

Original paper

Newly described uranium mineralization with ruthefordine from former arsenic mine Giftkies, Jáchymov ore district, Czech Republic

Michal ROLL^{1,2*}, Viktor GOLÍÁŠ¹, Jiří ZACHARIÁŠ¹, Jakub PLÁŠIL³, Lukáš FALTEISEK⁴

¹ Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague, Albertov 6, CZ–128 43, Prague 2, Czech Republic

² Institute of Geology of the Czech Academy of Sciences, Rozvojová 269, Prague 6, 165 00, Czech Republic, roll@gli.cas.cz

³ Institute of Physics of the Czech Academy of Sciences, Na Slovance 1999/2, 182 21 Prague 8, Czech Republic

⁴ Department of Ecology, Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic

*Corresponding author



The Giftkies mine is the only known locality of ruthefordine within the *Jáchymov ore district s.l.*, which is famous for the occurrence of many uranyl carbonates. Uranyl monocarbonate ruthefordine, $\text{UO}_2(\text{CO}_3)$, investigated in this study, has been found in significant amounts in the abandoned arsenic mine at Giftkies site (*Jáchymov*, Czech Republic), together with other uranyl carbonates, common liebigite and scarce agricolaite. The possible specific conditions of ruthefordine formation prompted the detailed study with the following analytical methods. XRD methods helped identify above mentioned minerals as well as other secondary minerals reported from this site, 31 minerals in total. The mineralization sequence was investigated and determined by both optical and scanning electron microscopy to be: quartz → early siderite → late siderite → pyrite → iron oxyhydroxides → ruthefordine. This microscale investigation of textural features and element admixtures helped to create above mentioned paragenetic scheme. Further on alpha spectrometry and radiometric dating of ruthefordine helped to build a timeframe. A daughter deficiency method using $^{230}\text{Th}/^{234}\text{U}$ isotopic pair provides late Holocene ages and suggests at least two ruthefordine formation episodes (4600–2600 years BP and 1350–300 years BP respectively). According to data, we claim that supergene processes that lead to ruthefordine crystallization at the site started at the beginning of the Subboreal period and lasted until nowadays.

Keywords: ruthefordine, uranyl carbonates, radiometric dating, SEM analysis, supergene weathering, *Jáchymov*

Received: 13 June 2023; **accepted:** 9 April 2024; **handling editor:** R. Skála

1. Introduction

Carbonate minerals containing hexavalent U as the uranyl ion $(\text{UO}_2)^{2+}$, are common alteration products of uraninite weathering under oxidizing conditions (Finch and Murakami 1999; Krivovichev and Plášil 2013). Uranyl carbonates are usually relatively soluble in aqueous solutions; aqueous uranyl-carbonate complexes are thermodynamically stable, and they are responsible for the migration of uranium in the environment on a large scale under low temperatures (Langmuir 1978; Clark et al. 1995). The most abundant complexes are uranyl monocarbonate, $[(\text{UO}_2)(\text{CO}_3)]^0$, uranyl dicarbonate, $[(\text{UO}_2)(\text{CO}_3)_2]^{2-}$ and uranyl tricarbate, $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$, with pKa values of 5.5, 7, and 9, respectively (Langmuir 1978). The most common uranyl carbonate minerals are those with a $\text{UO}_2:\text{CO}_3$ ratio of 1:3, which crystallize from solutions of a relatively high range of pH, from neutral to alkaline. The most common are uranyl tricarbonates, such as schröckingerite $\text{NaCa}_3[(\text{UO}_2)(\text{CO}_3)_3](\text{SO}_4)\cdot 10\text{H}_2\text{O}$ (Mereiter 1986; O'Brien and Williams 1983)

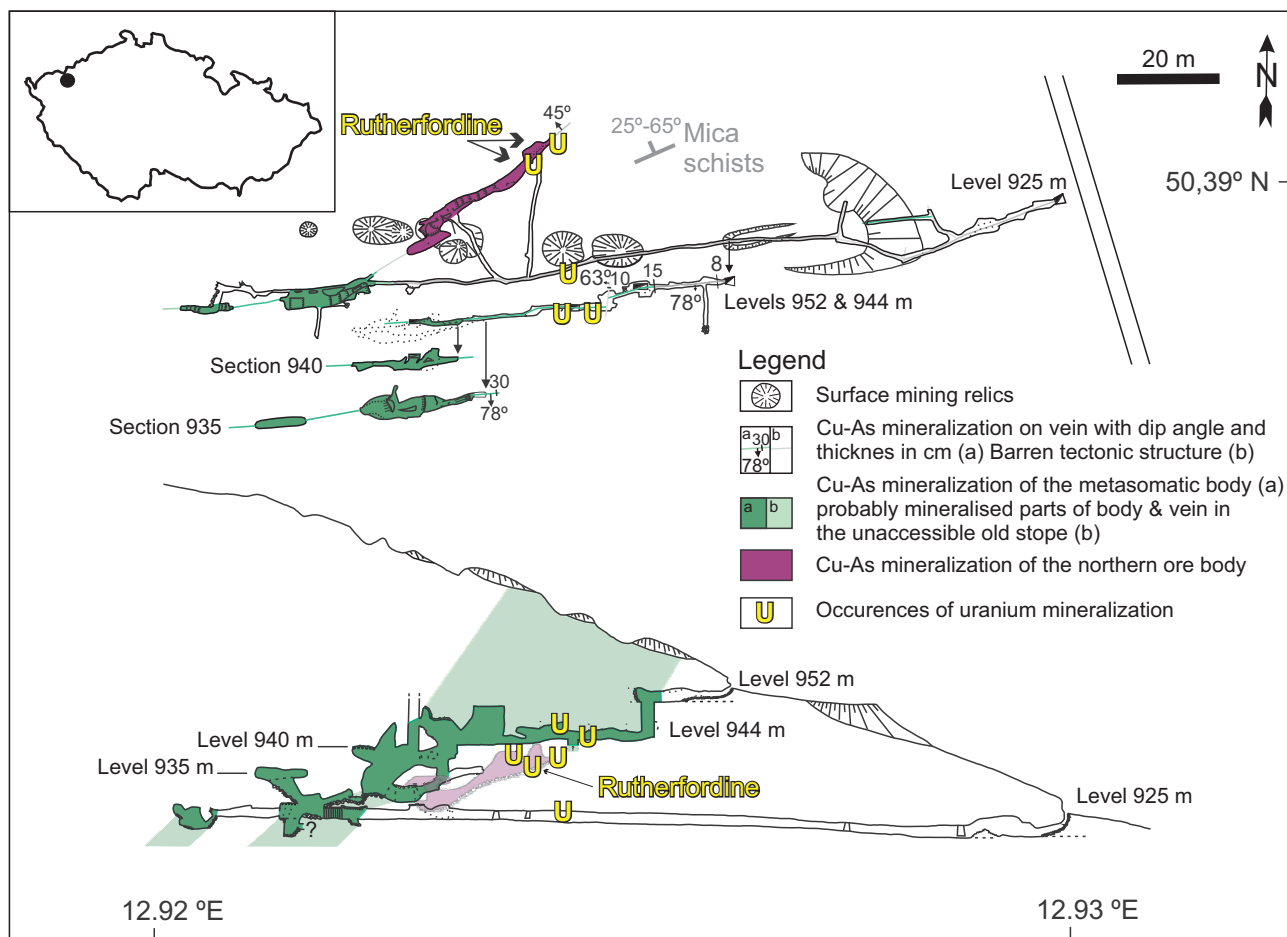
and liebigite $\text{Ca}_2[(\text{UO}_2)(\text{CO}_3)_3]\cdot 11\text{H}_2\text{O}$ (Frost et al. 2005). On the other hand, uranyl monocarbonates are not so abundant. Nevertheless, up to date, few monocarbonates have been reported as minerals: ruthefordine, $\text{UO}_2(\text{CO}_3)$ (Marckwald 1906), blatonite, $(\text{UO}_2)(\text{CO}_3)(\text{H}_2\text{O})$ (Vöchten and Deliens 1998), and joliotite, $(\text{UO}_2)(\text{CO}_3)(\text{H}_2\text{O})_{1.5-2}$ (Walenta 1976). The most common is ruthefordine, which has been reported from more than 60 localities worldwide (Mindat 2022). However, there are only a few sites where it has been found in significant quantities, as one of the major constituents of the oxidized portion of the ore: at Shinkolobwe (Kambove Territory, Democratic Republic of Congo), Krunkelbach (Black Forest Mountains, Germany) and *Jáchymov* (Krušné Hory Mountains, Czech Republic).

