

Original paper

The question of water content in parsonsite: a model case – occurrence at the Červené žíly vein system, Jáchymov (St. Joachimsthal), Czech Republic

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Strongly altered gangue, containing rich crystalline aggregates of parsonsite, was recently found at the outcrop parts of the Červené žíly vein system, the Jáchymov ore district, Czech Republic. Mineralogical research proved that in the crystal structure of parsonsite from Jáchymov is present a higher content of molecular water than expected. This conclusion is supported by the results of thermogravimetric analysis and infrared spectroscopy. The weight loss obtained from TG curve is 3.70 wt. %, corresponding to 1.93 mols of H₂O. The presence of a broad vibration band reflecting the O–H stretching vibrations of molecular water was ascertained in the infrared spectrum of studied parsonsite sample, suggesting that H₂O molecules are involved in the hydrogen-bonding network in the crystal structure of studied parsonsite. Inferred hydrogen bond lengths can vary in the range 2.6–3.0 Å, which is consistent with the distance between possible position of the molecular water and nearest neighbouring oxygen atom in the crystal structure of the synthetic parsonsite given in the literature. The chemical composition of the studied parsonsite from Jáchymov, 47.27 PbO, 13.38 P₂O₅, 1.60 As₂O₅, 0.16 SiO₂, 32.61 UO₃, 3.70 H₂O, total 98.71 wt. %, can be expressed as Pb_{1.99}(UO₂)_{1.07}[(PO₄)_{1.77}(AsO₄)_{0.13}·(SiO₄)_{0.03}]_{Σ1.93}·1.93 H₂O, based on electron microprobe and thermal analyses. Its refined unit-cell parameters for triclinic space group *P*-1, *a* 6.860(2), *b* 10.404(3), *c* 6.665(3) Å, α 101.46(3)°, β 98.30(3)°, γ 86.29(2)°, *V* 461.0(3) Å³ agree very well with the published data.

Keywords: parsonsite, Jáchymov, powder X-ray diffraction, EMPA, infrared spectroscopy, thermal analysis, O–H bonding

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1. Introduction

A detailed knowledge of crystal chemistry of uranyl minerals, i.e. hydrated oxysalts dominantly with layered structure, is of key importance in understanding their physical and chemical properties, such as stability and solubility (Schindler and Hawthorne 2008). These properties influence behaviour of the given mineral under oxidation conditions at surface and near-surface parts of the Earth's crust. Study of these phases is important in the context of uranium use as nuclear fuel. Related problems include sites of old mining, ore dressing settling pits, mine dumps or even spent nuclear fuel (“SNF”) management (Finch and Ewing 1992; Wronkiewicz et al. 1992, 1996; Finn et al. 1996; Murakami et al. 1997; Finch et al. 1999; Fayek et al. 2000; Čejka 2002; Shueneman et al. 2003; Catalano et al. 2004; Pittauerová and Goliáš 2006; Catalano et al. 2006; Procházka 2007; Procházka et al. 2009). Uranyl phosphates occur commonly as abundant phases in the supergene zones of most uranium deposits (Finch and Murakami 1999). Some uranyl phosphates

are remarkably stable and persist during prolonged storage in dumps or in bedrock outcrops (Pittauerová and Goliáš 2005).

Parsonsite is a member of the group of uranyl phosphates and arsenates with crystal structures based upon infinite chains of uranyl-anion polyhedra (Burns 2000; Locock et al. 2005). A similar uranyl-anion topology of crystal structure was reported for moctezumite (Swihart et al. 1993), derriksite (Ginderow and Cesbron 1983a), demesmakerite (Ginderow and Cesbron 1983b), walpurgite (Mereiter 1982), orthowalpurgite (Krause et al. 1995) and particularly for hallimondite, which probably represents an As-analogue of parsonsite (Locock et al. 2005). Even after extensive work on parsonsite crystal chemistry (Vochten et al. 1991; Burns 2000; Locock et al. 2005; Frost et al. 2006; Plášil et al. 2009), the role of molecular water in parsonsite remained problematic. This study aims to clarify these problems by a detailed mineralogical study of parsonsite from a new occurrence in the area of the Červené žíly veins in Jáchymov, Erzgebirge, western Bohemia.

2. Background information

Schoep (1923; 1930) estimated a chemical formula $\text{Pb}_2[(\text{UO}_2)(\text{PO}_4)_2](\text{H}_2\text{O})$ for natural parsonsite based on classic (wet) chemical analyses. Frondel (1950; 1958) mentioned parsonsite as $\text{Pb}_2[(\text{UO}_2)(\text{PO}_4)_2](\text{H}_2\text{O})_2$ based on analogy to hallimondite. Branche et al. (1951) studied a parsonsite sample from Reliez, Lachaux, Puy-de-Dôme, France, containing 2.1 wt. % H_2O . Bignand (1955) synthesized a phase corresponding to parsonsite which, however, was anhydrous. Guillemin (1958) also assumed parsonsite from Shinkolobwe, Katanga, to be anhydrous. Mazzi et al. (1959) presented the first crystal structure investigation on parsonsite. They estimated positions of heavy atoms only (U and Pb) in the crystal structure. Deliens et al. (1981) characterized parsonsite as dihydrate. Smith (1984) ascribed to parsonsite a chemical formula $\text{Pb}_2(\text{UO}_2)(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$. Vochten et al. (1991) prepared synthetic parsonsite crystals and provided results of thermogravimetric analysis, which indicated a formula $\text{Pb}_2[(\text{UO}_2)(\text{PO}_4)_2](\text{H}_2\text{O})_{0.5}$.

