



Liebigite recently formed from the dump of mine No. 16 (Příbram, Hájce), Bohemia, Czech Republic

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Abstract. Liebigite from Hájce near Příbram is orthorhombic $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3] \cdot 11 \text{H}_2\text{O}$ with $a = 16.708(4) \text{ \AA}$, $b = 17.557(4) \text{ \AA}$, $c = 13.713(3) \text{ \AA}$ and $V = 4023(1) \text{ \AA}^3$. It forms there coatings up to $2 \times 3 \text{ cm}$ (depth up to 0.5 mm) and rarely imperfectly formed isometric crystals up to 0.5 mm in their cavities. It has light yellowish-green colour, is transparent to translucent and very brittle. Intensive green fluorescence with weak bluish tint was observed in short- and long-wave UV radiation. Liebigite was found in the mine dump material of mine No. 16 (Hájce near Příbram) in the Příbram uranium district (Czech Republic). It recently originated in the mine dump material by crystallization from concentrated solutions of the uranyl-carbonate type on small fragments of calcite-type veins in dry places of the dump. These solutions were distinctly alkaline, with higher partial pressure of CO_2 and high prevalence of Ca^{2+} ions in relation to Mg^{2+} and Na^+ cations. The primary reddish calcite and uraninite and rarely secondary gypsum were determined in close association with studied liebigite. Tentative assignment and interpretation of the infrared absorption spectrum of liebigite and calculated U-O (uranyl) bond lengths are given.

■ Liebigite, uranyl, mineralogy, X-ray powder data, IR vibrational spectra, Příbram-Hájce, Bohemia, Czech Republic

INTRODUCTION

Liebigite, calcium uranyl tricarbonat hydrate, $\text{Ca}_2[\text{UO}_2(\text{CO}_3)_3] \cdot 11 \text{H}_2\text{O}$, was described by Smith in 1848 as a new mineral phase and the product of uraninite alteration in association with chalcopyrite and gypsite near Adrianopol, Turkey (Smith 1848, 1851). According to Smith (1851), the same mineral was found near Johannegeorgenstadt (Saxony). Vogl (1853, 1857) also described the same mineral from Jáchymov (Bohemia) and named it Uran-Kalk-Karbonat, later called flutherite (Weisbach 1875), and finally uranohallite (Schrauf 1882, Březina 1890). The identity of liebigite and flutherite had been supposed by Larsen (1917). Identity of liebigite, flutherite and uranohallite was finally established by Evans and Frondel (1950). Liebigite is an important representative of the family of uranyl carbonate minerals. This mineral is a secondary mineral formed from alkaline carbonate solutions. It occurs associated e.g. with calcite, schrockingerite, bayleyite and gypsum (Chernikov 1981, Finch et Murakami, 1999).

Liebigite was understood as a phase containing tetravalent (U^{4+}) uranium and the role of this cation in the crystal structure of liebigite was not known. Evans et Frondel (1950) assigned therefore the chemical formula $\text{Ca}_2\text{U}(\text{CO}_3)_4 \cdot 10 \text{H}_2\text{O}$ to liebigite. The presence of hexavalent uranium (U^{6+}) in the form of uranyl, UO_2^{2+} , in the mineral was established

by its analysis of Meyrowitz (written communication, Frondel, 1958) and Bachelet et al. (1952).

Liebigite occurs at many localities. Some of them have been mentioned by Frondel (1958) and later in a paper by Čejka et Urbanec (1976) in which practically all significant papers related to liebigite have been included. Many localities e.g. from Germany, Austria, Czech Republic, France, Great Britain, Turkey, U. S. A., and Canada are enumerated by an anonym in Lapis (1996). Matsubara (1976) described liebigite from Tsukiyoshi Orebody of the Tōnō mine, Gifu Prefecture, Japan. Walenta (1977) found liebigite in Schwarzwald. Meixner and Walenta (1979) presented liebigite from Kölnbreisperre, Maltatal, Kärnten, as a new mineral phase for Austria. Deliens (1985) described liebigite for the first time from Shinkolobwe, Shaba, Zaire (now Democratic Republic of Congo). Deliens et al. (1992) described liebigite from Rabejac et Mares. Kiss (1966) unsufficiently described a mineral phase from Mecsek, Hungary, and provisionally named it metaliebigite. This phase does not seem to be structurally related to liebigite. Recent data on liebigite from Jáchymov were published by Ondruš et al. (1997). Liebigite has never been observed in the region of uranium district Příbram.

