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Revision 2

Radiation effects in radioactive galena from burning heaps after coal mining from the Lower Silesian basin (Czech Republic)

MICHAL ČURDA[1,2,*], VIKTOR GOLIÁŠ[1], MARIANA KLEMENTOVÁ[3], LADISLAV STRNAD[4], ZDENĚK MATĚJ[5] AND RADEK ŠKODA[6]

[1] Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University, Faculty of Science, Albertov 6, 128 43 Prague 2, Czech Republic; *email: michal.curda@geology.cz
[2] Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic
[3] Institute of Inorganic Chemistry, Czech Academy of Sciences, 250 68 Husinec-Řež, Czech Republic
[4] Laboratories of the Geological Institutes, Charles University, Faculty of Science, Albertov 6, 128 43 Prague 2, Czech Republic
[5] Department of Condensed Matter Physics, Charles University, Faculty of Mathematics and Physics, Ke Karlovu 5, 121 16 Prague 2, Czech Republic
[6] Institute of Earth Sciences, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

ABSTRACT

The isotopic composition of lead ($^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$ and ^{210}Pb) in a recently-formed galena from burning heaps after coal mining in Radvanice, Markoušovice and Rybníček, the Lower Silesian basin, Czech Republic, was studied in detail. ^{210}Pb activity in galena varied from 135 ± 9 Bq/g to 714 ± 22 Bq/g and calculated integral doses ranged from 2.21×10^{11} α/g to 6.11×10^{11} α/g. The radioactivity of the galena causes micro-deformations in its crystal structure as indicated by the Williamson-Hall graphs, showing that the level of micro-strain depends on the length of time that galena samples were exposed to the radiation. However, the crystal structure of galena is affected very inhomogenously; according to TEM investigations there are domains of fully crystalline, polycrystalline and fully metamict galena within one crystal. Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the isotopic composition of the studied galena. The stable isotope ratios of Pb varied for $^{207}Pb/^{206}Pb$ from 0.8402 to 0.8435 and for $^{208}Pb/^{206}Pb$ from 2.0663 to 2.0836. The

average ratios $^{207}Pb/^{206}Pb = 0.8312$ and $^{208}Pb/^{206}Pb = 2.0421$ were obtained for coal from the same localities. These isotope ratios show that there is no isotopic fractionation taking place during the coal burning and subsequent galena crystallization from hot gases.

Running title: Radioactive galena from Czech Republic

Keywords: galena, radiation, lead-isotopes, radiation effects, metamict state

INTRODUCTION

^{210}Pb is an isotope in the decay series of ^{238}U with a half-life of 22 years, where it is a long-term radioactive daughter of ^{222}Rn. Thus, ^{210}Pb is usually enriched in metallic lead or galena under conditions where there is long-term contact with radon (e.g., during natural gas production) (Schmidt 1998; Schmidt et al. 2000).

Another geologic source of ^{210}Pb is outflow of hot volcanic gases through steam holes. Increased levels of ^{210}Pb were described in sulphur crusts precipitated on the Vulcano Island (Voltaggio et al. 1998) and on Mt. Etna (Le Cloarec et al. 1988; Le Cloarec and Pennisi 2001).

Groundwater in Triassic sandstone reservoirs with an elevated U content (up to 70 mg/kg) can be enriched in ^{210}Pb, as at the Wytch farm, southern UK. At Wytch farm water is rich in sulphates and ^{226}Ra precipitates in barite, whereas ^{210}Pb remains in solution (Worden et al. 2000).

Water enriched in ^{226}Ra occurs more commonly as chloride brines that originate from sedimentary sequences rich in uranium. Such waters are known from the Polish side of the described geological unit – the Lower Silesian Basin. Water pumped out from mines or from boreholes exhibit rather high activity, up to 85.5 Bq/l ^{226}Ra (Kozłowska et al. 2010), which is

very high as compared to global values. Fresh groundwaters typically have on the order of 0.01 – 0.03 Bq/l ^{226}Ra (Porcelli and Swarzenski 2003).