Burns (2000) reported refined crystal structure of natural parsonsite originating from a classic European locality, La Feye in France. According to Burns (2000), parsonsite structure consists of infinite chains of uranyl-phosphate polyhedra and does not contain any molecular water. These results are based on final difference Fourier maps that do not reveal any additional maxima connected with O of possible H_2O groups.

Later, Locock et al. (2005) published refined crystal structures of both end-member phases, synthetic parsonsite and its As-analogue, hallimondite. Based on study of synthetic parsonsite carried out by Locock et al. (2005), presence of molecular water in the parsonsite crystal structure is not evident. Their ATR-FTIR study did not prove the presence of O–H or H–O–H stretching and bending vibrations, in contrast to the synthetic hallimondite. Analysis of cavities in the crystal structure of synthetic parsonsite resulted in the fact that a void at special position 0, 0, 1/2 (like in synthetic hallimondite) is large enough for weakly bonded molecular water. Locock et al. (2005) commented the study by Vochten et al. (1995) with a note that content of molecular water in parsonsite is variable. It could be expressed by the structural formula $\text{Pb}_2[(\text{UO}_2)(\text{PO}_4)_2](\text{H}_2\text{O})_n$, where n is reliably proven in the range $0 \leq n \leq 0.5$.

Infrared and Raman spectra of parsonsite from the Ranger Mine (Australia) and La Feye (France) were published by Frost et al. (2006). Their conclusion was that the studied samples contained adsorbed water. Plášil et al. (2009) reported the content of 2 H_2O molecules for natural parsonsite from the Medvědin deposit (Czech Republic), based on result of TG analysis, with corresponding weight loss of *c.* 4 wt. %. Its refined unit-cell

parameters were slightly larger than those listed by Locock et al. (2005) for the synthetic parsonsite. The infrared spectrum of parsonsite from Medvědin contains bands probably belonging to stretching (3407 cm^{-1}) and bending (1643 cm^{-1}) vibrations of O–H bonds (Plášil et al. 2009). The uncertainty concerning the molecular water content in parsonsite is seen also in mineralogical compendia: Anthony et al. (2000) mentioned parsonsite as containing 2 molecules of molecular water but Back and Mandarino (2008) reported parsonsite as an anhydrous species.

3. Experimental

3.1. X-ray powder diffraction

The X-ray powder pattern of parsonsite from Jáchymov was collected on the powder diffractometer PANanalytical X'Pert Pro equipped with a secondary graphite monochromator and solid-state X'Celerator detector, using CuK_α radiation and operating at 40 kV and 30 mA. Sample was grinded and placed from acetone suspension onto a zero-background silicon holder. The powder pattern was collected in the Bragg–Brentano geometry in the range $7\text{--}60^\circ 2\theta$, step width of 0.02° and counting time of 300 s per step; the sample was rotated with a frequency of 2 s^{-1} . The position of each diffraction maxima was refined using Pearson VII profile function in the software Xfit (Coelho and Cheary 1997). Theoretical diffraction pattern of parsonsite, based on the structural data given by Locock et al. (2005), was calculated using PowderCell software (Krause and Nolze 2000). The experimental d_{obs} of the observed diffractions were assigned on the basis of the theoretical pattern hkl indices. Unit-cell parameters were refined by the least-square algorithm using software Celref (Laugier and Bochu 2002).

3.2. Electron microprobe analysis (WDS)

Chemical composition of parsonsite from Jáchymov was studied by Cameca SX100 microprobe (Laboratory of Electron Microscopy and Microanalysis the Masaryk University in Brno and Czech Geological Survey, operators R. Škoda and J. Sejkora), operating at accelerating voltage of 15 kV, beam current of 10 nA and beam diameter of 5 μm . For measurement, the following X-ray lines and standards were used, K_α : Si (sanidine), P (fluorapatite); L_α : As (InAs); M_α : Pb (vanadinite); M_β : U (U). Counting times (CT) at each of the diffraction positions were 20 s, counting time at background points was 1/2 CT. Measured intensities were re-calculated to element concentrations using “PAP” program (Pouchou and Pichoir 1985).



Fig. 1 Old mining dump at the area of Červené žily vein system outcrops, the Jáchymov ore district, Czech Republic. Photo by J. Tvrdý, November 2009.

3.3. Thermogravimetric analysis

Thermogravimetric study was undertaken on Stanton Redcroft Thermobalance TG 750 (Central Laboratories, Institute of Chemical Technology, Prague, analyst J. Ederová). Heating rate was set to $10\text{ }^{\circ}\text{C min}^{-1}$ in dynamic air atmosphere, with cooling rate 10 ml min^{-1} . Sample weight was 0.818 mg.