Synthesis of liebigite was described e. g. by Bachelet et al. (1952), Ambartsumyan et al. (1961), Čejka (1969), Meyrowitz et al. (1963), Jindra et Škrumovský (1966), Vochten et al. (1993a, b, 1994), Amayri (2002) and Amayri et al. (1998, 1999, 2001). Vochten et al. (1994) described a synthetic phase compositionally intermediate between liebigite and andersonite, $\text{Ca}_{1.54}\text{Na}_{0.61}[\text{UO}_2(\text{CO}_3)_3] \cdot x \text{H}_2\text{O}$ ($x = 5.38$). H_3O^+ ions should be present in this compounds because of the charge balance. Thermal analysis of synthetic liebigite was studied by Bachelet et al. (1952), Ambartsumyan et al. (1961), Čejka (1969), Vochten et al. (1993a), and Amayri (2002). Čejka et Urbanec (1979) presented thermal analysis of natural liebigite (from Jáchymov, Czech Republic) in comparison with that of its synthetic analogue (for details and references see also Čejka (1999) and Čejka et Urbanec (1990)). Empirical methods of prediction of thermodynamic properties of liebigite were published by Finch (1997) and Chen et al. (1999). Alwan et Williams (1980) determined free energy of formation of liebigite from solution studies at various temperatures. A theoretical study of the structures of $\text{UO}_2(\text{CO}_3)_3^{4-}$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10 \text{H}_2\text{O}$, and $\text{BaUO}_2(\text{CO}_3)_3^0$ using various methods was recently published by Tsushima et al. (2002). Single crystal structure of synthetic liebigite was unsufficiently described by Appleman (1956). A refinement of the single crystal structure of natural liebigite was published by Mereiter (1982). The structure of synthetic liebigite was also studied by EXAFS (e.g. Reich et al. 1998; Tsushima et al. 2002; Amayri 2002). Hemimorphy of liebigite crystals was described by Mereiter (1986).

According to Mereiter (1982), the crystal structure of liebigite contains $[\text{UO}_2(\text{CO}_3)_3]$ clusters with UO_2O_6 hexagonal dipyramids and three symmetrically distinct Ca polyhedra. One Ca cation is coordinated by seven ligands, two Ca cations are each coordinated by eight ligands. Each CaO_n polyhedron includes four H_2O groups and the remaining ligands are shared with $[\text{UO}(\text{CO}_3)_3]$ clusters. The $[\text{UO}_2(\text{CO}_3)_3]$ clusters are thus linked by two kinds of $\text{CaO}_4(\text{H}_2\text{O})_4$ and one kind of $\text{CaO}_3(\text{H}_2\text{O})_4$ polyhedron to form puckered $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 8 \text{H}_2\text{O}$ layers parallel to (001). These layers are interconnected only by hydrogen bonds, both directly as well as via three additional interlayer H_2O molecules, two of which show positional disorder (Burns 1999; Burns et al. 1996, 1997). A neutral dicalcium uranyl tricarbonate complex, $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (aq.) was recently discovered in uranium related waters (Bernhard et al. 1996a, b, c; Bernhard et al. 1998a, b, c, 2001; Geipel et al. 1999; Kalmykov et Choppin 2000).

