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Raman mapping of coal halos induced by uranium mineral radiation



SPECTROCHIMICA

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ABSTRACT

Raman mapping microspectroscopy was used as an advantageous high spatial resolution method for detailed assessment of the structure of radiation-induced halos in bituminous coal (Upper Paleozoic) with numerous inclusions of uraninite and coffinite. The uranium content in inclusions in the samples studied ranged from 40 to 50 wt %. Raman structural parameters such as full width at half maximum, the positions of the D-band and G-band peaks and their area ratios were calculated, and these correlated well with vitrinite reflectance. Using linear profiles across the entire halos, changes in the degree of radiolytic alteration of coal matter caused by ionising radiation resulting from the decay of uranium and its daughter products, were described. Using micro-ATR-FTIR, oxidative radiolytic alteration of coal was identified in halos, with oxidisation to alcohols, ketones and carboxyl groups, which were then converted to COO⁻ ions bound to the cations present, including UO₂²⁺. From our data, we conclude that the conversion of the original coal to a type of anthracite occurred during the process of C—H and C—C cleavage, dehydroaromatisation of naphthenic rings and oxidation resulting in the transformation of aliphatic structures into aromatic clusters. Generally, radiolytic alteration increased the structural organisation of coal. Monte Carlo simulations of the observed radiation alteration by the ionising energy loss and non-ionising energy loss were performed.

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1. Introduction

In 1950, seventy years ago, the German geologist Erich Stach first described the so-called halo in coal - an optical phenomenon he observed in polished thin sections of coal using an optical microscope [1]. A bright optical halo, a few tens of microns wide, was observed around an inclusion of thorium-containing zircon in the coal matrix. These halos were actually first observed as early as 1880, not in coal but rather in rocks, as Gentry [2] states in his extensive review. It was a mysterious phenomenon for scientists at that time, and only after the discovery of radioactivity the origin of these halos was explained [3,4].

Generally, these radiation-induced halos have been interpreted as radiation-altered areas, showing a different colour compared with non-altered material. They are the result of α particles that are emitted from mineral grains containing uranium or thorium and their daughter products. The emission of α particles produces a series of spherical areas that appear under the microscope as concentric circles or ellipses. The radii of the halos are directly proportional to the energy of the emitted

* Corresponding author. *E-mail address:* havelcova@irsm.cas.cz (M. Havelcová). α particles and range from 12 to 39 µm in the case of mica, which corresponds to the energy interval of ~4.2–7.7 MeV. The highest energies belong to polonium isotopes [2, and references therein]. Most of the halos in organic matter resulting from radiolytic alteration have a radius of between 40 and 60 µm, which corresponds to the energy of the incident particles of 4–7 MeV. Halos with a radius of more than 60 µm are considered to be the result of the action of β particles and γ rays [5].

Some halos in minerals show blurred features and it is not possible to distinguish individual halos of daughter nuclides. This phenomenon has been attributed to the size of mineral inclusion, so it appears when the inclusion is larger than ~1 μ m in size [6]. In the case of coal halos, it is not possible to microscopically distinguish individual energy contributions of radioactive particles as in minerals with narrow inclusions. Only adjacent to the radioactive mineral inclusion, thin dark zones can be found [7]. The impact range of α particles in the matrix of carbonaceous materials was calculated based on the density of the materials [8]. For example, the α particles with an energy of 5.3 MeV reached distances of 31 and 25 μ m in coalified woods with densities of 1.3 and 1.6 g/cm³, respectively [9].

Although alteration changes caused by radiation are known [5] and have been studied by spectroscopic methods, a detailed description of the halo structure itself has not been reported. Therefore, the aim of this work was to describe in detail internal features of halos with a focus on structural properties on a microscopic scale to better understand the very unusual optical phenomena associated with uranium. This was achieved by displaying the character of the changes on a microscale using Raman spectroscopy and by surveying the area of the halo, which usually surrounds the uranium mineral grain within a distance of 40–60 µm from its edge. The structural differences of organic matter inside and outside of halos were studied using attenuated total reflection Fourier transformed infrared spectroscopy (micro-ATR-FTIR) and optical microscopy. Local concentration distributions of uranium inside cracks filled with uranium minerals, and inside of halos, was determined by scanning electron microscopy coupled with energy-dispersive X-ray analysis (SEM/EDAX), and were compared with Raman spectroscopic structural parameters.

2. Material and methods

The coal samples (Upper Paleozoic) with uranium mineralisation studied were mined in the former Novátor coal and uranium mine at Bečkov, where coal was mined until 1959 [10]. Between 1952 and 1957 the coal was also mined as a source of uranium. The U content in coal was up to 2 wt%. This area is a part of the Žacléř Formation in the Upper Paleozoic Intra-Sudetic Basin located on the boundary between the Czech Republic and Poland. Uranium mineralisation formed small stratiform lenses (0.1–0.3 m thick) and included coffinite, uraninite and sooty pitchblende. Uranium was associated with Cu (up to 1.8 wt %), Zn (up to 0.9 wt%), Mo (0.6 wt%), and Pb (0.5 wt%) [10].