The Jestřebí Mountains with the Žaltman peak (739.1 m a.s.l.) are located in Eastern Bohemia between the Krkonoše (Giant Mts.) and Orlické hory Mountains. Coal has been mined in this area for more than 400 years in more than 200 mine workings (Jirásek 2006). Besides coal, copper ore from copper-bearing shales enriched with sulphides (chalcocite and bornite in nodules) and uranium from black coal beds bound onto Carboniferous sediments were also mined there (Pešek at al. 2001). The resulting mine heaps contained a large amount of lean coal enriched in Cu, U, Pb, Ge, Zn, Mo and other elements. The coal mass burnt on some of the heaps through time and leaking gases produced newly-formed mineral phases by desublimation. The richest (in terms of minerals and mineraloids) and also the most investigated locality is Radvanice. Various newly formed minerals and mineraloids of Cd, In, Ge, Zn, Bi, S etc. (e.g. greenockite, gunningite, GeO_2, Bi_2Te, GeS_2, GeAsS, $GeSnS_3$ etc.) were described there (Sejkora et al. 1998b; Žáček and Ondruš 1997). Amongst these is radioactive galena, the objective of the current study. As most localities have been remediated and collecting samples is almost impossible, these samples are rare.

GEOLOGICAL SETTINGS AND LOCALITY DESCRIPTION

The Lower Silesian Basin, also referred to as the Žacléř-Svatoňovice basin, is an upper-Paleozoic limnic basin. Only one third of the entire area of the Lower Silesian Basin (about 1800 km^2) lies in the Czech Republic in the vicinity of Žacléř and Broumov (Pešek et al. 2001; Hřebec and Veselý 1984; Sýkorová et al. 2016). Sedimentation in the basin started during the lower Carboniferous (Tournaisian) in the Polish portion, and sedimentation subsequently expanded to the Bohemian portion (Visean). At the beginning of the Visean, a sea flooded the entire area. However; at the end of this period the sea retreated and purely continental sedimentation (with some hiatuses) proceeded from the Carboniferous to the middle Triassic. Coal beds were formed during the Carboniferous in a humid climate (Pešek et al. 2001; Chlupáč et al. 2011; Košťák et al. 2011).

Radvanice – the Kateřina I mine (50°33'39.963"N, 16°3'58.648"E)

The main inclined shaft of the Kateřina I mine was opened in 1901 and served originally for black coal mining. Uranium mining operated by the Jáchymovské doly state enterprise mining company was performed there from 1953 until 1957, when a portion of the deposit was transferred the Východočeské uhelné doly (VUD, Eastern Bohemian coal mines) company. The mine was closed in 1993 (Cimala 1997; Jirásek 2003). An estimated 500,000 t of black coal and 60,000 t of radioactive coal were mined between 1952 and 1957. With an average grade of 0.29 % U in the coal it, mining recovered a total of 387.2 t of U (Sejkora et al. 1998a; Kafka 2003; Pauliš et al. 2007). Total black coal production from 1901 to 1994 is estimated at 10,500,000 t of coal (Cimala 1997).

The Kateřina I mine heap had an aerial extent of 40,000 m^2 (approximately 200 x 200 m) and a height reaching to 60 m. About 2,300,000 m^3 of mine waste was deposited there, 20% of which was radioactive lean coal remaining after uranium ore mining (Sejkora et al. 1998a). The exact time of heap-flaring is unknown. Initial attempts to extinguish the fire occurred from 1967 to 1969. Preparations for the final quenching started in November 1979. The remediation was finished at the end of 2006 (Němec 2006).

All galena samples from Radvanice were collected in 1998, when the heap was still burning, and the desublimation processes were active. Galena crystallised in deeper portions of the heap, at least 0.5 m beneath the surface. The temperature in the zone of crystallisation was 600–800 °C. Under such high temperatures the reductive association of metallic Pb, Sb, Bi (as liquid droplets), and Sb-Bi, Sn-Bi, Sn-Ge and Pb-Sn intermetallics were associated with galena (Sejkora and Tvrdý 1999). Galena formed as free, highly-lustrous (some tarnished) crystals, growing on the burnt rock. Crystals ranged from several millimeters up to 1.5 cm in diameter (Fig. 1), with masses from 0.024 g to 0.384 g, with an average of 0.122 g.