OCCURRENCE AND DESCRIPTION

The samples containing liebigite studied in this paper were found in dump material from the mine No. 16 (Háje) of the Příbram uranium district (Fig. 1). The mine No. 16, located approximately 500 m east of the village Háje (near a road Příbram – Kamýk n. Vlt.), initially it sunk in 1957 and in 1960 it reached the 22nd level. Further shaft sinking up to the final depth (88 m below the 32nd level) continued right to 1968. In 1976, the final depth 1838.4 m was here reached. At that time, this was the deepest vertical ore mine in Central Europe without overmining of ore materials (Litochleb et al. 2000). The mine No. 16 served as a mine shaft for mining of uranium and polymetallic ores up to the end of the eighties of the 20th century. In 1989–1998 the shaft was used as the main access, transport and mining work for building an underground gas reservoir having the volume over 620 000 m³. From the development of the mine No. 16, the material worked-out has been practically deposited on an indigenous hillside between the mines No. 16 and No. 10 (Bytíz), north of the mine No. 16; dimensions of yet mostly distributed dump get closer to 400 × 350 m. In the area of a former uranium ore-dressing plant, situated below the mine No. 16, a working for production of crushed and sorted rocks was established; up to 2000, practically all material from driving of gas reservoir has been processed. Later successive liquidation of the initial dump material continued. Some fragments of calcite containing gangue with macroscopically apparent coatings of recently formed supergene uranium mineral identified as liebigite were found during this work in 2000 in the central part of the dump approximately 10–15 m below the original surface (B. Bureš).

Liebigite was identified on fragments of tectonically strongly altered gangue (Fig. 2) having a thickness up to 1 cm formed by layers of reddish calcite and up to 3 mm thick layers of uraninite, some in reniform development. On calcite gangue, liebigite forms coatings having the surface up to 2 × 3 cm and depth up to 0.5 mm. Liebigite was also observed as smaller, very thin coatings directly on reniform aggregates of uraninite. Surface of liebigite coatings is uneven with greasy to vitreous lustre. Imperfectly formed isometric crystals, having size up to 0.5 mm, were also observed here and there in cavities of entirely non-continuous coatings (Fig. 3 and 4). Liebigite is light yellowish-green, transparent, in small fragments also translucent, very brittle. Its cleavage was not observed. Intensive green luminescence with weak bluish tint without any persistent effects was observed in short- (254 nm) and long- (366 nm) wave UV radiation. Studies samples of calcite gangue containing liebigite show higher radioactivity (of medium up to higher level) probably caused by also macroscopically apparent layers of uraninite. Besides uraninite, reddish to greyish, on its surface apparently corroded calcite was identified on the studied samples. Very small aggregates of transparent gypsum were sporadically observed in close association with liebigite.

The character of liebigite occurrence on the studied samples unambiguously proves that these mineral phases were recently formed under conditions of deposited dump material. A similar way of origin of liebigite was recently also described by Nekl et Goliáš (2002) on fragments of carbonated gangue containing uraninite in road grit of two streets in Klatovy. According to Meisser et al. (2002) and also other authors, complex $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ ions are stable in uranyl-sulfate and uranyl-carbonate types of waters, if they are alkaline in the pH range approximately 9–11. Simultaneously, partial pressure $p\text{CO}_2$ in these waters must be higher than that in the atmosphere. However, the influence



Fig. 1. The mine dump of the mine No. 16, Háje near Příbram. Photo J. Sejkora, 2002.

of pCO_2 on the formation of uranyl tricarbonates is not clear. Uranyl tricarbonates may form and exist also under normal temperature and atmospheric pCO_2 (see e.g. Čejka et Urbanec 1990; Chernikov 1981; Williams 1990). Higher pCO_2 probably may prevent hydrolysis of solutions from which uranyl tricarbonates crystallize. Other authors, e.g. Ondruš et al. (1997) assume that the stability field of $[UO_2(CO_3)_3]^{4-}$ ion is broader, approximately in the pH range 6.5–11.5. According to Williams (1990), high activity of Ca^{2+} ions and simultaneously low activities of Mg^{2+} and Na^+ ions are necessary, otherwise formation of andersonite, bayleyite, and other mineral phases is favoured.

At the studied locality, liebigite originates by crystallization from concentrated solutions of the uranyl-carbonate type on small fragments of calcite-type veins in relatively dry places of a dump (e. g. covered by greater rock fragments). Similarly, as in Jáchymov (Ondruš et al. 1997), liebigite forms in close association with uraninite and a gangue containing only minor amounts of pyrite and other Fe sulfides. As can be inferred from some published papers, mother solutions must be distinctly alkaline, probably with higher partial pressure of CO_2 and high prevalence of Ca^{2+} ions in relation to Mg^{2+} and Na^+ cations.