Before chemical analysis, samples were crushed, dried, and powdered. Standard analytical procedures were carried out to determinate moisture, ash content, and total carbon. The elemental composition of coal was determined using a CHNS/O micro-analyzer (Thermo Finnigan Flash FA 1112), and the oxygen content was calculated by difference from 100%.

Polished sections were prepared from the coal samples. Maceral analysis, the measurement of random reflectance of vitrinite and the actual reflectance of organic matter in halos were carried out using an Olympus BX51 microscope with a Zeiss Photomultiplier MK3 system and fluorescence mode using an immersion lens with $40 \times$ and $100 \times$ magnification. The Pelcon point counter was used for maceral analysis. Random and actual reflectance values were determined from particulate polished sections by SpectraVision software calibrated with sapphire (R = 0.596%), yttrium aluminium garnet (R = 0.894%), gadolinium-gallium-garnet (R = 1.717%), and cubic zircon (R = 3.12%) standards.

Infrared microspectra were measured with a Bruker IFS 66 FTIR spectrometer combined with a Hyperion IR microscope using an ATR objective containing a germanium crystal (diameter of 150 μ m). Resulting spectra were processed using the ATR correction. All spectra were recorded at a resolution of 2 cm⁻¹ with a zero-filling factor of 2. Spectra were collected from polished sections in the range 4000–650 cm⁻¹. The spectra were subjected to ATR correction, baseline adjustment and normalisation to the most intense band of the spectrum, which was the band of aromatic C—C stretching at 1600 cm⁻¹.

Raman spectra were collected from polished sections using a Thermo Scientific model DXR microscope equipped with a 532 nm line laser. Locations of interest were positioned using a motorised XY stage and an optical camera. The spot size of the laser focused by the $50 \times$ objective was ~1 µm in diameter on the sample. The laser power and time of sample excitation were adjusted to obtain high quality Raman spectra allowing the creation of spectral maps. A laser power of ca. 0.3 mW at the sample was used in this study. The scattered light was analysed by a spectrograph with holographic grating (900 per mm) and pinhole width 25 µm. The acquisition time was 10 s. Ten accumulations were added together to obtain a spectrum. A 3 µm step was selected for microspectroscopic line mapping using the OMNIC Atlµs imaging software program (ThermoFisher Scientific, Inc., MA, USA).

The semi-quantitative chemical compositions of the samples were analysed using an energy-dispersive X-ray microanalyser attached to the Quanta 450 scanning electron microscope (SEM/EDAX), with a 12.5 kV excitation electron beam. The analysis was carried out on selected spots of the polished sections prepared from the samples.

3. Results and discussion

3.1. Coal characterisation and properties

The samples were humic bituminous coal (Table 1) with a uranium concentration above 0.11 wt%, that was accompanied by high levels of Pb (<2 wt%), Cu (<1 wt%) and Zn (1 wt%). Uranium mineralisation consisted of grains of coffinite and uraninite scattered in coal matter. In addition, fissures in coal matter were probably filled by remobilised uranium minerals together with carbonates, quartz, kaolinite, chalcopyrite, sphalerite, galena, and dolomite. Coffinite contained 1.3–6.3 wt% SiO₂ with an admixture of 0.8–0.9 wt% Y₂O₃, and 0.8–0.9 wt% P₂O₅. The uraninite and coffinite grains were surrounded by anisotropic halos induced by the radiation, with thickness ranging from 35 to 100 μ m. The total volume of halos in the samples occurred in the range 4–14%.

3.2. Optical microscopy of halos

Maceral constituents of coal, according to morphology and reflectance fundamental to coal properties were carried out on samples CU-04 and CU-05: vitrinite was the major maceral constituent, liptinite and inertinite were less abundant. Generally, vitrinite is formed from the cell-wall material or woody tissue of plants through coalification, when physical and chemical properties of tissue change through the course; liptinite is derived from non-humifiable plant matter such as sporopollenin, resins, waxes and fats, and inertinite mainly originates from biodegraded or charred wood.

The degree of coalification, expressed as a vitrinite reflectance of about 0.73%, corresponds to the rank of highly volatile bituminous coal (Table 1). Vitrinite random reflectance is the parameter related to the reorganisation of carbonaceous material and an increase in aromatisation [11]. The reflectance can be increased not only by increasing carbonisation but also by the influence of radiation damage from uranium decay. In the samples studied, the halos surrounding grains of coffinite (or uraninite) were associated with detrital layers rich in vitrinite with disseminated fragments of inertinite and liptinite macerals, and the average reflectance of vitrinite increased in the halo bright zones as a result of radiation-induced alteration. Halos differed in reliefs and in the steepness of increasing reflectance, from about 0.7% R to 1.6–3.4% R in contact with the grain of uranium minerals.

Table 1			
Results	of chemical and	petrographic an	nalysis.