3.4. Infrared spectroscopy

Micro-DRIFTS spectrum of parsonsite was recorded by FTIR spectrometer Nicolet Magna 760 (in the range $4000\text{--}600\text{ cm}^{-1}$, resolution 4 cm^{-1} , 128 scans, Happ–Genzel apodization) equipped with Spectra Tech InspecIR micro-FTIR accessory. Crystals of parsonsite were mildly ground with KBr, without using pressure and immediately analyzed. The same KBr was used as a reference. Spectral manipulation was done using Omnic Spectra Tools software. For the decomposition of the spectra, Gauss–Lorentz profile function was applied. During the band fitting, the statistical agreement factors were checked until the fit converged to the final minimal value for the difference function.

4. Results

4.1. Description of the occurrence and samples

Sample of mainly quartz gangue ($30\times 20\times 15\text{ cm}$), containing the later detected parsonsite, was found on the dump

of an old mining work – a shallow shaft probably originating from the 1st half of the 16th century in Jáchymov (St. Joachimsthal). The shaft is located on the outcrop of the vein cluster known as the Červené žily system (area to the north of the shaft No. 14), Jáchymov ore district, Czech Republic (Fig. 1). A more detailed description of the vein is not possible, because of a complex situation of mining works and a lack of accurate archive materials and information. Parsonsite occurs as crystalline aggregates consisting of long prismatic, translucent to transparent crystals of yellow–orange to orange colour, up to 2 mm long (Fig. 2). It was found in the association with metatorbernite crystalline aggregates, locally strongly altered. The best-developed crystal of parsonsite was found in a most altered part of the gangue in layers with black, probably amorphous, ferric oxy-hydroxides.

4.2. X-ray powder diffraction

The powder X-ray diffraction pattern of parsonsite from Jáchymov (Tab. 1) is in excellent agreement both with theoretical diffraction data calculated from the parsonsite crystal structure (Locock et al. 2005) and other published data (e.g., Plášil et al. 2009). Observed intensities deviate only negligibly from the theoretical ones due to preferred orientation effect, which is induced by a very good cleavage of parsonsite crystals. Given the fact that in the powder pattern was detected only a single phase, without any admixture, the powder sample was further used for infrared and thermal analyses. Unit-cell parameters of parsonsite from Jáchymov (Tab. 2), refined based on positions of 35 diffractions, are consistent with data presented in the literature.



Fig. 2 Long prismatic parsonsite crystals in the cavity of the altered gangue. The width of photo is 0.8 mm. Photo by J. Sejkora (Nikon SMZ1500).

4.3. Chemical composition

A characteristic feature of the chemical composition of the studied parsonsite (Tab. 3) is the isomorphous substitution of the dominant $(\text{PO}_4)^{3-}$ anions in the tetrahedral positions by $(\text{AsO}_4)^{3-}$ anions up to ~10 mol. % in the position (Fig. 3). This substitution is characteristic of the isotypic series parsonsite–hallimondite (Locock et al. 2005). Interesting are also contents of $(\text{SiO}_4)^4-$ groups, even if they are very low (up to 0.16 wt. % SiO_2). With regard to detection limits and errors, the Si content is considered as reliable. According to Locock (2007), the anions $(\text{SiO}_4)^4-$ should not theoretically enter the uranyl-anion layers. A similar phenomenon has already been observed for a few other uranyl phosphates and arsenates (e.g., Sejkora and Čejka 2007; Sejkora et al. 2007; Plášil et al. 2009). Chemical composition of parsonsite from Jáchymov can be expressed by empirical formula (mean of three analyses, based on sum of atoms = 5 *apfu*):

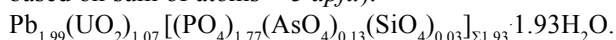
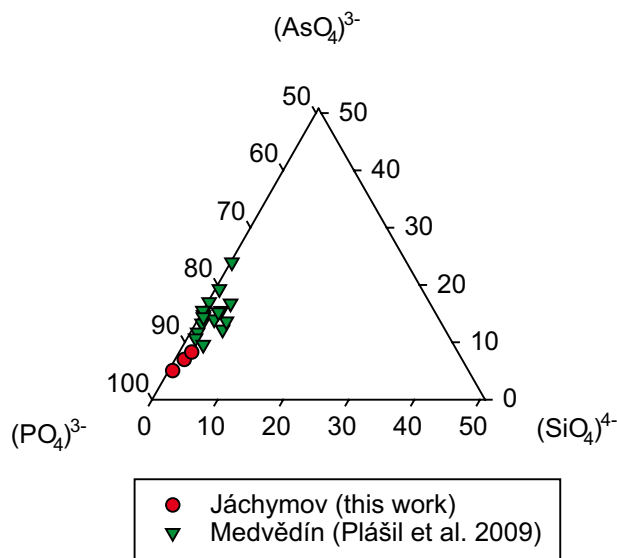


Fig. 3 The ternary diagram of anion contents (molar %) at tetrahedral sites of the studied parsonsite from Jáchymov.

