RUTHERFORDINE AND SHARPITE\*

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Infrared spectra ( $4000-400\text{ cm}^{-1}$ ) of solid samples in KBr microdisks were measured and interpreted for uranyl carbonate minerals, *viz.* rutherfordine and sharpite, and synthetic phases in the system  $\text{UO}_3\text{-CO}_2\text{-H}_2\text{O}$ ; the mineral schoepite was studied for a comparison as well. The  $\nu_3$  fundamental belonging to the  $\text{UO}_2^{2+}$  antisymmetric stretching vibrations in rutherfordine,  $\text{UO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$  ( $0.2 > x \geq 0$ ), lies in the same range as for the hydrothermal phases ( $985$  to  $978\text{ cm}^{-1}$ ), whereas in the case of sharpite,  $\text{UO}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  or  $(\text{UO}_2)_6(\text{CO}_3)_5(\text{OH})_{2.7}\text{H}_2\text{O}$  or  $\text{M}_{1-x}^{2+} \cdot (\text{H}_3\text{O})_{2x}(\text{UO}_2)_6(\text{CO}_3)_5(\text{OH})_{4 \cdot (6-2x)}\text{H}_2\text{O}$ , this vibration appears in the range where it is displayed by phases formed at normal temperature and pressure ( $954-953$  and  $914-913\text{ cm}^{-1}$ ). The IR spectrum of schoepite,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , is published for the first time.

IR spectra of uranium minerals are attracting particular attention. Apart from the more complex works<sup>1,2</sup>, only individual minerals or their groups have been treated, and IR spectroscopy was usually employed in combination with other methods, particularly for the identification and study of properties of new minerals or of known minerals found in new localities. Such works, however, lack usually a more detailed interpretation of the IR spectra obtained. In the present work, done as a part of systematic revision of secondary uranium minerals deposited in the mineralogical collection of the National Museum in Prague, we are dealing with the IR spectra of rutherfordine,  $\text{UO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$  ( $0.2 > x \geq 0$ ), sharpite  $(\text{UO}_2)_6(\text{CO}_3)_5(\text{OH})_{2.7}\text{H}_2\text{O}$  or  $\text{UO}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  or  $\text{M}_{1-x}^{2+}(\text{H}_3\text{O})_{2x}(\text{UO}_2)_6(\text{CO}_3)_5(\text{OH})_{4 \cdot (6-2x)}\text{H}_2\text{O}$  ( $\text{M} = \text{Ca}$  and probably also  $\text{Ba}$ , always in a separate phase), and for a comparison also of schoepite,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ . We include sharpite despite the fact that — as we suggested previously<sup>3</sup> — it is feasible that the cations may be present in the interlayer space in addition to molecular water; to this conclusion, we have come on confronting the data by Mélon<sup>4</sup> with the data of other workers which were determined on further mineral specimens from different localities, and with the results of interpretation of the sharpite's X-ray<sup>5,6</sup>, IR spectral data, and with the information available on its behaviour. A complete chemical analysis could not be so far performed because of the shortage of authentic material, and attempts at synthesis of sharpite failed. The results obtained

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were correlated with the data on the synthetic phases in the system  $\text{UO}_3\text{-CO}_2\text{-H}_2\text{O}$  as described previously<sup>7,8</sup>.

IR spectrum of rutherfordine has been reproduced in the paper<sup>1</sup> without any interpretation; it has been also mentioned along with that of sharpite in the paper<sup>8</sup>. A detailed analysis of these IR spectra is published in the present work for the first time. The IR spectrum of schoepite is here published for the first time too. Synthetic phases in the system  $\text{UO}_3\text{-CO}_2\text{-H}_2\text{O}$  have received more attention<sup>7-11</sup>. Interpretation of the IR spectra of the mentioned minerals exhibiting layer structure, in conjunction with the results of X-ray structure analysis and for the synthetic phases also of thermal analysis<sup>12-17</sup>, adds to a further improvement of our concepts concerning the origin of these minerals in the nature, their mutual relations, their structures and properties. It also contributes to the spectroscopy of the uranyl ion.