Sample W	V ^a (wt%)	A ^d (wt%)	C^{daf} (wt%)	H ^{daf} (wt%)	N ^{daf} (wt%)	S ^{daf} (wt%)	O ^{daf} (wt%)	SOM (%)	R_r (%)	U (ppm)	Vitrinite (vol%)	Liptinite (vol%)	Inertinite (vol%)
CU-04 4.	.5	13.2	79.4	4.6	2.7	1.5	11.9	1.3	0.74	1176	53.1	5.5	41.4
CU-05 4.	.2	17.8	78.9	4.7	3.2	0.7	12.5	0.7	0.73	569	68.4	9.3	22.3

a-as received, d-dry basis, daf-dry and ash-free basis; W, A-moisture and ash content; C, H, N, S -element content (oxygen content by difference); SOM = soluble organic matter, extract yields in dichloromethane; Rr = random reflectance, rank parameter; U-uranium content. Liptinite, compared with other macerals, usually comprises the lowest reflectance in a given rank, and in the samples studied, the liptinite reflectance increased from 0.3% to 0.9%, and reached 1.6%R in bright zone fissures. Simultaneously the fluorescent colour of liptinite changed from yellow and orange to reddish brown.

3.3. Micro-ATR-FTIR analysis

The first mention of a halo in coal only described this phenomenon [1], but in 1958 a more detailed study was presented [12]. The author concluded that the α particles emitted by the thorium present in zircon inclusions in coal broke down non-aromatic bonds that connected the lamellas of aromatic condensed rings while reducing hydrogen contents. Since then, infrared spectroscopy was applied to study either bulk coal samples containing dispersed radioactive minerals (e.g. [13,14]) or radiation-induced halos [10,15–17]. Most of these works have led to the realisation that the radiolytic alteration reaction schemes were very similar and not dependent on the origin and structure of the initial carbonaceous material. Alteration thus leads to destruction of aliphatic bridges and cleavage of substituents, to dehydroaromatisation of alicyclic (naphthenic) and heteroalicyclic structures. This free-radical mechanism leads to cross-linking of the degraded fragments while lowering the H/C and increasing the O/C atomic ratios due to oxidation and leakage of hydrogen, methane, and some other higher hydrocarbons and carbon oxides. The resulting radiolytically altered products are characterised by a much higher aromaticity and hence a degree of coalification/maturation, the degree of which is dependent on the radioisotope content in the sample and/or on the distance of the altered matter from the inclusion filled with radioactive mineral. The structural rearrangement of C-C and C-H bonds in materials is similar to that of thermal effects. The adjacent volume of organic matter outside the halos remains essentially unaffected by exposure to radiation.

The extend of bright radiation-induced halos in the vicinity of mineral grains is dependent on the nature of the material, in the case of coal on coalification, thus on its chemical and petrological composition, water content, thermal conductivity, texture (extent of cracks), as well as on the chemical composition of the radioactive minerals, and possibly on the degree of binding of radioactive elements to the coal matrix [15,18]. Radiolysis of water also produces hydroxyl radicals, whose reactions increase the degree of oxidation due to the formation of phenols, aromatic ketones, aldehydes, and carboxylic acids ([13] and reference herein, [17]).

Micro-ATR-FTIR describes in detail, structural differences between radiation-induced coal halos and radiolytically intact surrounding and radiation non-affected coal matrix. The typical microphotography of the halo and micro-ATR-FTIR spectra of the halo and coal matrix not affected by radiation are given in Fig. 1A and B. The measured area of ATR germanium crystal, which is used within the FTIR spectrometer, is relatively large (diameter 150 µm), and thus the spectrum of the halo also captures the spectrum of its own mineral inclusion, which contains a mixture of coffinite, uraninite and a small proportion of organic carbonaceous material. Both spectra are qualitatively similar and differ only in the intensity of some bands. The difference spectrum obtained by subtracting both spectra (i.e. spectra of the surrounding area from the spectra of the halo) was used to distinguish the main structural differences (Fig. 1C). There are clear visible negative signs of the stretching vibrations of aliphatic C—H bonds in the region of 3000–2700 cm⁻¹ with features at 2923 and 2855 cm⁻¹ from this difference spectrum. A band around \sim 3600 cm⁻¹ can probably be assigned to the hydroxyls of clay minerals (e.g. kaolinite, montmorillonite) that are present in the inclusion. The area of bending vibrations of aliphatic C—H bonds has a major negative feature at 1446 cm^{-1} . Next to the cleavage of aliphatic bonds, negative bands are visible in the range 3100-3000 (band at 3045) cm⁻¹ and 900-700 (bands at 857, 815, 750) cm⁻¹ due to stretching and out-of-plane vibrations of aromatic C-H bonds. The intensity decrease in the halo spectrum indicates a decrease in the degree of substitution of the aromatic condensed system and/or an increase in the degree of condensation. Similar results were found in the study of the coal halos by Rochdi and Landais [16].