Markoušovice locality – the Ignác mine (50°33'33.170"N, 16°0'35.890"E)

Coal mining in the surroundings of Markoušovice has a long and colorful history. Coal was mined there for more than 400 years, and is one of the oldest and longest operated mining districts in Bohemia. Mining operations ended in 1899 due to exploitation and flooding. Although uranium mineralisation lenses appear in the mined Bukov beds, the locality was classified uneconomical in the 1950s and uranium was not recovered (Jirásek 2003; Jirásek 2006).

The heap near the village of Markoušovice measures about 150–200 m in to dimensions, and has a height of about 20 m. 36,000 m^3 of waste material was deposited in these heaps. The coal mass fraction is

112 estimated at 40 %, i.e., approx. 18,000 t of coal. The heap flared in 2006. The fire was ignited by forest workers
113 burning waste wood. The fire was extinguished and remediation was complete in 2007 (Jirásek et al. 2008;
114 Pauliš and Kopecký 2010).
115 Galena samples selected for study from Markoušovice are tiny hexahedral crystals forming crust
116 covering a 10 cm diameter rock fragment (Fig. 2). Tarnishing was common.
117
118 *Rybníček locality – the Novátor mine (50°37'49.436"N, 15°58'51.838"E)*
119 The Novátor mining operation was located in the Bečkov and Rybníček cadastral areas, and had mine
120 several workings in the early Permian Rybníček radioactive bed. Prospecting for uranium was performed from
121 1947 to 1953. After uranium mining between 1952 and 1957, the mines were transferred to the Východočeské
122 uhelné doly (VUD) mining company for recovery of the remaining black coal from the columns. However, the
123 mine closed three years later. A total of 170.8 t U was mined here (Cimala 1997; Kafka 2003; Pauliš et al. 2007).
124 There are 13 coal heaps around the villages of Rybníček and Bečkov. Five of these contain an elevated
125 fraction of radioactive coal. The shaft No. 3 heap is formed by several ridges of approximately height 25 m.
126 100,000 m^3 of material were deposited on an area of about 12,000 m^2 (Kříbek et al. 2008). The heap flared about
127 1960. Today it is covered with birch, beech and spruce trees. The mineralogy of this locality was described by
128 Sejkora et al. (1998b). The Rybníček locality provided only tiny efflorescences of galena and one small, strongly
129 corroded crystal covered by anglesite (Fig. 3).
130
131 **EXPERIMENTAL METHODS**
132 *Gamma-spectrometry*
133 The activity of ^{210}Pb in the samples studied here was measured using a laboratory low-background
134 anticompton-anticoincidence gamma spectrometer SILAR (Faculty of Science, Charles University, Prague),
135 which is designed for measurements of low activities of low-energy γ-emitters in small volumes (Hamrová et al.
136 2010). The ^{210}Pb 47 keV energy was selected for mass activity determination, because strong sample matrix
137 effects of PbS are expected even at such a low γ energy. Shielding due to the heavy matrix was accounted for by
138 measuring 20 individual galena crystals, where the lower mass activity was detected in the cases of larger grains
139 (radiation from the crystal core is absorbed effectively by the layers close to the surface). We therefore chose a
140 constant mass measurement process, where the matrix effect is constant for all samples. A 50 mg portion of
141 milled galena in 1 mL AXYGEN ST 050 plastic bottle was measured for 1 hour. No standards or reference

material are available for this material (^{210}Pb in galena), so a secondary standard with a similar matrix and ^{210}Pb activity that approximates the studied samples was prepared. A 0.0020 g portion of radiogenic lead primary standard (SRM 983, NIST, USA) was ground to a powder, and had a certified ^{210}Pb activity of 16 kBq/g (in December 2004, the reference year). The activity was calculated for the current date, and the standard powder was diluted with 0.048 g of non-radioactive galena from the Příbram – Březové Hory deposit, which had a U activity lower than the detection limit (< 0.06 mg/kg). This artificial galena secondary standard had a ^{210}Pb activity of 484 Bq/g (on 24th May 2014).