At other places of the studied dump, apart from liebigite, occurrences of recently formed uranospinite (Sejkora et al. 2002), and probably of uranopilite were discovered. At a nearby dump of the mine No. 21 (Příbram-Háje), a recent occurrence of schröckingerite was described (Sejkora et Čejka 2002).

STRUCTURAL AND CHEMICAL PROPERTIES

The X-ray powder diffraction pattern of liebigite was obtained from a hand-picked sample using diffractometer HZG4-AREM/Seifert. To minimize complicated shape of background due to classic glass sample holder, the sample studied was placed on the surface of flat silicon wafer from alcoholic suspension. For unit cell parameters step-scanned ($0.05^\circ/7$ s) the powder X-ray diffraction pattern (Table 1) was collected in the range $8\text{--}54^\circ 2\theta$ $CuK\alpha$. Positions and intensities of reflections were calculated using the Pearson VII profile shape function by ZDS programme package (Ondruš 1995). The measured pattern was indexed by data calculated (Lazy Pulverix programme – Yvon et al.

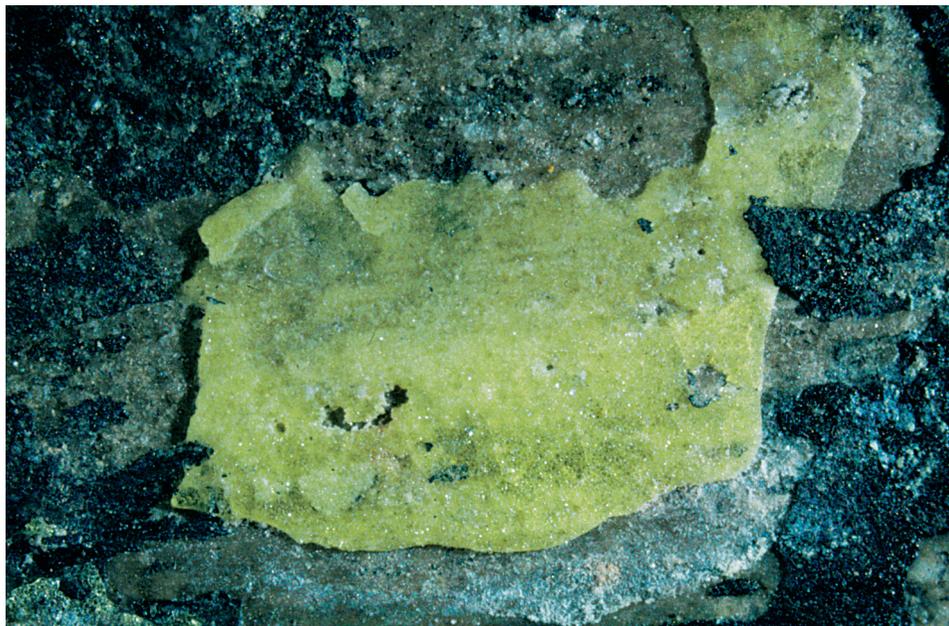


Fig. 2. The liebigitite coatings on gangue, Příbram-Háje. Photo J. Sejkora

1977) from crystal structure information of liebigitite (Mereiter 1982); unit cell parameters were refined by the programme of Burnham (1962).

It was proved that X-ray powder pattern of the studied liebigitite sample (Table 1) shows more diffractions than those given by Frondel et al. (1956) and in PDF file No. 11–296. The observed pattern, however, is in very good agreement with theoretical values calculated from crystal structure data of liebigitite by Mereiter (1982). Some differences between the observed and calculated intensities of individual diffraction peaks may be caused by the rather small preferred orientation of the $(0k0)$ type. The refined unit cell parameters of the studied liebigitite specimen agree very well with all data available and published for this mineral species (Table 2).