In this work, we have investigated uranyl carbonates (ruthefordine, liebigite, and agricolaite) found within ore stope of the second level of the Giftkies mine, sub-locality of *Jáchymov ore district s.l.* Other secondary minerals found at Giftkies mine are summarized in Tab. 1.

Tab. 1 Secondary minerals reported from the Giftkies mine, Jáchymov (Czech Republic).

<i>Carbonates</i>		<i>Uranyl oxides</i>	
agricolaite	$K_4(UO_2)(CO_3)_3$	becquerelite	$Ca[(UO_2)_6O_4(OH)_6] \cdot 8H_2O$
azurite	$Cu_3(OH)_2(CO_3)_2$	compreignacite	$K_2[(UO_2)_3O_2(OH)_3]_2 \cdot 7H_2O$
liebigite	$Ca_2(UO_2)(CO_3)_3 \cdot 11H_2O$	paulscherrerite	$(UO_2)(OH)_2$
malachite	$Cu_2(OH)_2CO_3$	masuyite	$Pb[(UO_2)_3O_3(OH)_2] \cdot 3H_2O$
metazellerite	$Ca(UO_2)(CO_3)_2 \cdot 3H_2O$	metaschoepite	$(UO_2)_2O_2(OH)_{12} \cdot 10H_2O$
UM1997-23-CO:CaCuHU*	$Ca_5Cu(UO_2)_4(CO_3)_6(OH)_8 \cdot 4H_2O$	vandendriesscheite	$Pb_{1.57}[(UO_2)_{10}O_6(OH)_{11}] \cdot 11H_2O$
rutherfordine	$(UO_2)(CO_3)$	schoepite	$(UO_2)_8O_2(OH)_{12} \cdot 12H_2O$
zellerite	$Ca(UO_2)(CO_3)_2 \cdot 5H_2O$		
<i>Arsenates</i>		<i>Silicates</i>	
geminite	$Cu(AsO_3OH) \cdot H_2O$	cuprosklodowskite	$Cu(UO_2)_2(SiO_3OH)_2 \cdot 6H_2O$
metazeunerite	$Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$	soddyite	$Mg(UO_2)_2(SiO_3OH)_2 \cdot 6H_2O$
slavkovite	$Cu_{13}(AsO_4)_6(AsO_3OH)_4 \cdot 23H_2O$	uranophane	$Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$
yvonite	$Cu(AsO_3OH) \cdot 2H_2O$	kasolite	$Pb(UO_2)[SiO_4] \cdot H_2O$
<i>Sulfates</i>			
antlerite	$Cu_3SO_4(OH)_4$		
brochantite	$Cu_4SO_4(OH)_6$		
jarosite	$KFe_3(SO_4)_2(OH)_6$		
posnjakite	$Cu_4SO_4(OH)_6 \cdot H_2O$		
rabejacite	$Ca_2[(UO_2)_4O_4(SO_4)_2] \cdot 8H_2O$		
uranopilite	$[(UO_2)_6(SO_4)_2O_2(OH)_6(H_2O)_6] \cdot 8H_2O$		
cyanotrichite	$Cu_4Al_2SO_4(OH)_{12} \cdot 2H_2O$		
chalcophyllite	$Cu_{18}Al_2(AsO_4)_4(SO_4)_3(OH)_{24} \cdot 36H_2O$		
beudantite	$PbFe_3(AsO_4)(SO_4)(OH)_6$		

*related to paddlewheelite $MgCa_3Cu_2[(UO_2)(CO_3)_3]_4 \cdot 33H_2O$ (Olds et al. 2018), from older literature also known as “Pseudo-voglite” (Ondruš et al. 1997).