## EXPERIMENTAL

The minerals studied are given in Table I. The preparations, X-ray patterns, and in some instances also thermal analysis curves (DTA or simultaneous DTA, TG, DTG curves) of the synthetic phases studied have been described in detail previously<sup>7,8,12-17</sup>. The IR spectra of the powdered minerals in KBr microdisks were measured on a grating spectrophotometer Perkin-Elmer 225 equipped with a beam condenser. The spectra of the synthetic phases were measured in addition on a prism instrument UR 10 (Zeiss, Jena) in nujol and fluorolube mulls. The minerals were identified by X-ray diffraction analysis (the Debye-Scherrer powder method, instrument Mikrometa, Chirana,  $\text{CuK}_\alpha$  radiation, Ni filter, chamber 114.6 mm diam., exposition 6 h, 20 mA, 40 kV), in some instances also optically, and the synthetic phases by chemical analysis as well. The thermal analysis was performed on a MOM Derivatograph, DTA apparatus Netzsch, micro-DTA apparatus according to Rosický<sup>18</sup>, or on a Microanalyzer 1 Mettler. The choice of the apparatus was determined by the quantity of the sample available.

## RESULTS AND DISCUSSION

Natural as well as synthetic phases in the system  $\text{UO}_3\text{-CO}_2\text{-H}_2\text{O}$  feature typical layer structures. We considered in this group in addition to rutherfordine,  $\text{UO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ , and schoepite,  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , also sharpite, so far taken for hydrated uranyl hydroxocarbonate<sup>3,4</sup>.

The linear uranyl ion exhibits three fundamentals in the IR spectrum<sup>19</sup>, in the regions  $900\text{--}700\text{ cm}^{-1}$  ( $\nu_1$ ),  $260\text{--}180\text{ cm}^{-1}$  ( $\nu_2$ ), and  $1000\text{--}850\text{ cm}^{-1}$  ( $\nu_3$ ). In the phases discussed, the uranyl ions form with the carbonate ions polyhedra in the uranyl carbonate layers — most probably hexagonal bipyramids, with oxygen atoms of the uranyl ion at the apexes and oxygen atoms of carbonate ions in the equatorial plane of the bipyramid. In the interlayer space, cations and/or water molecules may occur. The carbonate oxygen atoms in the equatorial plane can be replaced by the hydroxyl oxygen atoms during the alteration (hydrolysis) on the action of water. Penetration of cations or water into the interlayer space or of water and hydroxy

ions into the layers is in the nature very likely where the layers are not held by strong bonds; in rutherfordine, however, as follows from a comparison of the stability of the hydrothermal phases with phases prepared at normal temperature in system  $\text{UO}_3\text{-CO}_2\text{-H}_2\text{O}$  during hydrolysis in aqueous medium<sup>20</sup>, penetration of water into the interlayer space is very low.

The  $\nu_3(\text{UO}_2^{2+})$  antisymmetric stretching vibration of rutherfordine lies near  $980\text{ cm}^{-1}$  ( $985\text{--}978\text{ cm}^{-1}$ , Table II and Fig. 1) which corresponds to the experimentally found<sup>7,8</sup> values for synthetic hydrothermal phases possessing the rutherfordine structure ( $971\text{--}979\text{--}985\text{ cm}^{-1}$ ). On the other hand, for all the studied phases of the rutherfordine structure (as indicated by X-ray diffraction analysis) prepared at normal temperature and pressure<sup>7,8</sup>, this vibration is found in the range  $960$  to  $954\text{ cm}^{-1}$ , synthetic<sup>21</sup>  $\text{UO}_3\cdot 2\text{H}_2\text{O}$  displays it at  $960\text{ cm}^{-1}$ , natural schoepite at  $936\text{--}930\text{ cm}^{-1}$ , the phase  $\text{UO}_2\text{CO}_3\cdot 2\text{H}_2\text{O}$  (formed on a long-duration reaction<sup>7</sup> of atmospheric  $\text{CO}_2$  and  $\text{O}_2$  with an aqueous suspension of  $\text{U}_3\text{O}_8$ ) at  $930\text{ cm}^{-1}$ , and the sharpite examined at  $954\text{--}953\text{ cm}^{-1}$  with a very weak band or shoulder at

