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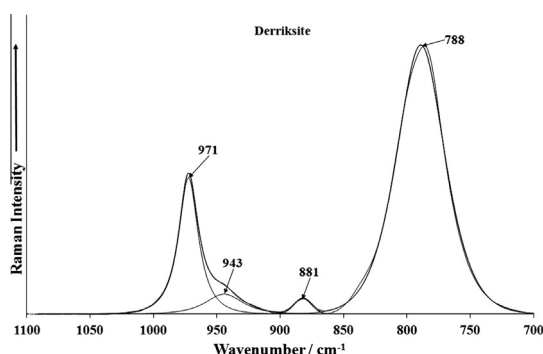
## Vibrational spectroscopic study of the uranyl selenite mineral derriksite $\text{Cu}_4\text{UO}_2(\text{SeO}_3)_2(\text{OH})_6\cdot\text{H}_2\text{O}$

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### HIGHLIGHTS

- We have studied the mineral derriksite  $\text{Cu}_4\text{UO}_2(\text{SeO}_3)_2(\text{OH})_6\cdot\text{H}_2\text{O}$ .
- A comparison was made with the other uranyl selenites.
- Namely demesmaekerite, marthozite, larisaita, haynesite and piritite.
- Approximate U–O bond lengths in uranyl and O–H···O hydrogen bond lengths were calculated.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Raman spectrum of the mineral derriksite  $\text{Cu}_4\text{UO}_2(\text{SeO}_3)_2(\text{OH})_6\cdot\text{H}_2\text{O}$  was studied and complemented by the infrared spectrum of this mineral. Both spectra were interpreted and partly compared with the spectra of demesmaekerite, marthozite, larisaita, haynesite and piritite. Observed Raman and infrared bands were attributed to the  $(\text{UO}_2)^{2+}$ ,  $(\text{SeO}_3)^{2-}$ ,  $(\text{OH})^-$  and  $\text{H}_2\text{O}$  vibrations. The presence of symmetrically distinct hydrogen bonded molecule of water of crystallization and hydrogen bonded symmetrically distinct hydroxyl ions was inferred from the spectra in the derriksite unit cell. Approximate U–O bond lengths in uranyl and O–H···O hydrogen bond lengths were calculated from the Raman and infrared spectra of derriksite.

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### Introduction

The crystal chemistry of selenium(IV) oxo-compounds shows great structural versatility expressed by the great number of different compounds [1]. Crystallochemical systematics of selenites was presented by Serezhkina et al. [2].

Uranyl anion topology of uranyl natural and synthetic compounds inclusive of uranyl selenites has been elaborated by Burns [3–6]. According to Finch and Murakami [7], uranyl selenites occur where Se-bearing sulfide minerals are undergoing oxidation and dissolution. Derriksite, demesmaekerite, guilleminite and marthozite are from the Musonoi Cu–Co mine, near Kalwezi, Katanga Province, Democratic Republic of Congo, piritite and also guilleminite from Shinkolobwe, Katanga Province, Democratic Republic of Congo, haynesite and larisaita from the Repete mine, San Juan Co., Utah, U.S.A [8,9].

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Structures of derriksite,  $\text{Cu}_4\text{UO}_2(\text{SeO}_3)_2(\text{OH})_6 \cdot \text{H}_2\text{O}$  [10,11], and demesmaekerite,  $\text{Pb}_2\text{Cu}_5[(\text{UO}_2)(\text{SeO}_3)_3]_2(\text{OH})_6 \cdot (\text{H}_2\text{O})_2$ , are characterized by infinite chains formed from uranyl and selenite ions [6,12], while those of the remaining uranyl selenite minerals, guilleminite,  $\text{Ba}[(\text{UO}_2)_3\text{O}_2(\text{SeO}_3)_2] \cdot (\text{H}_2\text{O})_3$  [13], marthozite,  $\text{Cu}[(\text{UO}_2)_3\text{O}_2(\text{SeO}_3)_2] \cdot (\text{H}_2\text{O})_8$  [14], larisaite,  $\text{Na}(\text{H}_3\text{O})[(\text{UO}_2)_3(\text{SeO}_3)_2\text{O}_2] \cdot (\text{H}_2\text{O})_4$  [9] and probably also haynesite,  $[(\text{UO}_2)_3(\text{SeO}_3)_2(\text{OH})_2] \cdot (\text{H}_2\text{O})_5$  [15,16] and piritite,  $\text{Ca}[(\text{UO}_2)_3(\text{SeO}_3)_2(\text{OH})_4] \cdot (\text{H}_2\text{O})_4$  [16] by uranyl oxo-hydroxo selenite sheets and phosphuranylite anion sheet topology. According to Chukanov et al. [9], the general formula of the minerals guilleminite, marthozite, haynesite, piritite and larisaite is  $\text{M}_{0-1}[(\text{UO}_2)_3(\text{SeO}_3)_2(\text{O},\text{OH})_{2-4}] \cdot n\text{H}_2\text{O}$ , where  $a = 3-8$ ,  $\text{M} = \text{M}^{2+}$ ,  $2\text{M}^+$ . In derriksite, the uranyl coordination polyhedra are formed from tetragonal (square) dipyramids  $\text{UO}_2\text{O}_4$ , in demesmaekerite pentagonal dipyramids  $\text{UO}_2\text{O}_5$ , and probably in all remaining natural uranyl selenites from pentagonal and hexagonal dipyramids  $\text{UO}_2\text{O}_5$  and  $\text{UO}_2\text{O}_6$ , respectively similarly as in phosphuranylite. According to Ginderow and Cesbron [11], derriksite contains the brucite-type layers of  $\text{CuO}_6$ . Derriksite is structurally related to deloryite,  $\text{Cu}_4(\text{UO}_2)(\text{MoO}_4)_2(\text{OH})_6$  and the difference in space group between the two minerals is the direct consequence of the replacement of the  $\text{SeO}_3$  trigonal pyramids in derriksite by the  $\text{MoO}_4$  tetrahedra in deloryite. Deloryite does not contain any molecular water. This differs from derriksite containing one water molecule. Ginderow and Cesbron [11] inferred from thermogravimetric curve (TGA) presented by Cesbron et al. [10], that the first dehydration step (up to approximately 300 °C) may be connected with adsorbed water. However, the original Cesbron's interpretation that this first TGA step corresponds with one molecule of water of crystallization [10] seems to be more correct.