2. Geological settings and exploration history

The western part of Krušné Hory Mountains is represented by the *Krušné Hory Crystalline Complex*, which consists of various granite bodies of Variscan age overlaid by gneisses and mica schists of the *Klínovec group* (Chlupáč et al. 2011). The *Jáchymov ore district s.s.* represents a classic example of five-element association (Ag–Ni–Co–Bi–As) and it is also one of the most world-recognized U hydrothermal deposits (Ondruš et al. 2003b), which is tectonically strictly separated from the other ore districts in the region (Ondruš et al. 2003a). Giftkies mine is located in the valley of Veseřice Creek (Elbecken or Ölbecken valley in archive materials), in the two upper Giftkies adits (Fig. 1). There are sharply developed subvertical ore veins of variable thickness ranging 15–30 cm, with transitions into metasomatic body of intensive silicification in the mica schist, following an E–W trending vein, approximately 150 m above underlying granite intrusion. Both historical adits follow this complex structure. The subvertical metasomatic body is 1.5 to 4 meters thick and approximately 15 to 20 meters long in a vertical section. Both vein and the metasomatic body are intensively mineralized by arsenopyrite, chalcopyrite and tennantite. Also, clusters of oxide minerals, represented mainly by large idiomorphic crystals of anatase (up to 2 mm) and dark blue cloud-like structured hematite, were observed locally in silicified host rock. The vein and the metasomatic body steeply inclined to the south, mineralized section generally inclined about 40° to the west. Sulfide mineralization was the subject of historical arsenic mining, which started at this site in the early 17th century. The ore deposit was opened from the surface by three adits, one above another. Two upper adits were excavated between 1618 and 1771, while the lowest adit was excavated during the exploration for uranium during the 1950's (Kořan and Mrňa 1967). Attempts to excavate uranium mineralization are still apparent in the mine, sparse blasting works were done in rather uncomfortable and unsuitable conditions of very narrow mining stopes and galleries. The difficulties connected with transportation of material from the underground and overall low-grade of uranium ore most probably stopped any other prospection works. Uranium mineralization formed cluster of ore lenses, those are not regularly developed, they have variable thickness, gangue is dominantly represented by quartz (of the amethyst to morion varieties), carbonates (dolomite and siderite) ap-

pear sporadically on microscale and they are mineralized by uraninite.

3. Materials and methods

3.1. Optical and electron microscopy

Three polished and three glass-covered thin sections were prepared from a gneiss sample. Thin sections were oriented in two mutually perpendicular directions, both perpendicular to metamorphic foliation. Thin sections were studied first by optical polarizing microscope Leica DLMP (magnification up to 1000×, photo-documentation by digital camera Jenoptik ProgRes® C5), both in transmitted and reflected light). Detailed mineralogy was studied using a TESCAN Vega scanning electron microscope equipped with an energy dispersive spectrometer (EDS detector X-Max 50 from Oxford Instruments) hosted at the Institute of Petrology and Structural Geology, Faculty of Science, Charles University. Operating conditions: 15 kV acceleration voltage, 1.5 nA beam current, focused beam diameter approx. 600 nm, live time acquisition 100 s, using an INCA data acquisition and processing software (Oxford Instruments).

3.2. X-ray diffraction

All secondary minerals listed in Tab. 1 were identified by powder X-ray diffraction (PXRD). For these analyses, a PANalytical Empyrean diffractometer (Institute of Physics, Czech Academy of Science) was employed using CuK α radiation in the range from 3° 2 θ to 70° 2 θ at room temperature. The integrated step size was set to 0.015° 2 θ and dwelltime to 3 s per step. Only kasolite and uranophane were identified by powder X-ray microdiffraction technique (μ -PXRD) on the PANalytical X'Pert PRO diffractometer (Faculty of Science, Charles University in Prague) was employed using CuK α radiation in the range from 3° 2 θ to 80° 2 θ at room temperature. The integrated step size was set to 0.05° 2 θ , virtual counting time 2 000 s and 800 μ m capillary optic was used. Both methods used HighScore Plus software.

3.3. Alpha spectrometry

Non-destructive alpha spectrometry was utilized for the determination of radionuclides and the type of radioactive equilibrium. Data were collected on a CANBERRA PIPS 450 mm² semiconductor detector with an ORTEC 142A pre-amplifier and CANBERRA 10 SERIES Plus multi-channel analyzer controlled by GENIE2000 software. Samples were separately powdered in an agate bowl with

⇐

Fig. 1 Giftkies mine, Jáchymov, underground map and the longitudinal projection. The mineralization is hosted in the gneisses and mica schists. Mapping was carried out between the years 2017–2019 by Lukáš Falteisek and Mária Mikšaníková, adjusted by Viktor Golíáš.

distilled water. Each powdered sample was deposited from the water suspension onto a polished stainless steel disc (22 mm in diameter), those were heated to dryness and then weighed. This non-destructive method (Plášil et al. 2010) has been modified after Killeen and Carmichael (1976). Obtained data were used for the evaluation of suitability for age determination via destructive alpha spectrometry. We assumed the Quaternary ages of collected minerals. In this regard, the $^{230}\text{Th}/^{234}\text{U}$ method was chosen. Suitable samples were treated with the following procedure for uranium and thorium separation introduced by Horowitz et al. (1992) further developed by Maxwell (1998), Carter et al. (1999), Skinner and Knight (2016) and appropriately adjusted by authors. The sample was dissolved in 65% HNO_3 (subsequently purified by sub-boiling distillation) having an aliquot activity of 1 Bq and spiked by the $^{232}\text{U}/^{228}\text{Th}$ (Harwell spike) of an equal activity. The sample was evaporated close to dryness, dissolved in 0.5M $\text{Al}(\text{NO}_3)_3$ in 4M HNO_3 and adsorbed onto activated UTEVA® chromatographic resin. The thorium fraction was stripped by 5 ml of 6M HCl and then the uranium fraction by 15 ml of 0.02M HCl . Each fraction was evaporated and diluted in 0.3M Na_2SO_4 in H_2SO_4 buffered at pH 1.6. Thorium and uranium targets were prepared by electrodeposition in teflon cell using Pt–Ir cathode (Crespo 2012) and polished stainless steel discs, which served as anode and bottom of the cell (using a current density of $0.22 \text{ A} \cdot \text{cm}^{-2}$ for uranium and $0.34 \text{ A} \cdot \text{cm}^{-2}$ for thorium). Newly prepared targets were sealed with ammonium solution, dried and subsequently measured by alpha spectrometry. For the analytic evaluation, an in-house standard: PU-1 (Příbram uraninite, Variscan pitchblende) (Feigl 2003) was used instead of scarce HU-1 (Harwell uraninite). This reference material provided following equilibrium: $^{234}\text{U}/^{238}\text{U} = 0.998 \pm 0.008$, and $^{230}\text{Th}/^{234}\text{U} = 0.991 \pm 0.054$ (1σ).

4. Results

4.1. Description of uranyl carbonates

Agricolaite, $\text{K}_4(\text{UO}_2)(\text{CO}_3)_3$ is a scarce mineral, first described from the Giftkies site by Skála et al. (2011). It has been found only in several specimens worldwide, including the one investigated in this paper. Mostly it forms an aggregate of irregular monoclinic crystals of yellow colour and vitreous luster. Agricolaite crystals cover the surface of the vein material, consisting of dominantly quartz gangue (including dark varieties), mica schists fragments, and hematite.