As described above, during radiolytic alteration, a significant oxidation of organic matter occurs, showing a positive broad band of the O—H bonds at 3430 cm⁻¹ in the differential spectrum, which is caused by the formation of phenols or alcohols. The formation of compounds containing a carbonyl group is indicated by several positive bands at 1740, 1690 and 1545 cm⁻¹ attributable to esters, carboxyl groups and COO⁻ ions. The presence of a positive band at 900 cm⁻¹ is the result of the anti-symmetric U—O stretching vibrations of the uranyl cation



Fig. 1. (A) Microphotography of the halo around a uraniferous mineral in the grey vitrinite bands with white inertinite and black liptinite admixtures in coal sample CU-05, analysed using micro-ATR-FTIR; (B) micro-ATR-FTIR spectra inside (blue line) and outside of the halo in the range $3800-650 \text{ cm}^{-1}$; (C) difference spectrum obtained by subtracting the outside from the inside micro-ATR-FTIR spectra of the halo. The halo is the whole bright part, having a different structure than the surrounding unaltered organic matter of coal. A darker band near the inclusion shows the highest degree of degradation. The uraniferous inclusion has a size of about $20 \times 10 \,\mu\text{m}$ and the thickness of the halo is of about $30-40 \,\mu\text{m}$.



Fig. 2. Curve-fitted micro-ATR-FTIR spectra in the region of 1800–1280 cm⁻¹: halo (upper spectrum) and surrounding matter (lower spectrum).

 UO_2^{2+} [19]. The asymmetric and symmetric stretching vibrations of the corresponding carbonyl groups can be found at 1580–1560 cm⁻¹ and 1400–1380 cm⁻¹ for UO₂-containing lignites [19]. Because the spectrum of the halo also includes the mineral inclusion, it can be assumed that the major part of the uranyl cation binding is directly in the inclusion and it is a relic of the uranyl reduction to a mineral containing U⁴⁺. In addition, carboxylate groups bound to other cations present (e.g. Pb, Ca, K and Fe) can also be present in the halo area. The C—O band at ~1270 cm⁻¹ decreased within the halo. This trend could be caused by the cleavage of ether C-O-C, whose spectral features were found in the range 1300–1100 cm⁻¹ in the study of coal [14,20].

The second-derivative was calculated to see the changes in oxygen function groups within the halo and unaltered organic matter of coal in detail (spectra in Supplementary Material). The spectrum of the non-altered matrix contains bands of carbonyl gorups such as ketones, aldehydes and carboxylic acids at 1727 and 1714 cm⁻¹, highly conjugated carbonyls (1659 cm⁻¹) and anhydrides (1812, 1784 cm⁻¹). Bands of aromatic C=C structures (1606, 1589, 1527, 1493 cm⁻¹) and deformation vibrations of aliphatic C—H bonds (1441, 1408, 1376, 1349 1326, cm⁻¹) are also visible in the spectrum. New bands appeared in the second-derivative spectrum of the halo (Supplementary Material) at 1734 cm⁻¹ (esters) and at 1568 and 1543 cm⁻¹, which probably belong to the antisymmetric vibrations of COO⁻. The mixed Gaussian-Lorentzian function was applied for a detail assessment of the structural

differences between the halo and surrounding matrix in the spectral range 1800–1280 cm⁻¹ (Fig. 2). At first glance, it is evident that the relative intensities of bending vibrations of aliphatic C—H bonds at 1440 and 1375 cm⁻¹ change in the spectra.

For an overview, Table 2 shows the structural parameters calculated as the ratio of the respective structural group (bond) band area to the area of the stretching vibrations of aromatic C=C bonds. A decrease in the ratio of A_{-1440}/A_{-1605} of more than half reflects the reduction of aliphatic bonds and substituents in the three-dimensional coal structure. The length and/or branching of the aliphatic structures can be inferred from the ratio A_{2926}/A_{2957} of the methylene and methyl group band areas, whose value decreased by more than half within the halo. Landais et al. [15] arrived at similar conclusions from uraniferous bitumens where, using nuclear magnetic resonance, they described a decrease in this ratio and also found a decrease (from 0.52 to 0.38) in the ratio displaying the degree of substitution of aromatic rings. Similarly, Sýkorová et al. [10] used a relationship between uranium concentration and the methylnapthalene ratio (based on the selective distribution of methylnaphthalene isomers) showing the effect of radionuclides on the chemical composition and structural ordering of organic matter similar to thermal alteration.

Oxidation during radiolytic alteration was most pronounced in carboxyl groups (A_{-1696}/A_{-1605}) and COO⁻ ions (A_{-1562}/A_{-1605}), as observed due to the increased ratios within the halo (Table 2). The changes in the content of ketones and highly conjugated carbonyls were not so expressive but from the obtained data, it can be concluded that during the oxidative radiolytic alteration of coal, a free radical mechanism takes place in which aliphatic structures break down to form larger aromatic lamellas and oxidise to alcohols, ketones and carboxyl groups. These change during the alteration to COO⁻ ions bound to the cations present, including UO_2^{2+} .