Tab. 1 Powder X-ray diffraction pattern of parsonsite from Jáchymov

I_{obs}	h	k	l	d_{obs}	d_{calc}
27	0	1	0	10.18	10.19
10	-1	0	0	6.78	6.78
1	0	0	1	6.47	6.47
3	0	-1	1	6.01	6.01
9	-1	-1	0	5.75	5.75
16	0	2	0	5.10	5.09
3	-1	0	1	5.03	5.03
2	-1	-1	1	4.87	4.87
16	-1	1	1	4.23	4.23
13	1	-1	1	4.20	4.20
17	-1	-2	0	4.15	4.15
4	-1	-2	1	3.94	3.95
2	0	2	1	3.68	3.68
100	0	3	0	3.40	3.40
3	0	-3	1	3.28	3.28
31	-2	-1	0	3.26	3.25
3	-2	1	0	3.18	3.18
5	1	2	1	3.16	3.17
13	-2	-1	1	3.15	3.16
5	1	3	0	3.08	3.08
3	0	-2	2	3.00	3.01
3	-1	1	2	2.803	2.803
9	-2	2	0	2.775	2.776
2	2	1	1	2.709	2.708
2	1	-2	2	2.610	2.609
1	1	3	1	2.559	2.560
2	-2	-1	2	2.550	2.550
1	1	4	0	2.414	2.414
1	1	-4	0	2.356	2.356
1	-3	0	0	2.262	2.261
3	-3	0	1	2.231	2.230
1	-2	-4	1	2.129	2.128
5	-1	-5	0	1.9723	1.9719
2	1	-5	0	1.9322	1.9320
2	-2	-3	3	1.8481	1.8479



Tab. 2 Unit-cell parameters of parsonsite from Jáchymov compared with published data (for the triclinic space group *P*-1)

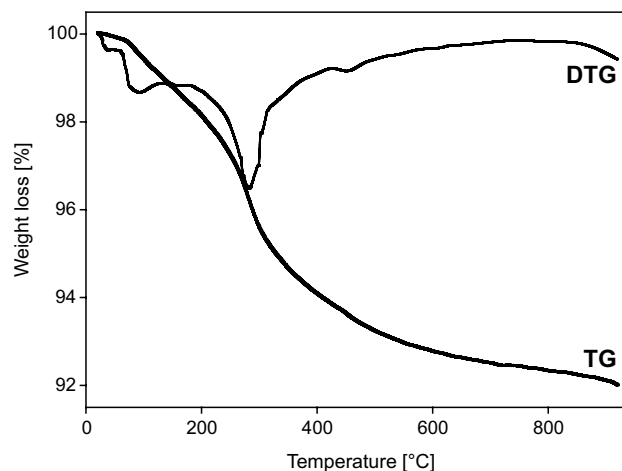
Mineral	parsonsite	parsonsite	parsonsite	parsonsite
Locality	Jáchymov	Jáchymov	Synt.	La Feye (France)
Reference	This work	Ondruš et al. (1997)	Locock et al. (2005)	Burns (2000)
<i>T</i> site	P _{1.847} As _{0.137} Si _{0.03}	P	P	P
<i>n</i> H ₂ O	~ 1.93	Not analyzed	0 ≤ <i>n</i> ≤ 0.5	0
<i>a</i> [Å]	6.860(2)	6.873(6)	6.8432(5)	6.842(4)
<i>b</i> [Å]	10.404(3)	10.416(5)	10.4105(7)	10.383(6)
<i>c</i> [Å]	6.665(3)	6.684(3)	6.6718(4)	6.670(4)
<i>α</i> [°]	101.46(3)	101.41(6)	101.418(1)	101.26(7)
<i>β</i> [°]	98.30(3)	98.358(7)	98.347(2)	98.17(7)
<i>γ</i> [°]	86.29(2)	86.39(1)	86.264(2)	86.38(7)
<i>V</i> [Å ³]	461.0(3)	463.8	460.64(5)	459.8(7)
Mineral	parsonsite	parsonsite	hallimondite	parsonsite
Locality	Medvědin	synt.	synt.	
Reference	Plášil et al. (2009)	Vochten et al. (1991)	Locock et al. (2005)	
<i>T</i> site	P _{1.667} As _{0.307} Si _{0.04}	P	As	
<i>n</i> H ₂ O	2	0.5	0.29	
<i>a</i> [Å]	6.852(6)	6.8487(2)	7.1153(8)	
<i>b</i> [Å]	10.395(7)	10.3599(4)	10.478(1)	
<i>c</i> [Å]	6.669(6)	6.6712(2)	6.8571(8)	
<i>α</i> [°]	101.20(6)	101.843(3)	101.178(2)	
<i>β</i> [°]	98.12(7)	98.233(3)	95.711(3)	
<i>γ</i> [°]	86.39(7)	86.361(3)	86.651(3)	
<i>V</i> [Å ³]	461.0(6)	458.2	498.64(3)	