Liebigite, $\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 11\text{H}_2\text{O}$ occurs within the anthropogenic debris at the floor of gallery, cementing the fragments or overgrowing the surface of rock frag-



Fig. 2 Spherical aggregates of rutherfordine with common overgrowths, and an example of goethite core (left upper part of the photo), field of view 2.1 mm, photo: L. Vrtiška.

ments, where it forms well-developed euhedral crystals of the yellow–greenish color and their aggregates cover areas up to the first tens of cm^2 . Among other uranyl minerals described from the debris, liebigite is relatively less abundant. The specimen investigated in this study was discovered approximately at 10 to 15 cm below the surface of the ground floor and apparently, the horizon has not suffered from the previous digging for a relatively long time (based on the character of the debris and the degree of compaction).

Rutherfordine, $(\text{UO}_2)(\text{CO}_3)$ was found both on the rock wall near the primary mineralization and within the anthropogenic debris. Mineral precipitated within tiny open fractures and cavities almost perpendicular to a metamorphic foliation. Mineral forms mostly spherical aggregates consisting of a core and outer rutherfordine shell, with common overgrowths (Fig. 2). Core is either iron oxyhydroxide phase (most likely goethite) or free space. The most suitable hypothesis for the missing solid core could be the presence of iron oxyhydroxide gel, which was overgrown by rutherfordine. Gel crystallized



Fig. 3 Thin, radial, plate-like crystals of rutherfordine with visible prismatic texture, underlined with carbonate, field of view 4.3 mm, photo: L. Vrtiška.

later to solid phase (most likely goethite again), and it was ripped off from the outer ruthefordine shell due to a volume contraction (water loss). Ruthefordine also forms radially plate-like aggregates, parallel with metamorphic foliation (Fig. 3). Fissures are locally coated by carbonates (mostly siderite). Ruthefordine crystals are mostly of pale yellow colour, only seldom of the bright yellow color that is more apparent, with individual reach up to 2 mm in diameter. Nevertheless, these aggregates form clusters, which may cover large areas of the quartz fissures and thin veinlets, up to dozens of cm². Among those three, only ruthefordine was suitable for radiometric dating (according to non-destructive alpha spectrometry).

4.2. Paragenetic relationships and EDS analysis

EDS-analysis of the polished thin-sections confirmed that most of the ruthefordine occurrences are related to tiny fractures (veins) and cavities (intra-vein cavities; Fig. 4a) that crosscut the metamorphic foliation at a high angle (Fig. 4b). Five separate episodes of mineral formation were identified in total (from oldest to youngest). Episodes (1–2) represent the main stage of hydrothermal evolution, episode (3) may represent a vanishing phase of previous hydrothermal activity (1–2), or a new one in time separated hydrothermal phase/input. Episode (4) by its oxygenated nature very likely indicates the onset of the supergene stage, followed by the formation of ruthefordine (5).

- 1) Quartz gangue locally with enclosed gneiss and mica fragments (Fig. 4b) most likely hydrothermal origin (analogy with *Jáchymov ore district s.s.*).
- 2) sideritic gangue, coarse-grained, locally with euhedral crystals, open cavities and gneiss and mica fragments (Fig. 4c). Two siderite generations systematically occurred in all thin sections, both exhibiting growth zoning (Fig. 4c–f) due to minor to moderate variations in Fe/Ca/Mn proportions. Subhedral to euhedral grains of the early siderite (Sd-1) contain numerous empty growth-like zones (Fig. 4f), the thickness of which is the same as that of siderite-filled growth zones. We were not able to prove if the empty zones were primary in nature, or if they contained a mineral phase that had been leached out. Late siderite (Sd-2) overgrows the early one, there is no visible evidence that any mineral phase would precipitate in between the two. Two prominent features are associated with the Sd-2: a) absence of “empty” growth zones in Sd-2; b) clear evidence of corrosion of several outermost growth zones of Sd-2 (Fig. 4c) and formation of open irregular microfractures (wedge-like; Fig. 4f). Both phenomena (corrosion and fractures) occurred prior to the onset of ruthefordine crystallization.
- 3) Rounded, concentric grains of pyrite (Py) locally overgrow the corroded or non-corroded surface of Sd-2

(Fig. 4c–d). The two phases (Sd-2, Py) therefore did not crystallize from the same fluid.

- 4) Iron oxyhydroxides (most probably goethite) contain a non-negligible admixture of uranium (1.9–5.3 wt. % UO₂), copper (1.3 to 5.0 wt. % CuO), zinc (1.0 to 2.2 wt. % ZnO) and occasionally also arsenic (0.6–1.2 wt. % As₂O₃). Iron oxyhydroxides generally postdate the siderite and most of pyrite grains were converted to pseudomorphs of goethite after pyrite (Fig. 4g–h). These are further overgrown by a thin continuous layer of iron oxyhydroxides, locally with an inter-layer, which is also enriched in copper, zinc (up to 2 wt. % each). Some parts of the siderite filling, typically the Sd-1, were transformed into a mixture of Sd-1 relics (complete or incomplete pseudomorphs of iron oxyhydroxides after Sd-1; Fig. 5a–b and Fig. 5c) intergrown with chemically homogenous (i.e. unzoned at BSE photos) anhedral siderite grains. This siderite (possibly Sd-2) lacks any evidence of corrosion or oxidation. We may speculate that postdates the formation of iron oxyhydroxides, or that formed prior to them; however, the fluid was not able to dissolve/corrode it.
- 5) Ruthefordine occurs as a) radial crust overgrowing the Sd-2 crystals (with or without overgrowing pyrite) in open cavities in the siderite gangue (Fig. 4a, c–e) and can contain micron-sized (1–20 µm) sheet-like particles (Figs 4d, 5d) of phyllosilicates (most likely kaolinite, dickite or some micas and eventually their oxidized products), containing mainly silica (15–43 wt. % SiO₂), alumina (11–35 wt. % Al₂O₃), iron (4.1–15.6 wt. % Fe₂O₃), potassium (1.4–6.8 wt. % K₂O), coupled with traces of magnesium (0.8–2.4 wt. % MgO), uranium (9–48 wt. % UO₂), copper (0.3–1.8 wt. % CuO) and sometimes also sulfur (0.7–1.0 wt. % SO₃). They formed during the early stage of ruthefordine precipitation (i.e., occur in the core of radial ruthefordine aggregates, while are missing in their peripheral zones). Locally, the multilayer ruthefordine aggregates (4c) are overlain by thin iron oxyhydroxide coating (Fig. 4h); b) thicker multilayer aggregates (Fig. 5c, e–f) with numerous concentrically-zoned botryoidal aggregates of iron oxyhydroxides (in thin section). Although enclosed in ruthefordine, we suggest they represent spurs of underlying iron oxyhydroxide layer and precipitated prior to ruthefordine. Some of the latter grains can also contain phyllosilicates (probably dickite or kaolinite infill or altered gneiss/mica fragments in their cores, Fig. 5f); and c) separate thin veinlets (ranging from 50 to 100 µm), usually monomineral, that crosscut the quartz gangue (Fig. 4b), the siderite gangue and the host-gneiss. The orientation of some veinlets turns from almost perpendicular into a metamorphic foliation parallel arrangement (Fig. 4b).