3.4. Raman mapping of radiation-induced halos in coal matrix

The radiation-induced halo volumes ranged from 4 to 14 vol% in the coal samples studied, as determined by optical microscopy. But the uranium content within mineral inclusions was up to 50 wt% while the uranium content in the bulk samples was relatively low (Table 1). The structure of the organic matter in the halo area and its properties contribute significantly to the general character of uraniferous coal. It is known that the physical and chemical properties within the halo are not constant, but vary from the outer boundary of the halo towards the inclusion of radioactive material. The properties across the coal halo have been described by optical microscopy based on the reflectance values of vitrinite and other macerals (Table 3). For a more detailed study of carbonaceous materials, it is advantageous to combine optical microscopy with Raman spectroscopy, in which spatial resolution below 1 µm can be achieved.

The very first Raman spectra of carbonaceous materials – graphites [21] and coals [22] were obtained in the 1970's and two prominent features were reported. The G band (graphic) in the region 1575–1620 cm⁻¹ was assigned to stretching vibrations of E_{2g} in graphite aromatic layers. The D band (disordered) in the region 1335–1380 cm⁻¹, corresponding to the graphite lattice mode A_{1g} , was connected with planar defects between the basic structural units or the presence of heteroatoms. The intensity ratio of both bands, full width at half maximum (FWHM), and band positions are parameters that can describe the structure of coals. A detailed description and use of these parameters

Table	2
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Structural micro-ATR-FTIR parameters of the halo and its surrounding area within sample CU-05.

	A ₂₉₂₆ /A ₂₉₅₇	A _{~1726} /A _{~1605}	$A_{\sim 1696}/A_{\sim 1605}$	$A_{\sim 1655}/A_{\sim 1605}$	A _{~1562} /A _{~1605}	A _{~1440} /A _{~1605}
Halo	1.170	0.176	0.364	0.397	0.260	0.210
Surrounds	2.860	0.182	0.209	0.455	0.179	0.375
Ratio halo/surrounds	0.41	0.97	1.74	0.87	1.45	0.56

Table 3

References concerning the study of coal halos.

Year	Material	Method	Radioactive element	Halo	Reference
1950	Hard coal	Optical microscopy	Th (in zircon)	n.s.	[1]
1952	Coal	Optical microscopy			[30]
1957	Coal	Optical microscopy	Th (in zircon)	n.s.	[31]
1958	High-volatile coal	Optical microscopy	Th (in zircon)	n.s.	[12]
1958	Coal	Optical microscopy	U	n.s.	[32]
1961	Coalified wood	Optical microscopy	U		[33]
1965	Coal	Optical microscopy	U	n.s.	[34]
1966	Asphaltised logs, low rank coals,	Optical microscopy	U (uraninite, coffinite, secondary uranium	20–50 µm	[7]
	anthracite		minerals)		
1974	Coal	Optical microscopy			[35]
1976	Coalified wood	Optical microscopy	U, Pb, Po	n.s.	[9]
1983	Bituminous coal	Optical microscopy	U	n.s.	[36]
1991	Bituminous coal	Optical microscopy	U	35–95 µm	[37]
2016	Bituminous coal	Optical microscopy, micro-FTIR, Raman	U (uraninite and coffinite)	35-100	[10]
		spectroscopy		μm	

has been studied in detail by [23,24]. To characterize organic matter in uranium deposits, Landais et al. [15] used Raman microspectroscopy to study the structure of Precambrian kerogens from Witwatersrand deposits (South Africa) and to display micro-textured variations. Spectral characteristics varied with respect to the uranium content, together with petrographic characteristics, and the diameter of the observed halos were 40–50 μ m, which, according to the authors, corresponded to the range of α particles.

For a more detailed examination of the coal microstructure, Raman microspectroscopy mapping is an appropriate method that was applied to the study of coal macerals [25] and tested in the study of coal halo structures [10].

Representative Raman spectra in the study of radiation-induced halos in coal contained, in the spectral region of 1800 to 800 cm⁻¹ two distinct spectral features, described above, at ~1600 (G) and ~1350 cm⁻¹ (D) bands. The intensities, positions and full width at half maximum yielded information about the rank, and correlated relatively well with the reflectance of vitrinite Ro and the atomic H/C ratio. When obtaining spectral parameters, Raman spectra are curve-resolved into multiple spectral bands, which sometimes can give results with many inaccuracies when analysed across the entire coal rank [24]. Because the degree of coalification varies dramatically from the outer boundary of the halo towards the centre, the curve fitting using two Lorentzian functions and a two-point linear baseline were used for the coal being analysed. According to the authors [24] this simple curve fitting technique yields fewer errors and can be used appropriately for the whole coal rank.

As the first step in this work, the vitrinite reflectance values and the corresponding Raman spectra were collected from polished samples at various sites in the coal. Raman spectra of coal from sites with R = 0.80 and 2.42% are presented in Fig. 3A, as well as a correlation between the full width at half maximum of the Raman D bands (FWHM-D) and

the vitrinite reflectance R, which was chosen as a suitable spectral parameter describing the coal rank. The relatively good linear dependence (R = 0.89) in the R range from 0.5 to 3.5% indicates the appropriate use of the Raman spectral parameter (FWHM-D) to describe coal in terms of degree of coalification/graphitisation.