Liebigitite from Příbram has been analyzed semiquantitatively by energy dispersive micro-analyzer Link ISIS at electron scanning microscope CamScan 4 (acceleration potential 20 kV, a sample current 2.5 nA and 2 μm electron beam size). A natural unpolished sample surface has been analyzed. This analysis proved that liebigitite contained U, Ca, C and O as major constituents; this well agrees with its ideal formula $\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 11 \text{H}_2\text{O}$. The presence of H_2O , $(\text{UO}_2)^{2+}$ and $(\text{CO}_3)^{2-}$ was inferred from the IR analysis (see below).

INFRARED ABSORPTION SPECTROSCOPY

Infrared spectrum (4000–400 cm^{-1} range) of liebigitite from Příbram (Fig. 5) was measured with the FTIR Nicolet 740 type apparatus (absorption spectrum of the mineral phase dispersed in KBr disk). Infrared spectrum of liebigitite was interpreted by Čejka et Urbanec (1976), Urbanec et Čejka (1979a, b), Čejka (1999) and Amayri (2002) and discussed in relation to other anhydrous and hydrated uranyl carbonates possessing the $\text{UO}_2(\text{CO}_3)_3^{4-}$ cluster in their structure by Urbanec et Čejka (1979a) and especially by Čejka (1999).



Fig. 3. Irregular crystal of liebigite up to 60 μm , Příbram-Háje. TESLA BS 320, SEM photo by J. Sejkora and A. Gabašová.

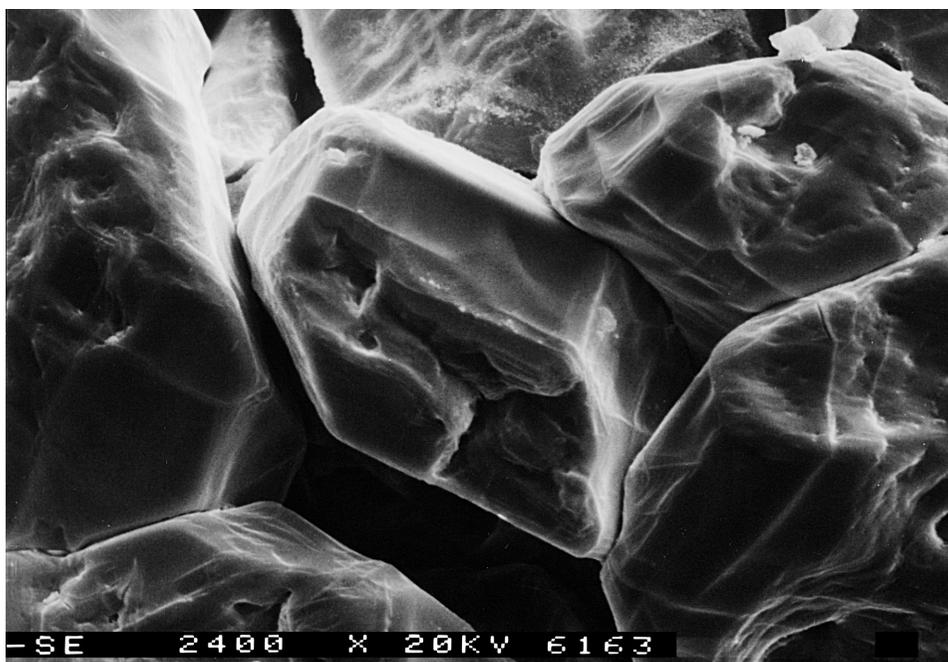


Fig. 4. Irregular crystals of liebigite up to 30 μm , Příbram-Háje. TESLA BS 320, SEM photo by J. Sejkora and A. Gabašová.

Table 1. X-ray powder diffraction pattern of liebigite from the dump of the mine No. 16 (Příbram-Háje).