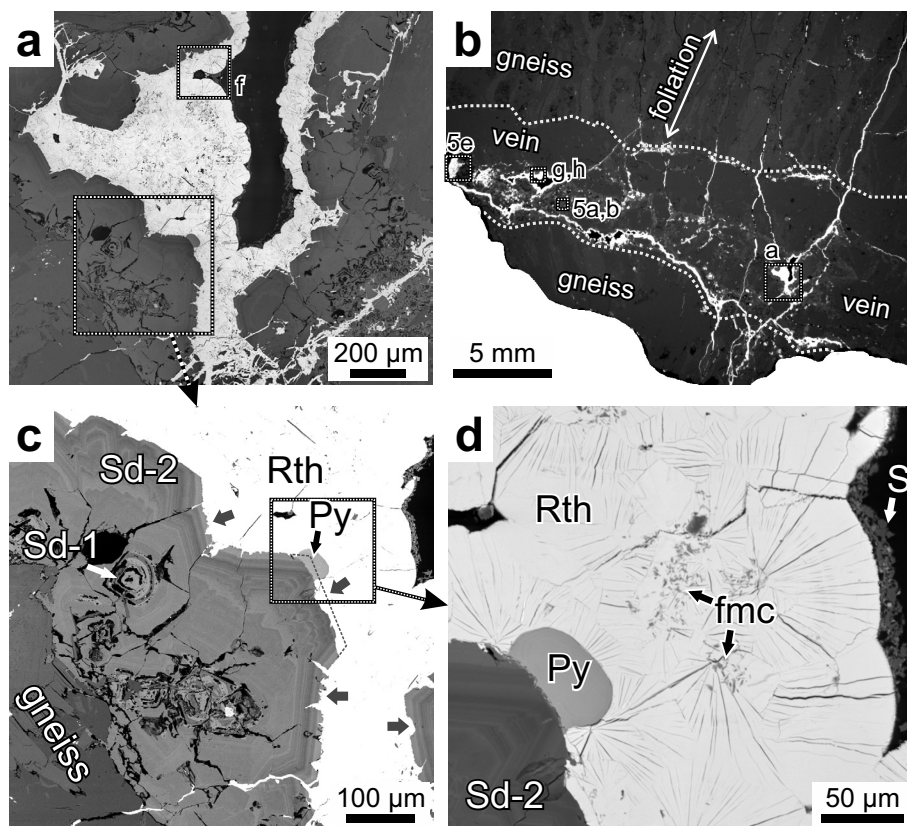


Fig. 4 Documentation of textural relations in the sample with rutherfordine (BSE photos of a thin polished section): **a** – an overview of vein margin with siderite infill and a cavity incompletely filled in with rutherfordine (Rth); **b** – a general overview of the sample. The outlines of the composite quartz-siderite-rutherfordine vein are highlighted by dotted yellow lines. Rutherfordine veinlets and coatings are white, mostly parallel with vein margins, but also parallel with metamorphic foliation; **c** – detail of siderite infill overgrown by rutherfordine. The red arrows mark fracturing and/or corrosion of siderite (Sd-2) prior to rutherfordine crystallization. A thin dotted red line outlines the hypothetical extent of siderite crystal before its corrosion; **d** – detail of the corroded surface of Sd-2 overgrown by pyrite (Py) and rutherfordine. Note the presence of tiny phyllosilicates most likely mica/clay phases (fmc) in the core of rutherfordine aggregate; **e** – corroded surface (red arrow) of Sd-2 overgrown by rutherfordine; **f** – detail from **d** of growth zones in Sd-1 and Sd-2. The black zones in the Sd-1 are empty; **g** – rutherfordine overgrowing the siderite (Sd-2). Note the presence of a thin continuous layer of iron oxyhydroxides (Gt) in between rutherfordine and siderite; **h** – detail view of the iron oxyhydroxide layer from the previous photo.