Tab. 3 Chemical composition of parsonsite from Jáchymov

	mean	1	2	3
PbO	47.27	47.78	46.85	47.17
SiO ₂	0.16	0.16	0.08	0.24
As ₂ O ₅	1.60	1.53	1.23	2.04
P ₂ O ₅	13.38	12.33	14.16	13.64
UO ₃	32.61	33.39	31.59	32.85
H ₂ O	3.70	–	–	–
Total	98.71			
Pb	1.995			
Si	0.025			
As	0.131			
P	1.775			
Σ <i>T</i> site	1.931			
U	1.074			
H ₂ O	1.93			

4.4. Thermogravimetric analysis

Thermogravimetric study of parsonsite from Jáchymov (Fig. 4) proved that with increasing temperature parsonsite loses its weight in several steps. Strictly speaking, the weight loss in the range of 20–280 °C can be described in three, relatively distinct steps. Its weight loss up to 300 °C, that is up to the temperature, where the molecular water release can be expected, corresponds to ~ 3.70 wt. %. This value equals to ~ 2 H₂O molecules. The same result has been obtained in case of thermal analysis of the sample from Medvědin (Plášil et al.

**Fig. 4** The thermogravimetric curve (TG) and its derivation (DTG) for parsonsite sample from Jáchymov.

2009). Contrary to the Medvědin sample, the TG curve of parsonsite from Jáchymov is better defined and each decomposition step is visible. The first step is present in the range 20–100 °C (with the corresponding maximum on DTG curve at ~ 40 °C). This weight loss corresponds to approximately 0.2 wt. % (~ 0.1 mol H₂O). This change can be connected with release of adsorbed water. The dehydration step, which follows, significantly differs (different slope of TG curve) and proceeds approximately in the temperature range of 100–200 °C, with a weight

loss 1.68 wt. %, corresponding to 0.88 mol H₂O (~ 1 mol H₂O). Weight loss in the range 200–280 °C corresponds to ~ 1.82 wt. %, i.e. 0.95 mol H₂O (~ 1 mol H₂O). Decomposition is not finished until the highest observed temperature 920 °C, with weight loss of 4.31 wt. %. This process is connected with destruction of the parsonsite crystal structure and probable formation of polyphosphate phases. This weight loss is probably a result of As₂O₃ and O₂ release from decomposition of As₂O₅ and O₂ release from decomposition of UO₃ to UO_{2.67}.

4.5. Infrared spectroscopic study

The infrared spectrum of parsonsite from Jáchymov is comparable to the results of Frost et al. (2006) and Plášil et al. (2009). Dominating vibration bands in the parsonsite spectrum (Fig. 5) correspond to the antisymmetric stretching vibration ν_3 (PO₄)³⁻ (~ 1050 cm⁻¹). In the range of ~1000 to 860 cm⁻¹ are present vibration bands belonging to the symmetric stretching vibration

ν_1 (PO₄)³⁻ and the antisymmetric stretching vibration ν_3 (AsO₄)³⁻. At lower values (~860–800 cm⁻¹) occur overlapping bands of the antisymmetric stretching vibration ν_3 (UO₂)²⁺ and a symmetric stretching vibration ν_1 (UO₂)²⁺ with stretching modes ν of (AsO₄)³⁻. The position of the stretching vibration bands of (UO₂)²⁺ was calculated on the basis of the empirical relations carried out by Bartlett and Cooney (1989), using the bond length U–O_{ur} published by Locoock et al. (2005) for synthetic parsonsite and by Burns (2000) for natural parsonsite (1.78 Å). The position of the antisymmetric stretching vibration ν_3 (UO₂)²⁺ 906 cm⁻¹ and the symmetric stretching vibration ν_1 (UO₂)²⁺ 831 cm⁻¹ corresponds to these empirical relations. Towards the low-wavenumber region, the splitting bending modes ν_4 (δ) (PO₄)³⁻ and libration modes of H₂O occur. The vibration bands of weak intensity below 1500 cm⁻¹ are probably overtones. Although this assignment is the most probable one, we have to point out that the wavenumbers of these bands are similar with those of U–OH deformations. But presence of the hydroxyls