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs.}	<i>I</i> / <i>I</i> ₀	<i>d</i> _{calc.}	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs.}	<i>I</i> / <i>I</i> ₀	<i>d</i> _{calc.}
0	2	0	8.783	100	8.778	4	2	4	2.537	11	2.537
2	0	0	8.361	36	8.354	6	2	2	2.475	16	2.475
0	0	2	6.865	79	6.857	1	6	3	2.439	36	2.438
1	2	1	6.768	98	6.761	3	2	5	2.369	15	2.369
2	2	0	6.048	28	6.052	7	1	1	2.331	9	2.331
0	2	2	5.408	85	5.404	1	4	5	2.301	13	2.034
2	0	2	5.303	34	5.300	5	4	3			2.298
3	1	1	4.961	5	4.951	3	6	3	2.254	24	2.254
2	2	2	4.539	46	4.537	5	6	1	2.169	25	2.174
0	4	0	4.394	25	4.389	1	8	1	2.148	34	2.149
4	0	0	4.174	27	4.177	3	4	5			2.146
1	4	1	4.053	94	4.055	5	5	3	2.138	12	2.139
1	2	3	3.939	37	3.940	2	2	6			2.138
4	2	0	3.773	26	3.772	6	2	4	2.098	23	2.099
0	4	2	3.697	21	3.697	7	4	1	2.074	17	2.073
4	0	2	3.570	36	3.567	8	2	0	2.027	35	2.032
3	4	1	3.346	30	3.343	2	8	2			2.028
4	2	2	3.306	41	3.305	3	8	1	2.020	12	2.020
5	1	1	3.192	30	3.193	1	6	5	1.9867	55	1.9869
0	2	4			3.193	5	6	3			1.9834
2	0	4	3.170	31	3.172	1	8	3	1.9667	20	1.9647
1	4	3	3.111	69	3.111	4	2	6	1.9542	7	1.9547
4	3	2	3.047	23	3.046	8	2	2	1.9469	21	1.9481
5	2	1			3.045	5	4	5	1.9047	21	1.9091
4	4	0	3.026	7	3.026	3	6	5	1.8832	22	1.8832
3	3	3			3.025	3	8	3	1.8647	18	1.8643
2	2	4	2.988	19	2.983	7	6	1	1.8338	20	1.8330
5	3	1	2.840	11	2.839	8	4	2	1.8194	17	1.8184
1	6	1	2.821	31	2.821	5	8	1			1.8182
4	4	2	2.768	9	2.768	2	8	4	1.8028	15	1.8047
3	4	3	2.751	21	2.752	1	4	7	1.7800	18	1.7787
0	4	4	2.702	25	2.702	7	6	3	1.7160	25	1.7145
6	2	0	2.656	28	2.654	1	8	5	1.7028	27	1.7046
5	4	1	2.610	22	2.610	3	4	7			1.7032
3	6	1	2.554	21	2.545						

X-ray powder diffractometer HZG4-AREM/Seifert, step-scanning 0.05°/7 s in the range 8°–54° 2θ CuKα.

The recent assignment of infrared spectrum of liebigite presented by Amayri (2002) is based on the mentioned papers by Čejka et Urbanec. Jones et Jackson (1993) published the infrared spectrum of liebigite without any interpretation. Infrared spectrum of liebigite described in this paper practically agrees with the published spectra (Table 3).

Table 2. Unit cell parameters of liebigite (for orthorhombic space group *Bba2*)

		a	b	c	V
Příbram-Háje	this paper	16.708 (4)	17.557 (4)	13.713 (3)	4022.6 (1.2)
Jáchymov	Mereiter (1982)	16.699 (3)	17.557 (3)	13.697 (3)	4015.7
Klatovy	Nekl, Goliáš (2002)	16.71 (1)	17.55 (2)	13.71 (1)	4020.6
Rožná	Řidkošil et al. (1993)	16.659 (7)	17.53 (1)	13.670 (9)	3992.1
synt.	Appleman (1956)	16.740	17.540	13.720	4028.5