A halo in coal sample CU-05 around elongated mineral inclusion (9 \times $24 \,\mu\text{m}$) and containing 49.7 wt% uranium as a mixture of uraninite (UO₂) and coffinite (USiO₄) was chosen as the first example of the analysis. For Raman microspectroscopic mapping, a suitable rectangular area with dimensions $126 \times 93 \,\mu\text{m}$ (with mapping step 3 μm) was selected in the polished section of the halo. The microphotography with measured points (1302 points) is shown in Fig. 4A. Based on the measured spectra, a correlation map describing differences inside the halo, and outside the halo - in the radiolytically unaltered coal matrix, was produced. The correlation map was calculated by comparing the spectral features from the spectrum at the inner edge of the halo (e.g. at the boundary of halo and inclusion) with the other spectral characteristics from the area. The appearance of the correlation map is largely influenced by changes in the slope and shifts of the baseline, which are largest - due to strong fluorescence - at the less altered coal structures close to the outer edge of the halo. The correlation map illustrates well the structural differences within the halo itself and its boundaries with the mineral inclusion as well as with the unaltered region of the coal sample.

For a more detailed analysis of the halo, three profiles (129 spectra in total) were extracted from the measured mapping spectra, which cross horizontally across the mapped area (Fig. 4B). Structural parameters were obtained by curve fitting the Raman spectra into two Lorenz bands, and used for a detailed description of changes within the halo area. The relationship of FHWM-D with distance from the centre of the halo (zero coordinates) towards the outer part of the halo in both profiles, up to the radiolytically unalterated regions, is presented in



Fig. 3. (A) Raman spectra of two coal samples with two differing degree of coalification; (B) Correlation between average vitrinite reflectance and FWHM-D parameter of coals.

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Fig. 4. (A) Microphotography of the halo in the CU-05 coal sample with the indicated measurement points (1302 points) and measured area ($126 \times 93 \mu m$); (B) correlation map of halo; (C) development of the FWHM-D values across the halo; D) and (E) corresponding correlations for D and G band positions with distance within the halo; (F) the values of A_D/A_G ratio depend on the distance from the mineral inclusion; (G) and (H) correlations of the D and G band positions with FWHM-D and FWHM-G values; (I) the difference in G and D band positions with FWHM-D values.

Fig. 4C. It is clear from the dependence that there was a continuously increasing radiolytic alteration of the coal matrix towards the mineral inclusion in the centre, as given by the decrease in FWHM-D values. The maximum degradation (degree of coalification) of the sample was at a distance of about $\pm 15\,\mu m$ from the mineral inclusion. From these minimum FWHM-D values, however, the values increased again towards the inclusion. The whole dependence, similar to "butterfly wings", was not symmetrical about the vertical axis and did not have a smooth course. This was also noted but not explained by Jedwab [7] in his work when obtaining a similar dependence for vitrinite reflectance on the distance from the radioactive mineral inclusion. These phenomena can probably be attributed to asymmetry of the mineral inclusion and possibly to uneven distribution of macerals in the sample. The scattering of the results was evident, mainly in the range of distances of 40-60 µm (Fig. 4), in the spectra of which there was strong fluorescence, which also contributed to errors in the determination of FWHM-D values. The maximum and minimum values of the full width at half maximum of the Raman D bands were 300 and 230 cm⁻¹ and the corresponding values of the vitrinite reflectance can be subtracted from the correlation in Fig. 3, as Ro 0.7 and 1.95%. These reflectance values indicate that radiolytic alteration leads to changes in the coal structure from the original high-volatile bituminous coal to a semi-anthracite type [26].

During radiolytic alteration of high-energy α particles, the C—C and C—H bonds are broken down, recombined, and gaseous reaction products dominated by hydrogen are released. Similarly, to coal coalification, aromaticity increases, i.e. the content of aromatic carbons and hydrogens. For example, in the interval Ro = 0.7–1.95%, which corresponds to a carbon content of 80–90%, the content of Car-Car bonds increased by 25%, Car-H by about 20%, while Cal-Cal and Cal-H decreased by 25 and 55%, respectively [27]. These data indicate cleavage of aliphatic bridges and substituents, dehydroaromatisation of naphthenic rings and the formation of highly condensed aromatic structures.

Moreover, the positions of the D and G bands depended on the measuring point within the halo area (Fig. 4D and E): the mutual relations of the bands corresponded in shape to the "butterfly wings". The ranges of the positions of the D and G bands were 1335–1355 cm⁻¹ and 1590–1595 cm⁻¹, respectively. These differences also corresponded to the conversion of the original coal structure to a semi-anthracitic type in the halo area. To document the progress in coalification/ graphitisation, the ratio of the peak areas of the D and G bands, i.e. A_D/A_G , is often used. The relationship of this ratio to the distance from the mineral inclusion (Fig. 4F) clearly shows a decrease in the ratios from the periphery of the halo towards the inclusion. Our results show that radiolytic alteration increased the structural organisation of the coal: lower A_D/A_G ratio indicates a higher structural order. In the case of crystalline graphite, only the G band is in the spectrum and the ratio is zero. Fig. 4 was further supplemented by correlations between positions and the full width at half maximum of the Raman D and G bands (Figs. 4G and H), from which it is clear that the decrease in FWHM values during radiolytic alteration led to a 20 cm⁻¹ decrease in D band position, while the G band position increased by only 5 cm⁻¹. The change in these values with coalification is also well illustrated by the "band separation" parameter, calculated from the difference between the peak positions of the G and D bands. This parameter increased with coalification and is represented in the graph by FWHM-D values (Fig. 4I).