Alpha-spectrometry

Non-destructive semi-conductor alpha-spectrometry was used to determine and evaluate the presence of alpha-active radionuclides in the samples. A powder sample was prepared from galena from the Radvanice site. A suspension of the galena powder was placed on a holder and dried. The sample weight was 280 μg, as determined by a micro-balance. The spectrum was collected over 24 hours using a semi-conductor alpha detector PIPS 450 mm^2 (CANBERRA). The signal was processed by the multi-channel analyser CANBERRA Series 10.

Alpha-autoradiography

The distribution of radionuclides in the galena matrix was investigated using the alpha autoradiography method. A film LR – 115A (KODAK) was placed on top of a polished section from the Radvanice sample, and the film was exposed for one week. Subsequently the film was developed using standard etching methods in a 10 % NaOH solution at 60 °C.

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) was performed utilizing an X´Pert Pro (PANalytical) diffractometer operating with Cu*K*α radiation. Data collection was done for the range of 24–80° 2θ with a step 0.02° 2θ and a counting time of 300 s/step (continuous mode). The HighSore Plus (PANalytical) with PDF – 2 (ICDD, 2003) database was used for phase analysis. Profile fitting was done using HighScore Plus (PANalytical) and the pseudo-Voigt profile function, which was chosen because it provided the best fits to the experimental profiles. This function is a sum of Gauss and Cauchy functions with a free parameter weighing both components (Kužel 2003). Unit cell parameters of galena were refined using the least squares method by the HighScore Plus (PANalytical) program. The diffraction data were corrected for shift of the sample from the goniometer plane

(sample displacement).

The LaB_6 standard was used for testing the resolution of the instrument (*FWHM*). A synthetic PbS sample was prepared in the Laboratory of Experimental Mineralogy of the Czech Geological Survey to compare the structure of natural and synthetic material.

Transmission electron microscopy

Transmission electron microscopy (TEM) was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB_6 cathode, point resolution 1.7Å) with an Oxford Instruments Energy Dispersive X-ray (EDX) detector attached. Images were recorded on a CCD camera with resolution 1024x1024 pixels using the Digital Micrograph software package. Electron diffraction patterns were evaluated using the Process Diffraction software package (Lábár 2005). Powder samples were dispersed in ethanol and the suspension was treated by ultrasound for 5 minutes. A drop of very dilute suspension was placed on a holey-carbon-coated copper grid and allowed to dry by evaporation at ambient temperature.

Electron-probe microanalysis

Qualitative and quantitative chemical analyses were performed using a CAMECA SX-100 electron microprobe equipped with four crystal spectrometers (operator M. Fridrichová, Institute of Geology, ASCR, v.v.i.). A TESCAN Vega scanning electron microscope with an EDS X-max 50 (Oxford Instruments) detector and acceleration voltage 15 kV, beam current 1.5 nA was used for BSE imaging (operator M. Racek, Faculty of Science, Charles University, Prague).

Mass spectrometry

Uranium, lead and thorium contents, as well as the isotopic ratios of Pb were measured using a X Series II Thermo Scientific quadrupole mass spectrometer (operator L. Strnad, Faculty of Science, Charles University, Prague). Galena samples were dissolved in 10 mL of concentrated HNO_3. After evaporation, a further 5 mL of concentrated HNO_3 was added and the solution was evaporated again. The remaining salts were placed in 25 mL HDPE bottles filled with 2 % (v/v) HNO_3. Coal samples were ground and 0.5 g ± 0.0005 g of material was placed on platinum plates and fired in a furnace at 450 °C for four hours. The maximum temperature was reached after gradual increasing the temperature at a rate of 50 °C/60 min. $HClO_4$ and HF were used for mineralisation of the ashes. For details of the analytical protocol and correction strategy see Strnad et al. (2005)

and Ďurišová et al. (2015). The external reproducibility of this method was monitored using the reference material NIST 1632b (Bituminous coal, NIST, USA). ^{74}Ge, ^{103}Rh and ^{187}Re isotopes were used as internal standards. Standard reference material SRM 981 (Common lead, NIST, USA) and SRM 983 (Radiogenic lead, NIST, USA) were used for lead isotope measurement verification.