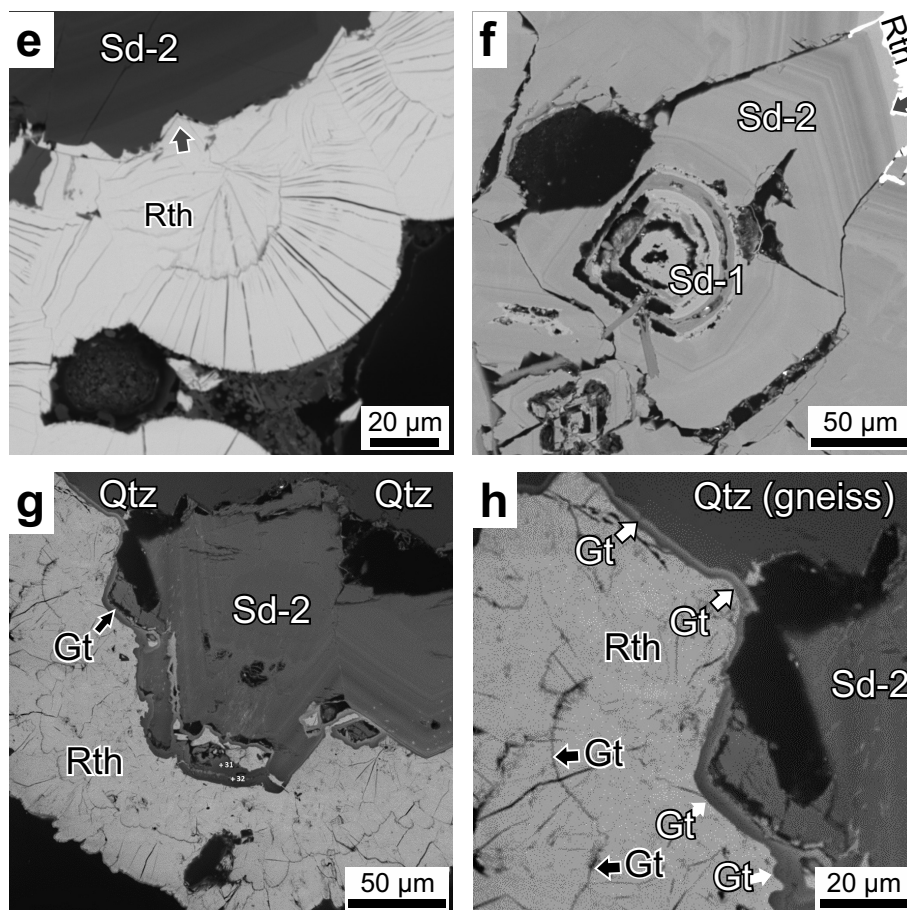
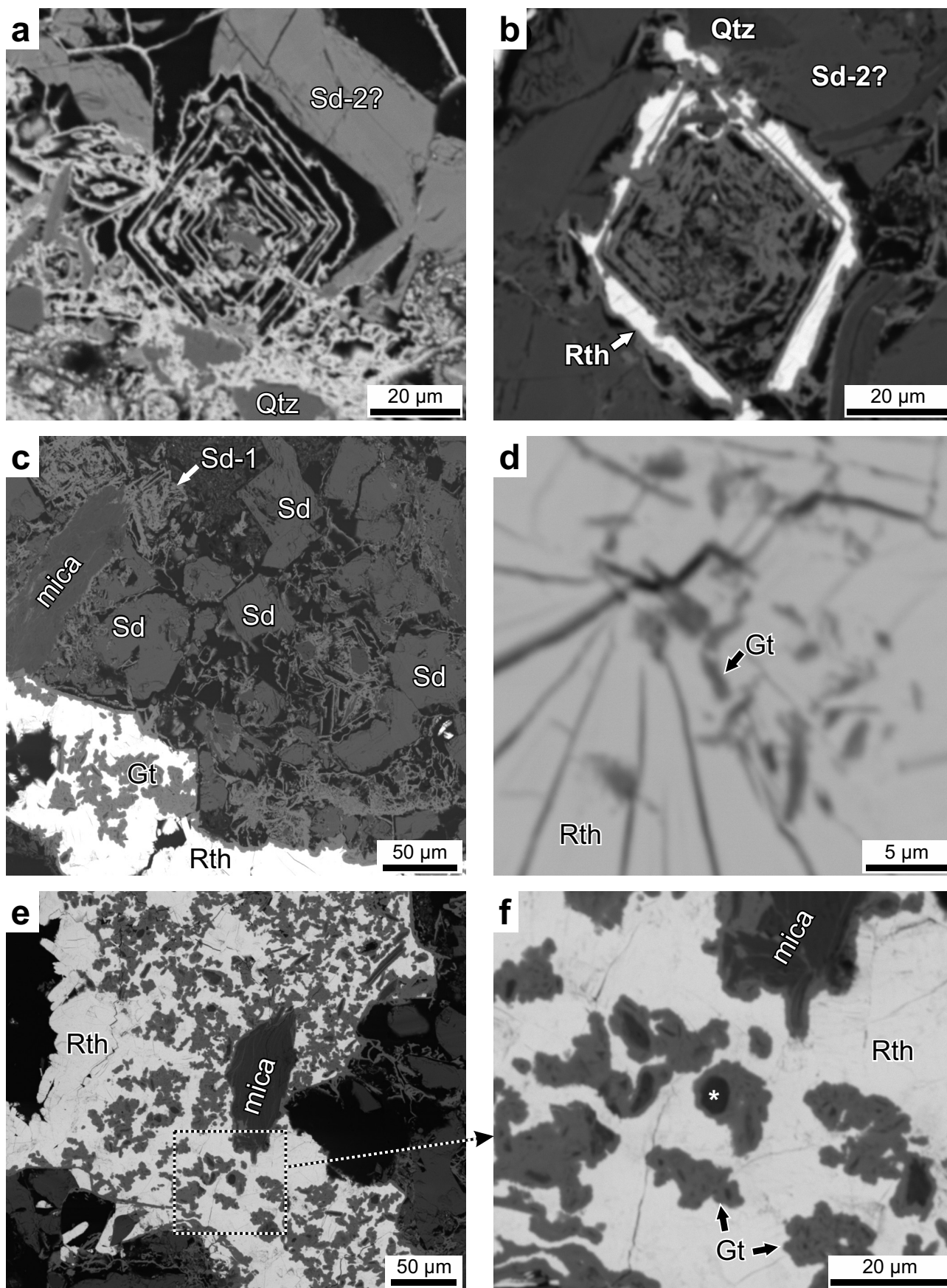


Fig. 5 Documentation of textural relations in the sample with rutherfordine (BSE images): **a** – pseudomorphs of iron oxyhydroxides after early siderite (Sd-1) intergrown with late siderite (Sd-2?); **b** – similar situation as the previous photo, except for rutherfordine (white) filling in void space between the outermost layers of iron oxyhydroxides. Empty space is black; **c** – an overview of the sample margin with a mixture of siderite (Sd) intergrown with iron oxyhydroxides, most likely goethite (Gt), both phases overgrown by rutherfordine; **d** – detail view of iron oxyhydroxides particles (Gt, medium grey) from the core of rutherfordine aggregate; **e** – massive rutherfordine aggregate overgrowing rim of the sample. It contains numerous iron oxyhydroxide aggregates (Gt, dark grey); **f** – detail of the previous photo, botryoidal iron oxyhydroxide aggregates (light grey) with cores filled in with phyllosilicates (most likely micas).



4.3. Rutherfordine ages

The ratio of $^{230}\text{Th}/^{234}\text{U}$ and 2σ values also $^{234}\text{U}/^{238}\text{U}$ ratio and 2σ values were calculated from activity measured by alpha spectrometry, using a set of equations presented by Majer (1981). For an age determination, the initial $^{234}\text{U}/^{238}\text{U}$ ratio was estimated and the age of the mineral was calculated iteratively. A corresponding initial $^{234}\text{U}/^{238}\text{U}$ ratio was simultaneously calculated via an Excel spreadsheet and subsequently replacing the original estimation for this age. After this readjustment, all calculations were repeated in the same way to obtain a more precise age. Six ages calculated for rutherfordine together with activity ratios for other minerals studied in this work are shown in Tab. 2.

Although all samples were collected with the highest emphasis on the crystals' integrity and purity, rutherfordine no. 3 exhibits extremely large age tolerance, for that could be several possible reasons: accidentally picking up a conglomerate crystal or crystal with incremental zones both can cause a "mixture of ages", contamination with some unwanted material (e.g. siderite) or affected by imperfect uranium and thorium separation. Either way sample is misleading, therefore it will be excluded from further interpretation. Other uranyl carbonates (agricolaite and liebigite) were also excluded from further interpretation due to very young age (we assume first decades to first hundreds of years).