TABLE I  
The Minerals Studied

Mineral	Deposit	Designation (inv. No)	Collection <sup>a</sup>
Rutherfordine $\text{UO}_2\text{CO}_3\cdot x\text{H}_2\text{O}$ ( $0.2 > x \geq 0$ )	Shinkolobwe, Zaire	M1, M2	A
Sharpite $(\text{UO}_2)_6(\text{CO}_3)_5(\text{OH})_2\cdot 7\text{H}_2\text{O}$	Shinkolobwe, Zaire	M22, (US NM 115 318 = = RGM 2767)	B
$\text{UO}_2\text{CO}_3\cdot \text{H}_2\text{O}$ or	Shinkolobwe, Zaire	M23, (NM 45 146)	C
$\text{M}_1^2 \pm_x(\text{H}_3\text{O})_{2x}(\text{UO}_2)_6(\text{CO}_3)_5(\text{OH})_4\cdot$ $(6 - 2x)\text{H}_2\text{O}$ (M = Ca, Ba)	Shinkolobwe, Zaire	M24, (RGM 2768)	D
Schoepite $\text{UO}_3\cdot 2\text{H}_2\text{O}$	Shinkolobwe, Zaire	M6, M7	A
	Delta, Mine, Utah, USA	M8	A

<sup>a</sup> A Pinch Mineralogical Museum, Rochester, New York, USA, BUS National Museum, Smithsonian Institution, Washington, D. C., USA, C National Museum, Prague (from the collection of R. Nováček), D Musée royal de l'Afrique Centrale, Tervuren, Belgium.

982  $\text{cm}^{-1}$ . The high wavenumber of the  $\nu_3$  vibration of rutherfordine and of hydrothermal phases indicates a stronger uranium–oxygen bond in the uranyl ion which is due to the weaker (disturbing) ligand field<sup>22</sup>.

In sharpite, two types of uranium coordination obviously occur; one of them maintains the uranyl nature, similar as in  $\text{UO}_3 \cdot 2 \text{H}_2\text{O}$ , whereas in the other the inter-layer oxygen atoms are strongly affected either by the hydrogen bond with molecular water or oxonium, or by the presence of other cations (Table II, Fig. 2). Wilkins<sup>2</sup> has identified the  $\nu_3(\text{UO}_2^{2+})$  vibration at 985  $\text{cm}^{-1}$  for rutherfordine. The differences in the positions of this vibration for the various phases are essential and can serve for a consideration of the conditions of formation. Rutherfordine and the hydrothermal carbonate phases are virtually identical from the IR spectroscopic point of view — they are formed at elevated temperatures and partial pressures of carbon dioxide. On the other hand, the  $\nu_3(\text{UO}_2^{2+})$  values for sharpite, synthetic and natural schoepite, and the phase  $\text{UO}_2\text{CO}_3 \cdot 2 \cdot 2 \text{H}_2\text{O}$  prepared by us show that these minerals form under conditions of nearly normal temperature and atmospheric partial pressure of  $\text{CO}_2$ . We suppose that under similar conditions the Walenta's<sup>23</sup> joliotite,  $\text{UO}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$ , is formed, too. It is of interest that the X-ray patterns of hydrothermal phases and phases prepared by saturating aqueous suspensions of  $\text{UO}_3 \cdot x \text{H}_2\text{O}$  with carbon dioxide at normal temperature are virtually identical (the same sublattice of the uranium atoms in layers), which can mislead to the idea of completely identical structure. Differences follow just from the infrared spectra, for example.