The thickness of the halo analysed was about $35-40 \ \mu m$ (Fig. 4). As described above, the intensity of radiation-related change in coal structure is dependent on the energy of emitted particles, on material properties of the organic and inorganic fractions (chemical composition, maceral composition, degree of coalification, material density, porosity, texture), as well as external conditions such as pressure, temperature and time during the process of radiolytic alteration. The size, shape and composition of the radioactive mineral inclusions plays a major role. Linear energy transfer for alpha particles increases to a maximum shortly before the end of their range and this must be a principal effect controlling the observed coalification pattern with a maximum within the halo area located about $15-20 \ \mu m$ from the uranium inclusion.

For simulation of the observed radiation alteration of coal matter, FLUKA – a fully integrated particle physics Monte Carlo simulation Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 246 (2021) 118996

package - was employed. It has many applications in high energy experimental physics and engineering, shielding, detector and telescope design, cosmic ray studies, dosimetry, medical physics and radiobiology [28]. The ionising energy loss and non-ionising energy loss were computed. The ionising energy loss is a dominant contribution of the energy deposition from charged particles. It affects the temperature and stress of material but does not lead to direct radiation damage in materials. The non-ionising energy loss is associated with nuclear interactions which cause lattice defects and hence radiation damage. The simulation assumed a mineral inclusion $(15 \times 15 \times 3 \,\mu\text{m})$ with a hypothetic uniform density 4.7 g/cm³ (close to 5.1 g/cm³ of coffinite) in a material with elemental composition of the sample C-05 and density 1.45 g/cm³, and geometry similar to that shown in Fig. 4. The entire ²³⁸U decay series (i.e., 8 α particles with energies 4.2–7.7 MeV) was assumed. The simulation results are illustrated by Fig. 5. The simulation indicates that the blurred character of coal halos may be attributed, besides relatively great size of the inclusion, to a significant contribution of the ionising energy loss. On the other hand, the non-ionising energy loss better corresponds to the coalification pattern including its asymmetry observed by Raman microspectroscopy.

The extent of radioactive halos in relation to other factors was evaluated by several authors. For example, the relationship between the intensity of α particle penetration into the coal matrix and the density of coal was studied by Gentry [9]. The author concluded that particles with an energy of 5.3 MeV reached 31 and 25 μ m into the fossilised wood



Fig. 5. Monte Carlo simulations of the ionising energy loss (top) and non-ionising energy loss (bottom) for α particles in the ²³⁸U decay series released from a uranium mineral inclusion in a coal sample roughly corresponding to sample C-05. The graphs on right represent a horizontal profile crossing the bottom edge of the inclusion similarly to a profile used for evaluation of structural parameters from Raman microspectroscopic mapping (cf. Fig. 4B–F).

with a density 1.3 and 1.6 g/cm³, thus the range of α particles equal in energy was inversely proportional to the density of the matter studied. Coal density is similar to fossilised wood; it changes during coalification, but not continuously: initially decreasing in the direction from younger coal (1.50 g/cm³) and passes through a minimum (1.25 g/cm³) at a carbon content of about 80%. It then rises to about 1.45 g/cm³ [29]. These complex changes in coal density could partially contribute to the coalification pattern observed in our coal samples. A semi-anthracitic stage with high density values is reached at this point, according to the Raman parameters and the vitrinite reflectance. Another halo was selected as the second example of the analysis, also from sample CU-05 coal, differing from the first halo in the size and having a mineral inclusion of $27 \times 59 \,\mu\text{m}$ (Fig. 6A). To study the Raman spectral parameters, the spectra from horizontal and diagonal single-line maps were separated, as indicated in the correlation map (Fig. 6B). Relationships between FWHM-D and the distance from inclusion again have the shape of "butterfly wings" in both (horizontal and diagonal) directions, and the maximum and minimum of FWHM-D reached values of 310–210 and 320–220 cm⁻¹, corresponding with reflectances of 0.70–2.31 and 0.70–2.04% respectively, and can be



Fig. 6. (A) Microphotography of the area in a polished section from coal sample CU-05 selected for Raman microspectroscopic mapping; (B) correlation map of halo; (C) and (D) development of the FWHM-D values across the horizontal and diagonal halo profiles; (E) and (F) changes in weight percent uranium content across the horizontal and vertical halo profiles.