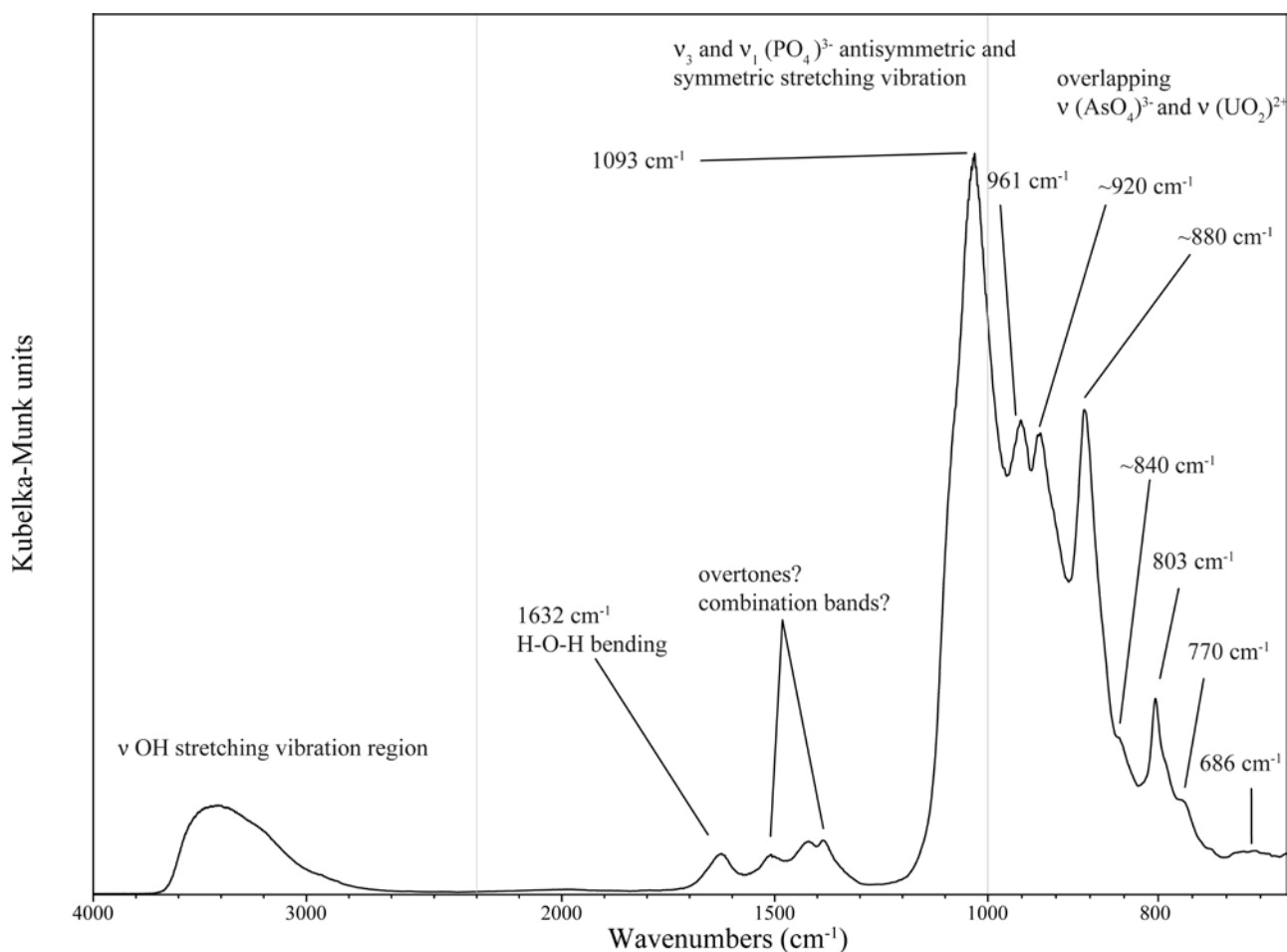


Fig. 5 The infrared spectrum of parsonsite from Jáchymov with assigned and displayed fundamental vibration modes with wavenumbers for clarity.

within the sheet is not possible since the OH groups were not detected by the single crystal studies (Burns 2001; Locock et al. 2005).

Broad, to the lower wavenumbers positioned asymmetric vibration band, occurring at $\sim 3400\text{ cm}^{-1}$, corresponds to stretching ν_1 and ν_3 O–H of the H_2O molecules (Fig. 5). As a mathematical deconvolution of the spectrum in this region shown in Fig. 6 indicates, this broad band possibly consists of several overlapping bands. The nature and structure of this broad band suggests that H_2O molecules, responsible for these vibrations, are involved into hydrogen bonding network (Čejka 1999). The empirical relation (Libowitzky 1999) describes the dependence of stretching frequencies (wavenumber) ν O–H on bond lengths $\text{O}\cdots\text{O}$ in relevant hydrogen bonds $\text{O}-\text{H}\cdots\text{O}$. The approximate range of hydrogen bond lengths present in the crystal structure of parsonsite from Jáchymov is 2.6 to 3.0 Å. The lengths of hydrogen bonds (based on bond length $\text{O}\cdots\text{O}$), determined by structure analysis in an analogous case of synthetic hallimondite, are in the

range of 2.5–2.9 Å. A vibration band at 1632 cm^{-1} (Fig. 5) belongs to the deformation vibrations ν_2 (δ) H–O–H, definitely due to the molecular water. It is a symmetric, non-splitting band of lower intensity, which is nevertheless clearly defined.

5. Discussion

Locock et al. (2005) presented refined crystal structures both of parsonsite and hallimondite, two isostructural phases. In case of hallimondite, the oxygen atom, corresponding to the molecular water, was found at special position. Inspecting Fig. 7, we can easily compare both structures. Hallimondite contains molecular water within the channels in its crystal structure, while parsonsite does not, although it exhibits the same nature of the structure. Locock (personal communication, 2009) derived a distance from the possible atom (centre) in the special position (0, 0, 1/2), within the void/cavity in a parsonsite