The absorption bands of the  $\text{CO}_3^{2-}$  groups were compared for the hydrothermal phases and phases prepared in normal conditions in the system  $\text{UO}_3\text{--CO}_2\text{--H}_2\text{O}$  of rutherfordine and sharpite and were found to be identical in the case of the  $\nu_1$ ,  $\nu_2$ , and  $\nu_4$  vibrations — approximately 1115 ( $\nu_1$ ), 806 ( $\nu_2$ ), 783 ( $\nu_{4a}$ ), and 704  $\text{cm}^{-1}$  ( $\nu_{4b}$ ) (the exceedingly high splitting of the  $\nu_4(\text{CO}_3^{2-})$  bending vibration is remarkable). Differences were found only in the positions of the components of the split degenerate  $\nu_3$  vibration: in the spectrum of the low-temperature products the wavenumbers

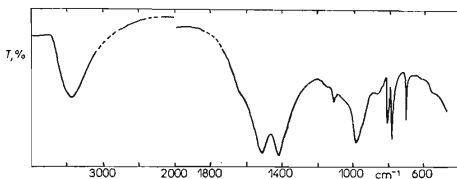


FIG. 1

Infrared Absorption Spectrum of Rutherfordine (sample M2) in Potassium Bromide Microdisk

(1432 and 1555  $\text{cm}^{-1}$ ) are higher and the splitting (123  $\text{cm}^{-1}$ ) greater than in the case of the hydrothermal products, where the positions are variable — 1432 to 1420  $\text{cm}^{-1}$  and 1529 to 1509  $\text{cm}^{-1}$  — and the magnitude of splitting varies from 82 to 100  $\text{cm}^{-1}$ . A greater deformation of the carbonate group can be inferred for the low-temperature products. For rutherfordine, the wavenumbers of the  $\nu_3(\text{CO}_3^{2-})$  vibrations found are 1418–1415 and 1510–1503  $\text{cm}^{-1}$ , splitting  $\sim 90 \text{ cm}^{-1}$ , which is in a good relation with the hydrothermal phases. The lower splitting reflects a smaller influence of the surrounding crystal field. The symmetry of the carbonate groups obviously reduces from  $D_{3h}$  to  $C_{2v}$ , the problematic criterion of the splitting value cannot be, however, employed successfully for a decision if the carbonate groups are monodentate or bidentate; this question remains open. In addition to the original assumption that in the bipyramid equatorial plane of rutherfordine, two bidentate and two monodentate bonded carbonate groups occur<sup>24–27</sup>, it has been also suggested<sup>28,29</sup> that only three bidentate carbonate groups are present, which agrees well<sup>30,31</sup> with the layer structures of the compounds of the type  $\text{MXO}_2\text{CO}_3$  with  $\text{M} = \text{K}, \text{Rb}, \text{Cs}, \text{and } \text{NH}_4$ , and  $\text{X} = \text{Np}^{5+}, \text{Pu}^{5+}, \text{and } \text{Am}^{5+}$ .

Sharpite contains carbonate groups of two types (Table I, Fig. 2). If a point symmetry lower than  $D_{3h}$  is assumed for the  $\text{CO}_3^{2-}$  group, then the originally doubly degenerate modes (the in-plane bending  $\nu_4(\text{CO}_3^{2-})$  mode and the  $\nu_3(\text{CO}_3^{2-})$  stretching mode) are split. From the occurrence of a pair of doublets in the  $\nu_4(\text{CO}_3^{2-})$  range (691 and 705  $\text{cm}^{-1}$  and 761 and 776  $\text{cm}^{-1}$ ) and of at least four bands in the  $\nu_3(\text{CO}_3^{2-})$  range (1381, 1418, 1445, (1456), and 1540  $\text{cm}^{-1}$ ) in the infrared spectrum of sharpite, it can be inferred that this substance involves two nonequivalent carbonate groups of symmetry lower than  $D_{3h}$ .