Fig. 7. Microphotography of in area in a polished section from coal sample CU-04 chosen for Raman microspectroscopic mapping (A), correlation map of halos (B), development of FWHM D values across the horizontal (C) and vertical (D) halo directions.

attributed to the scale range from highly-volatile bituminous coal to semi-anthracite, which is in the same range as the previous halo. Other parameters such as the positions of the D and G peak maxima and their area ratio (not shown) exhibited very similar values and correlations. The distance of FWHM-D minima from the edges of the inclusion was about $8-10 \mu m$ in the case of the horizontal map, passing through a relatively narrow part of inclusion, while in the case of a diagonal line map passing through a much wider part of inclusion, the distance was about $16-18 \mu m$. The diameters of the halo (covering also the inclusion) recorded in horizontal and diagonal directions were estimated at 105 and 135 μm respectively.

The average uranium content within the inclusion was 49.73 wt%. In addition to uranium, lead (2.47 wt%) and silicon (6.75 wt%) were detected. The uranium concentrations spread throughout the halo and mineral inclusions in horizontal and diagonal directions were measured by electron microscopy (Fig. 5E, F), and it is apparent from the dependencies that the maximum uranium contents were in the centre of the inclusion (70 wt% U). The concentration decreased sharply towards the periphery and was practically zero in the organic matter of the coal matrix.

As a third example, the so-called "double eye" was chosen; two halos lying close together, the centres of which were about 40 μ m apart, and the inclusions had dimensions of 12 \times 5 and 11 \times 4 μ m (Fig. 7A). The uranium content in the inclusions was about 51 wt%. A horizontal profile through both inclusions and a vertical profile through the left inclusion were selected for micro-Raman study (Fig. 7B). From the dependence of FWHM-D on position it was estimated that the left halo had a radius of about 35 μ m and the right halo of about 20 μ m. In the space between the two inclusions, the halos intersected. The

minima of FWHM-D values were in the outer edges of the inclusions, had values for the left and right inclusions of 202 and 188 cm⁻¹, and corresponded to a 2.48% and 2.79% vitrinite reflectance respectively - to values showing the transition from original highly-volatile bituminous coal to the anthracite type. Between inclusions there was an area with an FWHM-D of 202 cm⁻¹, whose value corresponds to a semi-anthracite with $R_o = 2.48\%$. The vertical single-line map of the first inclusion shows a similar minimum half-width value in proximity to the inclusion of about 210 cm⁻¹, which corresponds to semi-anthracite with a reflectance of 2.31%. In the interspace between inclusions, both halos were difficult to distinguish by optical parameters, and therefore Raman mapping microspectroscopy appears to be an effective tool for assessing the structure of a complex "double eye".

4. Conclusions

This study of structural changes within halos surrounding uranium mineral inclusions in coal revealed that:

- The degree of radiolytic alteration increased steadily from the outer edge of the halo towards the radioactive inclusion, and the maximum structural and chemical changes in coal matrix were found at about 15–20 µm from the edge of the inclusions.
- The thickness of the halos and progress of dependent alterations, such as variations in the D band FWHM in Raman spectra with distance from inclusion, are ascribed to the character of energy transfer of α particles, the size and shape of the three-dimensional inclusion, the reaction scheme, and density of the original coal and altered coal whose

density increases by alteration while the range of particles is shortened.

- The energy of ionising particles causes the Cal-Cal and Cal-H bonds to split while the Car-Car and Car-H content increases; this indicates a cleavage of aliphatic bridges linking aromatic nuclei, shortening of aliphatic substituents, dehydroaromatisation of naphthenic rings forming highly condensed aromatic structures with a high degree of structural organisation.
- Using micro-ATR-FTIR, oxidative radiolytic alteration of coal were identified in halos, with oxidisation to alcohols, ketones and carboxyl groups, which converted to COO⁻ ions bound to the cations present, including uranyl cation UO₂²⁺.

Even after seventy years post-discovery, the coal halo has not lose its attractiveness. It shows to coal scientists and technologists that within a micro-space of about 100 µm a range of physical and chemical features can be found, corresponding to highly-volatile through to low-volatility bituminous coal, and semi-anthracite to anthracite. In addition to the well-established methods of optical microscopy, which are based on reflectance of macerals, microspectroscopic methods such as micro-ATR-FTIR and Raman spectroscopy appear to be very efficient tools to study the effect of radiation on coal matter. With the development and use of high spatial resolution analytical micromethods, the halo can provide valuable data on radiation-driven changes in the structure of organic matter. Raman mapping is an automated method reducing subjective observation that optical microscopy has. On the other hand, Raman spectroscopy cannot distinguish the maceral composition and thus the high heterogeneity of organic materials. Therefore, both methods are complementary and complement each other well.

CRediT authorship contribution statement

Vladimír Machovič devised the project, the main conceptual ideas and proof outline.

Material preparation, and data analysis were performed by Martina Havelcová, Ivana Sýkorová, Lenka Borecká and Ladislav Lapčák.

Jiří Mizera and Bohdan Kříbek contributed to the design and implementation of the research, and to the analysis of the results.

Pavel Krist performed the Monte Carlo simulations.

The first draft of the manuscript was written by Vladimír Machovič and all authors commented on previous versions of the manuscript.

All authors read and approved the final as well as revised manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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