5. Discussion

5.1. Age interpretation

At this moment, we are not able to firmly prove how many generations of rutherfordine are present at the site in total, but according to radiometric data, we can assume the presence of at least two generations of rutherfordine. The upper border of "older" generation is calculated as

age of rutherfordine no. 1 plus its tolerance, lower border is calculated as the age of rutherfordine no. 2 minus its tolerance (values were rounded if appropriate), therefore we obtained two possible intervals: 2σ interval (95.4% of certainty) 4600–2600 years and tighter 1σ interval (68.2% of certainty) 4150–3020 years. The other interval was calculated by the same principles from rutherfordine no. 5 and 6, 2σ interval is 1350–300 years and 1σ interval is 1180–450 years, but with regard to other samples (other uranyl carbonates) and other supergene processes, which can be spotted at the site. It is possible that this interval can be semi-closed (1350–present, 1180–present respectively). Rutherfordine no. 4 even though it overlaps both interval was set aside as a separate analysis due to uncertainty. With all the above mentioned, we believe that rutherfordine formation started at the very beginning of the Subboreal period (or at least not significantly earlier) and lasts till nowadays. We also assume that one of the main factors which led to the crystallization of rutherfordine was fluctuations in underground water level, which was most likely caused (periodically) by significant deforestation. This process has been linked to mining and smelting activities that took place in Krušné Hory Mountains since the Bronze Age till the late Medieval (Bodálková et al. 2018).

5.2. Indirect evidence for the origin of rutherfordine

The following observations are crucial for the discussion of rutherfordine origin/nature. 1) Textural relations indicate the unambiguously very late formation of rutherfordine. We did not identify any mineral phase overgrowing it. 2) No elements other than uranium were identified, by the SEM-EDS analyses, in the rutherfordine; 3) micron-sized phyllosilicates enclosed in the core rutherfordine radial aggregates (Figs 4d, 5d) always contain an admixture of uranium (9–48 wt. % UO_2) and copper (0.3 to 1.8 wt. % CuO). While the highest admixture of uranium may be affected by partial irradiation of the enclosing rutherfordine, the admixture of copper clearly must be of other origins. 4) Pseudomorphs of iron oxyhydroxides after early siderite (Sd-1; Fig. 5a–c) suggest an influx of oxidized acidic waters into the gangue before the precipitation of the rutherfordine. A collateral admixture of copper, zinc, arsenic and uranium in these iron oxyhydroxides and those underlying rutherfordine

Tab. 2 Results of alpha spectrometry of radionuclides in the studied samples from Giftkies mine, Jáchymov.

sample	Activity ratios		Calculated age B.P.
	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$	
rutherfordine 1	0.990 ± 0.022	0.034 ± 0.007	$3\,725 \pm 845$
rutherfordine 2	0.938 ± 0.021	0.031 ± 0.008	$3\,470 \pm 900$
rutherfordine 3	1.105 ± 0.154	0.021 ± 0.019	$2\,335 \pm 2\,185$
rutherfordine 4	0.989 ± 0.011	0.023 ± 0.010	$2\,550 \pm 1\,130$
rutherfordine 5	0.897 ± 0.012	0.009 ± 0.003	$1\,010 \pm 340$
rutherfordine 6	0.972 ± 0.005	0.006 ± 0.004	635 ± 375
agricolaite	$0.405 \pm 0.010^{**}$	N/A	<1 000
liebigite 1	1.116 ± 0.269	0.003 ± 0.006	<1 000*
liebigite 2	$1.065 \pm 0.022^{**}$	N/A	<1 000

* Outside of the dating range, the theoretical age calculated is 280 years.

** Theoretical ratio, indirectly calculated from non-destructive alpha-spectrometry measurement.

N/A – Not available, due to very young age, samples were not investigated by destructive alpha-spectrometry, therefore $^{230}\text{Th}/^{234}\text{U}$ values are not available.

aggregates (Fig. 4g–h) testifies for the supergene origin of acidic waters (i.e., cold and descending) and for leaching of hydrothermal ores, probably uraninite-bearing, located in between the surface and the sample site. 5) The contrast between the massive destruction of early siderite (Sd-1) in some parts of the gangue (Fig. 5a), and only subtle corrosion of some tips of the late siderite (Sd-2; Fig. 4c) may indicate either two separate phases of acidic corrosion or two-stage precipitation of siderite. 7) Precipitation of rutherfordine itself, suggests neutral to weakly alkaline fluid (Hazen et al. 2009; Antoniou et al. 2009; Szecsody et al. 2013).

6. Conclusions

The appearance of rutherfordine investigated in this study is quite unique, this mineral is often associated with uranyl silicates (uranophane, kasolite, cuprosklodowskite) and some other secondary uranyl minerals such as schoepite or phosphuranylite, but in this case, rutherfordine stands alone, even though some above mentioned minerals and numerous more supergene minerals listed in Tab. 1 were reported from the site, none of them is closely associated with this mineral.

Chemical composition of rutherfordine is also surprising. Despite the primary ores are source of arsenic, copper and zinc, as directly evidenced from iron oxyhydroxides enriched with these elements, yet rutherfordine contains only uranium. Therefore, we assume that the solutions from which rutherfordine was formed must have been highly depleted in all those elements except uranium.

Mineralization most probably evolved through a wide span of pH conditions, from highly acidic (iron oxyhydroxides) to highly alkaline (siderite, pyrite), which can be partially explained by climatic fluctuations of groundwater level. We claim that from the beginning of Subboreal period (probable onset of rutherfordine crystallization) till nowadays, pH conditions must have been stable and close to neutral, thus rutherfordine as other uranyl monocarbonates has only a narrow window of precipitation, pH ranging roughly from 4.9 to 6.1, in this narrow section also completely dominates over generally more abundant uranyl tricarbonates which are precipitating mostly in alkaline conditions (pH from 6.0 to 9.5).

Acknowledgments. Authors would like to thank Mária Mikšaníková for her substational help during geological mapping and Luboš Vrtiška for high quality photos of rutherfordine. We would like to also thank František Veselovský and Petr Mikysek for their detailed reviews and insightful comments. Editorial handling by Roman Skála and Vladimír Rappich is also greatly appreciated.

This work was financially supported by project PROGRES Q45 from Charles University in Prague, institutional support RVO67985831 provided by Institute of Geology of the Czech Academy of Sciences and partly by the Czech Science Foundation (GACR 20-11949S).