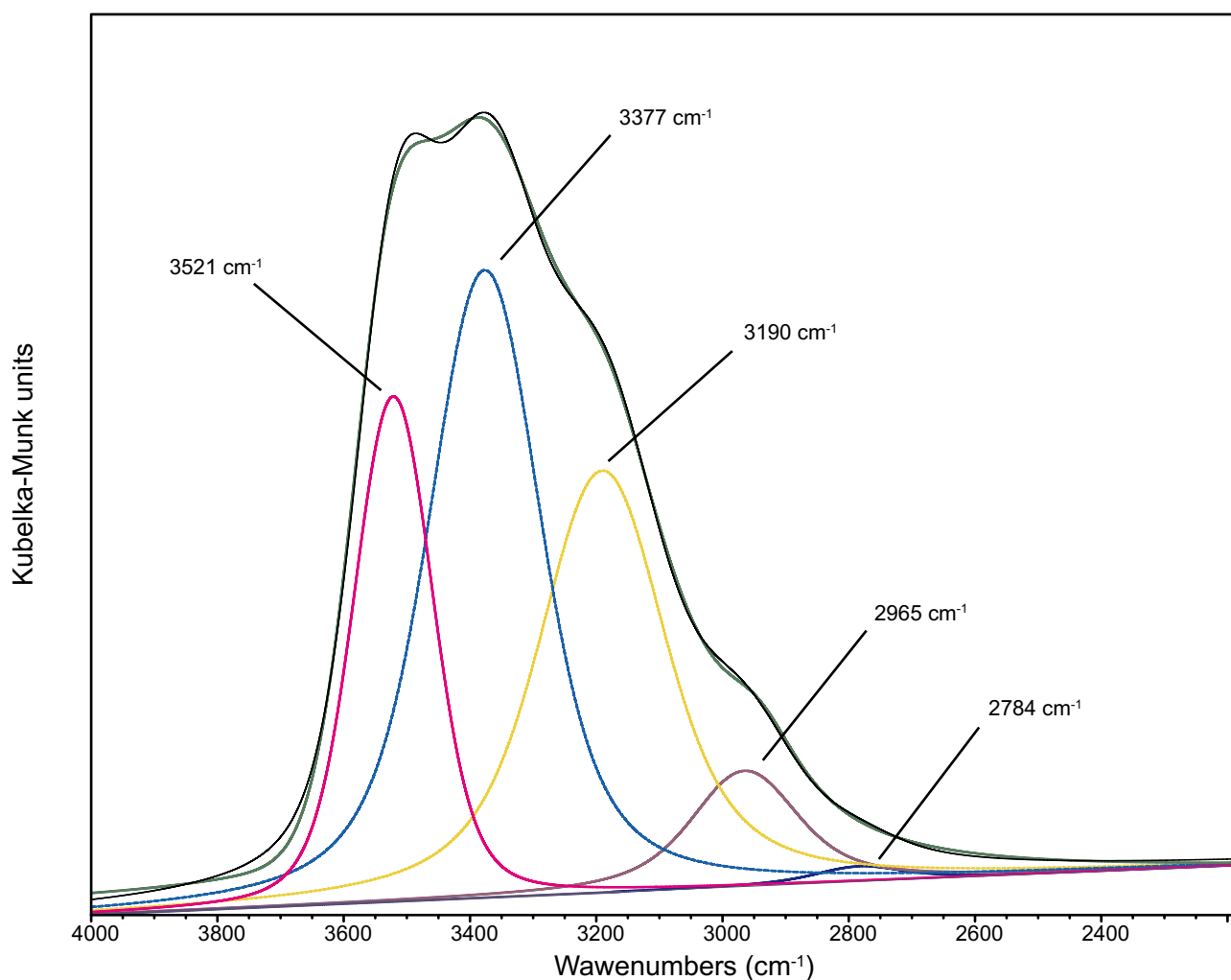


Fig. 6 Decomposition of the parsonsite spectrum in the region of the ν OH stretching vibrations.