RESULTS

When the coal heap material enriched in uranium caught fire, Pb – including its radioactive isotope ^{210}Pb – was released into the escaping gases. The liberated Pb was incorporated within the structure of galena during crystallization due to de-sublimation of hot gases. The radioactivity of this recently-formed galena is caused by the presence of radioactive ^{210}Pb and its decay products that have accumulated in the galena structure. The studied galena contains radionuclides of the ^{238}U decay chain, specifically at least its three final radionuclides as well as the final daughter, stable (non-radioactive) Pb, respectively:

$$^{210}Pb \xrightarrow[22.26y]{\beta-} {}^{210}Bi \xrightarrow[5{,}012d]{\beta-} {}^{210}Po \xrightarrow[138{,}376d]{\alpha} {}^{206}Pb$$

A major part of the γ activity of the studied galena is caused by secondary nuclear effects associated with the high β activity ^{210}Bi with very "hard" energy (β_{max} = 1.162 MeV). For the heavy galena matrix, the characteristic radiation lines Pb-X (72.8 to 84.9 keV, lines Pb*K*β and Pb*K*α composite) appears and Bremsstrahlung is also strongly emitted up to the energy corresponding to the above mentioned β_{max}. These effects are apparent in the γ spectrum of the galena from Radvanice (Fig. 4).

Alpha-spectrometry revealed the main α emitter is ^{210}Po (Eα 5304 keV), which is a daughter after ^{210}Pb (Fig. 5). ^{212}Po (E_α = 8785 keV) from the ^{232}Th decay chain was also detected in almost negligible amounts. As there are no lead isotopes having a longer lifetime in that decay chain, mechanical contamination from the surrounding rock is the most probable explanation (Fig. 5).

226 According to the autoradiographic picture, different α track densities (corresponding
227 with ^{210}Po α activity) are present in different crystals (Fig. 6). This is perhaps due to an
228 uneven burning of the inhomogenous heap material (with respect to the U and thus also ^{210}Pb
229 content). The $PbCl_2$ vapors were the most likely transport medium for lead (Wang and Tomia
230 2003). Ammonium chloride crusts found in the overburden of the crystallised galena from
231 Radvanice strongly support this theory.

232 At the time the samples were collected from the burning Radvanice heap, the galena
233 radioactivity was very high and decreased rapidly within a few hours (indicated by qualitative
234 Geiger counter measurements by R. Škoda). This may have been caused by the presence of
235 the short-lived radionuclides ^{214}Pb ($t^{1/2}$ = 26.8 min) and ^{214}Bi ($t^{1/2}$ = 19.9 min), which were
236 also originally present in newly-formed galena.

237 Due to the short half-life of ^{210}Pb ($t^{1/2}$ = 22.26 years), the total activity of this nuclide
238 in galena has decreased significantly since crystallization. Today, the average radioactivity of
239 galena from Radvanice is 624 ± 59 Bq/g (the galena age is 16 years). Galena from
240 Markoušovice has a measured activity of 684 ± 20 Bq/g (the galena age is 8 years), and for
241 Rybníček galena the activity is only 135 ± 9 Bq/g (the galena age is about 50 years). As the
242 ages of the galena crystals are known the original mass activity of ^{210}Pb at the time of
243 crystallisation can be calculated. The original activity of Radvanice galena is 1026 Bq/g
244 (integral dose for the 16 years is 4.34×10^{11} α/g), that of Markoušovice galena is 877 Bq/g
245 (dose for the 8 years is 2.21×10^{11} α/g), and that of Rybníček galena is 724 Bq/g (dose for the
246 ~ 54 years is 6.11×10^{11} α/g). The activity of the galena samples at the time of their formation
247 is quite similar at all studied localities (Fig. 7). The calculated integral dose of the galena
248 samples studied is quite low. For example, the integral dose is seven orders of magnitude
249 lower that in some cases of metamict zircon, where the typical dose is up to $12\text{-}14\times10^{18}$ α/g
250 (e.g. Farnan et al. 2007, Nasdala et al. 2005, and others).