Molecular water is present only in the low-temperature phases in the systems  $\text{UO}_3\text{-CO}_2\text{-H}_2\text{O}$  ( $\nu_2(\text{H}_2\text{O}) \sim 1666 \text{ cm}^{-1}$ ),  $\text{UO}_3\cdot 2\text{H}_2\text{O}$  ( $\nu_2(\text{H}_2\text{O}) \sim 1625 \text{ cm}^{-1}$ ),

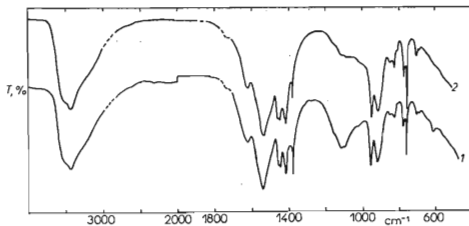


FIG. 2

Infrared Absorption Spectra of Sharpite in Potassium Bromide Microdisks

1 Sample M22, 2 sample M24.

TABLE II

Interpretation of the Infrared Spectra of Rutherfordine, Sharpite, and Schoepite

Band positions in  $\text{cm}^{-1}$ . Intensity: VS very strong, S strong, M medium, W weak, VW very weak; peak character: s sharp, b broad, sh shoulder. Values in parentheses were read with a precision poorer than 0.5%, bands given in square brackets are uncertain. Assignment:  $\nu$  stretching vibration,  $\delta$  in-plane bending vibration. Numbering of the vibrational modes of the  $\text{UO}_2^{2+}$ ,  $\text{CO}_3^{2-}$ , and  $\text{SO}_4^{2-}$  ions as for non-interacting species.

Rutherfordine			Sharpite			Schoepite	
M1	M2	assignment	M22	M24	assignment	M7	assignment
	554 W	impurity <sup>a</sup>				$\begin{pmatrix} 520 \\ 545 \end{pmatrix}$ Wb	$\nu(\text{U}-\text{O}_{II})$
607 VW	615 VW	$\nu_2(\text{SO}_4)$	612 W				
638 VW		$\nu_2(\text{SO}_4)$	688 VW	691 VW			
(691) sh	(695) sh	7 $\text{CO}_3^b$	703 W	705 W		(720) VW	
702 Ws	703 Ms	$\nu_4(\text{CO}_3)$	759 Ms	761 Ms	$\nu_4(\text{CO}_3)$		
(770) sh <sup>b</sup>		$\nu_4(\text{CO}_3)$	773 Ws	776 Ws	$\nu_4(\text{CO}_3)$		
781 Ms	782 Ss	$\nu_4(\text{CO}_3)$					
804 Ws	806 Ms	$\nu_2(\text{CO}_3)$	811 VWs	813 VWs	$\nu_2(\text{CO}_3)$	841 M	$\nu_1(\text{UO}_2^{2+})$ $\nu(-\text{O}-\text{U}-\text{O}-)$
	(865) Wb	impurity <sup>a</sup>	825 Ws	824 Ws			
			845 VWb	845 VWb			
	(945) sh	impurity	913 S	914 S	$\nu_3(\text{UO}_2^{2+})?$		
(940) sh			954 Ss	953 Ss	$\nu_3(\text{UO}_2^{2+})$	930 S	$\nu_3(\text{UO}_2^{2+})$
985 M	981 S	$\nu_{as}(\text{UO}_2^{2+})$	982 VW	(982) sh			
			(1 017) VWb	1 010 W		1 018 M	$\delta(\text{OH})$