References

- ANTONIOU S, KOLOKASSIDOU C, POLYCHRONOPOULOU K, PASHALIDIS I (2009) Effect of humic acid on the solid phase stability of UO_2CO_3 . *J Radioanal Nucl Chem* 279/3: 863–866
- BOHDÁLKOVÁ L, BOHDÁLEK P, BRÍZOVÁ E, PACHEROVÁ P, KUBĚNA AA (2018) Atmospheric metal pollution records in Kovářská Bog (Czech Republic) as an indicator of anthropogenic activities over the last three millennia. *Sci Total Environ* 633: 857–874
- CARTER HE, WARWICK P, COBB J, LONGWORTH G (1999) Determination of uranium and thorium in geological materials using extraction chromatography. *Analyst* 124: 271–274
- CHLUPÁČ I, BRZOBHATÝ R, KOVANDA J, STRÁNÍK Z (2011) *Geologická minulost České republiky*. Academia, Prague, pp 1–436 (in Czech).
- CLARK DL, HOBART DE, NEU MP (1995) Actinide carbonate complexes and their importance in actinide environmental chemistry. *Chem Rev* 95: 25–48
- CRESPO MT (2012) A review of electrodeposition methods of the preparation of alpha radiation sources. *Appl Radiat Isot* 243: 322–338
- FEIGL M (2003) Aplikace nové metody pro alfaspektrometrické stanovení obsahu izotopického složení uranu v hutních struskách, uranem barvených skel a produktech jejich alterace. [Master's thesis] Faculty of Science, Charles University in Prague, pp 1–44 (in Czech)
- FINCH RJ, MURAKAMI T (1999) Systematics and paragenesis of uranium minerals. In: BURNS PC, FINCH RJ (eds) *Uranium: Mineralogy, Geochemistry and the Environment*. Mineral Soc Amer Rev Mineral Geochem 38: 91–180
- FROST RL, ERICKSON KL, WEIER ML, CARMODY O, ČEJKA J (2005) Raman spectroscopic study of the uranyl tricarboxylate mineral liebigite. *J Mol Struct* 737/2–3: 173–181
- HAZEN RM, EWING RC, SVERJENSKY DA (2009) Evolution of uranium and thorium minerals. *Amer Miner* 94/10: 1293–1311
- HOROWITZ EP, DIETZ, ML, CHIARIZIA R, DIAMOND H, ES-SLING AM, GRACZYK D (1992) Separation and preconcentration of uranium from acidic media by extraction chromatography. *Anal Chim Acta* 266: 25–37
- KILLEEN PG, CARMICHAEL CM (1976) Determination of radioactive disequilibrium in uranium ores by alpha-spectrometry. *Geol Surv Canad* 75: 1–17

- KOŘAN J, MRŇA F (1967) Jáchymovské ložisko v minulosti a dnes. Sbor Dějiny přír věd a techn 12: 35–110 (in Czech)
- KRIVOVICHEV SV, PLÁŠIL J (2013) Mineralogy and crystallography of uranium. In: BURNS PC, SIGMON GE (eds) Uranium: From Cradle to Grave. Mineral Assoc Canada Short Courses 43: 15–119
- LANGMUIR D (1978) Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim Cosmochim Acta* 42: 547–569
- MAJER V (1981) Základy jaderné chemie. SNTL, Prague, pp 1–612 (in Czech)
- MARCKWALD W (1906) Ueber Uranerze aus Deutsch-Ostafrika. *Zbl Mineral Geol Paläont Abh* 761–763 (in German)
- MAXWELL SL (1998) Rapid actinide-separation methods. *Radioact Radiochem* 8: 36–44
- MEREITER K (1986) Crystal structure and crystallographic properties of a Schröckingerite from Joachimsthal. *Tschermak's mineral petrogr Mitt* 35: 1–18
- MINDAT. Accessed on September 8, 2022, at <https://www.mindat.org/min-3484.html#autoanchor18>
- O'BRIEN T, WILLIAMS P (1983). The aqueous chemistry of uranium minerals. 4. Schröckingerite, grimselite, and related alkali uranyl carbonates. *Mineral Mag* 47: 69–73
- OLDS TA, PLÁŠIL J, KAMPF AR, DAL BF, BURNS PC (2018) Paddlewheelite, a New Uranyl Carbonate from the Jáchymov District, Bohemia, Czech Republic. *Minerals* 8/11: 511–527
- ONDROUŠ P, VESELOVSKÝ F, SKÁLA R, CÍSAŘOVÁ I, HLOUŠEK J, FRÝDA J, VAVŘÍN I, ČEJKA J, GABAŠOVÁ A (1997) New naturally occurring phases of secondary origin from Jáchymov (Joachimsthal). *J Czech Geol Soc* 42/4: 77–108
- ONDROUŠ P, VESELOVSKÝ F, GABAŠOVÁ A, HLOUŠEK J, ŠREIN V (2003a) Geology and hydrothermal vein system of the Jáchymov (Joachimsthal) ore district. *J Czech Geol Soc*, 48/3–4: 3–18
- ONDROUŠ P, VESELOVSKÝ F, GABAŠOVÁ A, DRÁBEK M, DOBEŠ P, MALÝ K, HLOUŠEK J, SEJKORA J (2003b) Ore-forming processes and mineral parageneses of the Jáchymov ore district. *J Czech Geol Soc* 48/3–4: 157–192
- PLÁŠIL J, ČEJKA J, SEJKORA J, ŠKÁCHA P, GOLIÁŠ V, JARKA P, LAUFEK F, JEHLIČKA J, NĚMEC I, STRNAD L (2010) Widenmannite, a rare uranyl lead carbonate: occurrence, formation and characterization. *Mineral Mag* 74: 97–110
- SKÁLA R, ONDRUŠ P, VESELOVSKÝ F, CÍSAŘOVÁ I, HLOUŠEK J (2011) Agricolaite, a new mineral of uranium from Jáchymov, Czech Republic. *Mineral Petrol* 103: 169–175
- SKINNER M, KNIGHT D (2016) The behaviour of selected fission products and actinides on UTEVA® resin. *J Radioanal Nucl Chem* 307: 2549–2555
- SZECSDY JE, TRUEX MJ, QAFOKU NP, WELLMAN DM, RESCH T, ZHONG L (2013) Influence of acidic and alkaline waste solution properties on uranium migration in subsurface sediments. *J Contam Hydrol* 151: 155–175
- VOCHTEN R, DELIENS M (1998) Blatonite, $\text{UO}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, a new uranyl carbonate monohydrate from San Juan County, Utah. *Canad Mineral* 36: 1077–1081
- WALENTA K (1976) Widenmannit und Joliotit, zwei neue Uranylkarbonatminerale aus dem Schwarzwald. *Schweiz mineral petrogr Mitt* 56: 167–185 (in German)