Raman spectroscopy was proven most useful for the characterization of secondary uranyl containing minerals [17–23]. The aim of this research is the study of Raman spectra of the natural uranyl selenite derriksite, complemented by its infrared spectra. The paper is a part of systematic vibrational spectroscopic research of secondary minerals formed in the oxidation zone, inclusive uranyl minerals originating during hydration–oxidation weathering of primary uranium minerals, such as uraninite. Raman spectroscopy was proven most useful for the characterization of secondary uranyl containing minerals. In order to identify and characterize the Raman and infrared spectra of derriksite, this research reports the Raman and infrared spectrum of derriksite and relates the spectra of derriksite to the structure of the mineral.

## Experimental

### Mineral

For the development of this work, one single crystal of derriksite was chosen for our investigation. Sample was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais with sample code SAB-098. The crystal is deep green and transparent, with up to 2.0 mm in length and occurs in association with malachite. The studied sample is from Musonoi Mine, Katanga, Democratic Republic of Congo and can be considered a type material.

The chemical analyses of the mineral have been made. These are included in [Supplementary information](#).

### Raman microprobe spectroscopy

Crystals of derriksite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10 $\times$ , 20 $\times$ , and 50 $\times$  objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a

monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He–Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2  $\text{cm}^{-1}$  and a precision of  $\pm 1 \text{ cm}^{-1}$  in the range between 200 and 4000  $\text{cm}^{-1}$ . Repeated acquisitions on the crystals using the highest magnification (50 $\times$ ) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the 520.5  $\text{cm}^{-1}$  line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

### Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525  $\text{cm}^{-1}$  range were obtained by the co-addition of 128 scans with a resolution of 4  $\text{cm}^{-1}$  and a mirror velocity of 0.6329  $\text{cm/s}$ . Spectra were co-added to improve the signal to noise ratio. The infrared spectra are given in the supplementary information.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectralcalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of  $r^2$  greater than 0.995.

## Results and discussion

The Raman spectrum of derriksite over the full wavenumber range is illustrated in [Fig. 1a](#). This figure displays the position and relative intensities of the Raman bands of derriksite. It may be observed that there are large parts of the spectrum where no intensity is found; therefore the spectrum is subdivided into sections based upon the type of vibration being studied. The infrared spectrum of derriksite over the full wavenumber range is illustrated in [Fig. 1b](#). This spectrum shows the position and relative intensities of the infrared bands of derriksite. The Raman spectrum of derriksite over the 700 to 1400  $\text{cm}^{-1}$  spectral range is reported in [Fig. 2a](#). The infrared spectrum of derriksite over the 600 to 1400  $\text{cm}^{-1}$  spectral range is reported in [Fig. 2b](#). The Raman spectra of derriksite over the 300 to 700  $\text{cm}^{-1}$  and 100 to 300  $\text{cm}^{-1}$  spectral ranges are reported in [Fig. 3](#). The Raman and infrared spectra of the OH stretching region (2600–4000  $\text{cm}^{-1}$ ) are shown in [Fig. 4](#). The Raman and infrared spectra in the water bending region (1300–1800  $\text{cm}^{-1}$ ) are given in [Fig. 5](#).

The free linear uranyl group  $(\text{UO}_2)^{2+}$ , symmetry  $D_{\infty h}$ , has four normal vibrations, but only three fundamentals: the  $\nu_1$  symmetric stretching vibration, Raman active (approximately 900–700  $\text{cm}^{-1}$ ), the  $\nu_2$  ( $\delta$ ) doubly degenerate bending vibration, infrared active (approximately 300–200  $\text{cm}^{-1}$ ), and the  $\nu_3$  antisymmetric stretching vibration, infrared active (approximately 1000–850  $\text{cm}^{-1}$ ). Distortion of the uranyl group or change in the local symmetry can result in the removal of the degeneracy and therefore Raman activation of the  $\nu_2$  mode and infrared activation of the  $\nu_1$  mode [24].

The chemistry of the selenite ion and selenite containing compounds resembles the chemistry of the sulphite ion and its compounds. The polyhedron of the selenite ions is similar to that of sulphite ions, which is trigonal pyramid with one vacant orbital

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