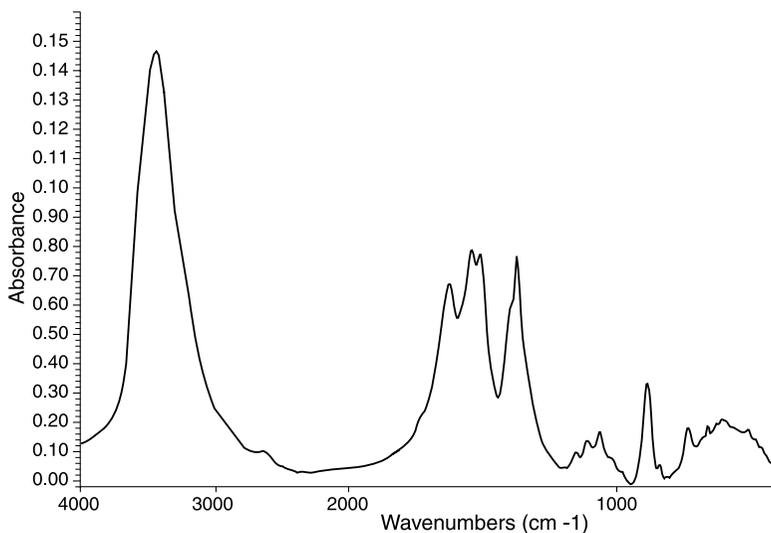


Fig. 5. The infrared absorption spectrum of liebigite, Příbram-Háje (FTIR Nicolet 740).

A band at 894 cm^{-1} was assigned to the antisymmetric stretching vibration $\nu_3\text{ UO}_2^{2+}$. Because of the symmetry lowering of the UO_2^{2+} group, the symmetric stretching vibration, $\nu_1\text{ UO}_2^{2+}$, becomes infrared active. A band related to this vibration should be located in the range $817\text{--}840\text{ cm}^{-1}$ as calculated from two empirical relations expressing the dependence of the symmetric stretching vibration $\nu_1\text{ UO}_2^{2+} = f(\nu_3\text{ UO}_2^{2+})$ (for details see e.g. Čejka 1999).

The U-O_I bond length in uranyl, UO_2^{2+} , was calculated with a set of empirical relations published by Veal et al. (1975), Barlett et Cooney (1989), Glebov (1989), Syt'ko et al. (2001, 2003) and Čejka et al. (in preparation). These empirical relations express the dependence of the U-O_I bond length (Å) on the $\nu_3\text{ UO}_2^{2+}$ antisymmetric stretching vibration (cm^{-1}) ($R_{\text{U-OI}} = a + b\nu_3^{-2/3}\text{ Å}$) (for details see e.g. Čejka 1999). Calculated U-O_I bond lengths in uranyl vary in the range $1.770\text{--}1.794\text{ Å}$ and excellently agree with the U-O_I bond length from the X-ray crystal structure analysis 1.779 Å (Mereiter 1982) and EXAFS 1.804 Å (Amayri 2002). A very weak band at 821 cm^{-1} may be assigned to the $\nu_1\text{ UO}_2^{2+}$. This band is located in the range mentioned above. Barlett et Cooney (1989) published also an empirical relation expressing $R_{\text{U-OI}}(\text{cm}^{-1}) = f(\nu_1)\text{ Å}$. The wavenumber 821 cm^{-1} corresponds with $R_{\text{U-OI}} = 1.789_6\text{ Å}$, this is also in agreement with calculated bond lengths using the $\nu_3\text{ UO}_2^{2+}$.

The infrared spectrum of liebigite indicates that the symmetry of the CO_3^{2-} ion is reduced from D_{3h} lower than C_{2v} (inferred from site symmetries of all constituents if the space group of liebigite is $Bba2 - C_{2v}^{17}$) (Ross 1972, Nakamoto 1986). All vibrations of CO_3^{2-} ions are therefore infrared active and doubly degenerate vibrations ν_3 and ν_4 are split. An absorption band at 1074 cm^{-1} may be assigned to the $\nu_1\text{ CO}_3^{2-}$ symmetric stretching vibration. Some other weak absorption bands in the region $989\text{--}1206\text{ cm}^{-1}$ may be probably related to the ν_3 antisymmetric and ν_1 symmetric stretching vibrations of

Table 3. Infrared spectrum of liebigite from Příbram in comparison with the published data