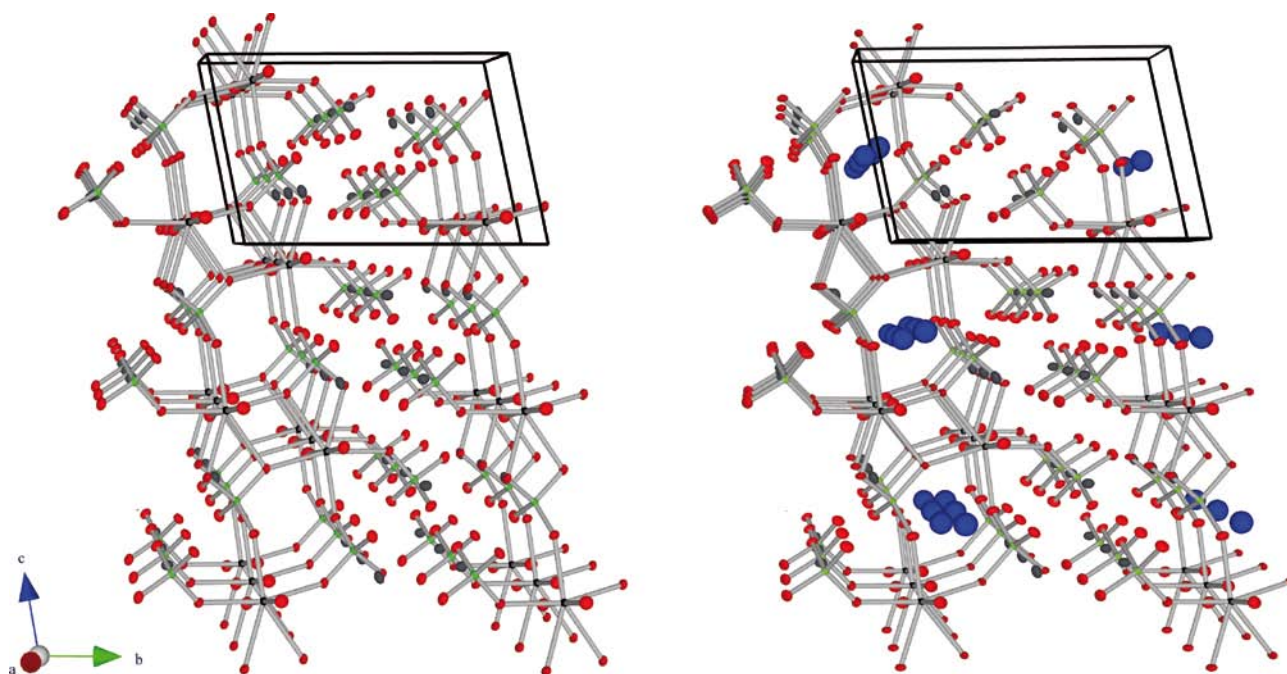


Fig. 7 Crystal structures of isostructural parsonsite (left) and hallimondite (right) after Locock et al. (2005) in a perspective projection along *a* axis. The unit-cell edges are marked by solid black line. Uranium atoms are of black colour, phosphorus/arsenic atoms are green, oxygen atoms are red and oxygen atoms belonging to the molecular water are blue.

crystal structure, to the neighbouring oxygen atom in the following range: 2.5–2.9 Å. This value is very similar to that obtained for the parsonsite from Jáchymov, based on the position of the OH stretching band in the infrared spectrum. It is highly probable that the molecular water is located along these structural channels and that its content in parsonsite is variable, depending on many variables (conditions of forming, relative humidity in the air etc.).

7. Conclusions

Parsonsite, recently found at the Jáchymov ore district, has clearly defined contents of molecular water. This feature is based on the results of thermal analysis (TG) and infrared spectroscopic study and corresponds to the structural arrangement of parsonsite. The weight loss obtained from the thermal analysis nevertheless underlines the fact that molecular water content in parsonsite can be slightly higher. The obtained weight loss is 3.7 wt. % up to 280 °C, corresponding to 1.91 mol H₂O (~ 2 mol H₂O). Asymmetric, differentiated broad band of the stretching O–H vibrations and their wavenumbers suggest that the water molecules are involved in the hydrogen bonding network with possible O··O bond lengths of 2.6–3.0 Å. Therefore, we propose that the chemical formula of parsonsite can be better described as Pb₂[(UO₂)(PO₄)₂](H₂O)_{*n*}, 0 ≤ *n* ≤ 2.

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Otázka obsahu molekulární vody v parsonsite: modelový případ – výskyt na Červených žilách v Jáchymově, Česká republika

Parsonsite byl identifikován v silně alterované žilovině nalezené na výchozech Červených žil v Jáchymově (Česká republika). Mineralogický výzkum prokázal, že obsah molekulární vody v krystalové struktuře parsonsite je vyšší, než bylo očekáváno. Tento závěr je podložen výsledkem termogravimetrického studia a infračervenou spektroskopii. Hmotnostní úbytek zaznamenaný křivkou TG činí 3.70 hm. %, což odpovídá 1.93 mol H_2O . V infračerveném spektru studovaného parsonsite byla zjištěna přítomnost širokého vibračního pásu, náležejícího valenčním O–H vibracím molekulární vody, naznačujícím, že molekuly H_2O jsou zapojeny do systému vodíkových vazeb v krystalové struktuře studovaného parsonsite. Odvozené délky vazeb O··O se pohybují v rozmezí 2.6–3.0 Å, což je v souladu s možnými vzdálenostmi mezi pozicí kyslíku molekulární vody a nejbližšího sousedního kyslíku, dle modelu syntetického parsonsite uvedeného v literatuře. Chemické složení studovaného parsonsite z Jáchymova 47.27 PbO, 13.38 P_2O_5 , 1.60 As_2O_5 , 0.16 SiO_2 , 32.61 UO_3 , 3.70 H_2O , suma 98.71 hm. %, může být vyjádřeno jako $Pb_{1.99}(UO_2)_{1.07}[(PO_4)_{1.77}(AsO_4)_{0.13}(SiO_4)_{0.03}]_{\Sigma 1.93} \cdot 1.93 H_2O$, na základě mikrosondové a termické analýzy. Vypřesněné mřížkové parametry, pro triklinickou prostorovou grupu $P-1$, a 6.860(2), b 10.404(3), c 6.665(3) Å, α 101.46(3)°, β 98.30(3)°, γ 86.29(2)°, V 461.0(3) Å³ souhlasí s literárními údaji.