(1 070) sh Wb			(1 090) VWsh	(1 090) VW		1 072 Ms	$\delta(\text{OH})$
(1 100) Mb		$\left(\begin{matrix} \nu_1 \\ \nu_3 \end{matrix}\right) ? (\text{SO}_4)$ $\nu_3(\text{SO}_4)$					
1 112 VWs	1 104 VWsh <sup>b</sup> 1 112 Wsh	$\nu_1(\text{CO}_3)$	1 118 M (1 158) sh (1 195) sh 1 381 Ss	(1 112) Wb	$\nu_1(\text{CO}_3)$	(1 115) sh	
1 415 Ss	1 415 VS	$\nu_3(\text{CO}_3)$	1 418 S 1 445 s } M 1 456 }	1 381 Ms 1 418 S 1 445 s } M 1 456 }	$\nu_3(\text{CO}_3)$ $\nu_3(\text{CO}_3)$ $\nu_3(\text{CO}_3)$	[1 400] M	
1 503 S	1 510 VS	$\nu_3(\text{CO}_3)$	1 540 VS	1 540 VS	$\nu_3(\text{CO}_3)$		
[1 740] Wb	1 640 shb [1 740]	$\nu_2(\text{H}_2\text{O})$ impurity?	1 622 M [1 740]	1 622 M [1 740]	$\nu_2(\text{H}_2\text{O})$ impurity?	1 624 S [1 742]	$\nu_2(\text{H}_2\text{O})$ impurity?
1 900 VWs		impurity?		1 863 VW			
3 430 M	3 435 S	$\nu(\text{OH})$	2 635 VW (3 150) shb (3 250)	2 635 VW (3 200) shb		(3 160) Wb	
			3 425 S 3 500 sh 3 540 shW	3 435 S 3 500 sh 3 540 shW	$\nu(\text{OH})$	3 440 VS	$\nu(\text{OH})$

<sup>a</sup> Sklodovskite? <sup>b</sup> isotopomer  $^{13}\text{C}$  (1-1% in natural material).

schoepite ( $\nu_2(\text{H}_2\text{O}) \sim 1615-1624 \text{ cm}^{-1}$ ), and sharpite ( $\nu_2(\text{H}_2\text{O}) \sim 1622 \text{ cm}^{-1}$ ). In rutherfordine, a smaller amount of water (up to  $\sim 1\%$ ) can be present according to analyses<sup>32</sup>. The intensity of the  $\nu(\text{OH})$  bands in the infrared spectra measured by us indicates, however, that in the samples M1 and M2 the water content is considerably higher (a part of it can be associated with the presence of sulfate or silicate impurities in the mineral samples). It is not clear, however, whether this is molecular water or  $\text{OH}^-$  ions, which can be in relation to surface hydrolysis and a partial replacement of the carbonate groups in the layers; at any rate, however, this phenomenon is associated with a distortion of the ideal compact structure of  $\text{UO}_2\text{CO}_3$ . Frondel<sup>32</sup> regards the presence of this "water" as significant in the structure of rutherfordine. The wavenumbers of the stretching modes of molecular water indicate rather strong hydrogen bonds. It is also conceivable that sharpite involves in its structure also hydroxyl ions, giving rise to the bending mode band at  $1010 \text{ cm}^{-1}$ , or also  $\text{H}_3\text{O}^+$  ions, as can be inferred from the weak absorption at  $1150$  and  $1740 \text{ cm}^{-1}$  (the origin of the latter is, however, not clear).

The character of the IR spectrum of schoepite (Table II, Fig. 3) is analogous to that of synthetic  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ , except for the antisymmetric stretching  $\nu_3(\text{UO}_2^{2+})$  vibration whose lower wavenumber value can result from the effect of the conditions of formation of the phases and possibly also from the experimental conditions of the sample preparation for the IR spectral measurements<sup>33</sup>. This problem lies beyond the scope of this treatment. The complexity of the  $\text{UO}_3\text{-H}_2\text{O}$  system has been recently pointed out by Hoekstra and coworkers<sup>34</sup>.

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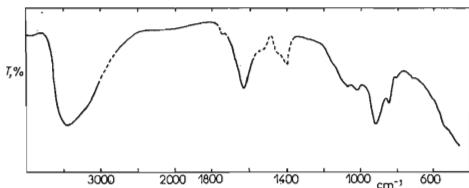


FIG. 3

Infrared Absorption Spectrum of Schoepite (sample M7) in Potassium Bromide Microdisk



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