Příbram-Háje (this paper)	Colorado, USA (Jones, Jackson 1993)	Jáchymov (Čejka, Urbanec 1976)	synthetic (Amayri 2002)	Tentative assignment
3573 sh 3446 vs 3260 sh	3484	3450 ssh	3402	ν OH stretch
2622 vw	2622			$(\nu_1+\nu_3)$ CO_3^{2-}
1745 sh				$(\nu_1+\nu_4)$ CO_3^{2-}
1638 s	1624	1632 wsh 1590 sw	1620 s	δ H_2O bend
1551 s 1520 s 1405 sh 1385 s	1549 1515 1379	1538 s 1504 sh 1395 sh 1378 vs	1537 vs 1404 s 1385 w	ν_3 CO_3^{2-} antisymmetric stretch
1206 vw 1161 vw 1119 w	1159	1110 w		ν_3 SO_4^{2-} antisymmetric stretch (?)
1074 wm 1020 sh	1070	1069 wm 1020 wm	1076 w	ν_1 CO_3^{2-} symmetric stretch
989 vw				ν_1 SO_4^{2-} symmetric stretch (?)
894 m	902 893	sh 890 s	899 s	ν_3 UO_2^{2+} antisymmetric stretch
846 w 821 vw	846 823 799	841 w	847 w	ν_2 CO_3^{2-} out-of-plane bend and/or ν_1 UO_2^{2+} symmetric stretch
742 wm 669 m	742	737 mw 682 w	743 vw 691 w	ν_4 CO_3^{2-} in-plane band
633 m 611 m 515 m				libration modes of water molecules and/or ν_4 SO_4^{2-} bend

FTIR spectrophotometer Nicolet 740 (absorption spectrum of the mineral phase dispersed in KBr disk). Character of absorption maxima: sh – shoulder, b – broad. Intensity scale: vs – very strong, s – strong, ms – medium strong, m – medium, mw – medium weak, w – weak, vw – very weak.

SO_4^{2-} ions (liebigite may be contaminated by traces of gypsum). Amayri (2002) presented the infrared spectrum of very pure synthetic liebigite, in which only the band at 1074.7 cm^{-1} ($\nu_1 \text{CO}_3^{2-}$) is present. The spectrum does not contain any additional bands in this region. The bands at 842 and 821 cm^{-1} may be connected with the $\nu_2 \text{CO}_3^{2-}$ out-of-plane bending vibration. However, the very weak band at 821 cm^{-1} may be related to the $\nu_1 \text{UO}_2^{2+}$ symmetric stretching vibration, as mentioned above. Wavenumbers of the split $\nu_3 \text{CO}_3^{2-}$ antisymmetric stretching vibrations lie at 1551 , 1520 , 1404 and 1385 cm^{-1} . Bands at 742 and 669 cm^{-1} are assigned to the $\nu_4 \text{CO}_3^{2-}$ in-plane bending vibrations. The number of observed vibrations is lower than expected from the presence of three structurally nonequivalent carbonate groups in the crystal structure of liebigite (Mereiter 1982). A shoulder at 1745 cm^{-1} is connected with $(\nu_1 + \nu_4) \text{CO}_3^{2-}$ combination vibration and a very weak broad band at 2621 cm^{-1} with $(\nu_1 + \nu_3) \text{CO}_3^{2-}$ combination vibration (Taravel et al. 1973).

The presence of water molecules is manifested by the ν_2 (δ) H_2O bending vibration at 1638 cm^{-1} , and the ν OH (ν_1 and ν_3) stretching vibrations appearing at 3573 (sh), 3446

and 3260 (sh) cm^{-1} . Some bands with low intensity below 670 cm^{-1} may be assigned to libration modes of water molecules. A very strong band with two shoulders assigned to the νOH stretching vibrations corresponds to the presence of structurally nonequivalent water molecules bonded with various strength in layers and in the interlayer of the crystal structure of liebigite. This agrees with crystal structure (Mereiter 1982) and thermal analysis of natural and synthetic liebigite (Čejka 1969, 1999; Čejka et Urbanec 1979; Amayri 2002). The observed wavenumbers of the νOH stretching vibrations show that water molecules form hydrogen bonds with O-H...O bond lengths approximately 3.1, 2.95 and 2.73 Å (Libowitzky 1999). This is practically in agreement with hydrogen bonds inferred from the crystal structure of liebigite (Mereiter 1982).

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