Broadening of powder diffraction profiles in the studied galena samples shows a strong anisotropy, *i.e.* a strong *hkl*-dependence. This is typical due to contributions from defects such as dislocations or stacking faults. Such an anisotropy was observed previously in studies of Ungár et al. (1999) in ball-milled galena. For studies of structural micro-deformation in such materials it is more convenient to use a modified form of the Williamson-Hall plot method. XRD line broadening due to lattice defects is sensitive, similar to electron microscopy, to the mutual orientation of *hkl* diffraction vectors and dislocation lines, as well as to the character of the deformation fields, and can be strongly influenced by the crystal elastic anisotropy. For the powder diffraction case this can be accounted for by "dislocation orientation factors" C_{hkl} (Ungár et al. 1999). The expected linear dependence of XRD line broadening on the length of the diffraction vector (sin θ) is then modified by the square root of the orientation factors C_{hkl}. In case of the cubic material the orientation factors C_{hkl} are a simple function of the well-known cubic Γ_{hkl} invariant:

$$C_{hkl} = C_{h00} * (1 + q\Gamma_{hkl}), \qquad where \quad q\Gamma_{hkl} = \frac{h^2k^2 + k^2l^2 + l^2h^2}{(h^2 + k^2 + l^2)^2} \qquad (1)$$

Parameters C_{h00} and q above are material constants characteristic of the dislocation type (edge or screw) and the active dislocation slip system. These can be calculated using theory provided in Klimánek and Kužel (1988) or *e.g.*, the software ANIZC (ANIZC, 2003). It was shown that for many materials the C_{h00} constant is very similar for edge and screw dislocations of a particular slip system, whereas parameter q differs significantly. The most common slip system for *fcc* materials is {111}⟨110⟩; however, for galena the {100}⟨110⟩ slip system was reported to be most active (Deeb et al. 2004). Ungár et al. (2002) reported a high q = 6.5 value calculated for the Zener anisotropy ratio of PbS A_z = 0.311. A calculation based on the general theory (Klimánek and Kužel 1988) and using Wolfram Mathematica gives q_s = 1 for ⟨110⟩ screw dislocations and q_e = 4.3 for {100}⟨110⟩ edge dislocations. Hence the q parameter was optimized to obtain the best linear correlation in the modified Williamson-Hall

plot assuming that it is in the range of 1.0 to 4.3. In our case a higher q equates to stronger *hkl*-anisotropy. The density of dislocation defects is then proportional to the slope in the modified Williamson-Hall plot (Fig. 8). Samples from Radvanice, Příbram and synthetic PbS show strong anisotropy, hence $q = 4.3$ was used and the modified Williamson-Hall plot gives better a correlation than the simple linear version, whereas for samples from localities in Markoušovice and Rybníček the anisotropy is not so strong, and the modified method does not provide significant improvement and consequently a lower q (= 1) was used. Concerning the crystallite size and micro-deformation, the graph shows (Fig. 8) that the size-effect on diffraction line broadening is unimportant, but the presence of strain in galena caused by micro-deformations varies within samples. The lowest values of micro-strain are observed for synthetic galena, which should ideally contain no micro-deformations, although this is not the case. Rapid cooling of synthetic galena upon removal from the furnace may have caused this difference from the ideal state. The structure data of the studied galena show that the extent of crystal structure damage depends on the duration of the radiation exposure. A high level of strain occurs for Rybníček galena (age ~50 years), and lower values occur for Radvanice galena (age is 16 years). The galena sample from Markoušovice (age is 8 years) exhibits the lowest structural damage. These micro-deformations are caused by the presence of the ^{210}Pb emitter and its daughters that produce destructive ionizing particles (mainly α and recoil daughters) in the crystal structure of galena.

Investigations using HRTEM showed that micro-deformations in galena from Radvanice are caused mainly by metamictization of the galena structure. Three stages of structure damage were observed: 1) fully crystalline, 2) polycrystalline (nano-crystalline) and 3) fully metamict ("amorphous" PbS) (Fig. 9). We find it very interesting that fully metamict galena occurs as a ball-like crystalline cluster of nanometric size (Fig 9 / 4b). This feature probably represents a process of self-recrystallization of amorphous PbS, as was also

documented for metamict zircon (e.g. Palenik et al. 2003, Ewing et al. 2003) and in other minerals containing radioactive elements (Ewing et al. 2000).

The existence of distinct degrees of structural damage within one sample (macro-crystal) could relate to the primary differences in initial ^{210}Pb content in galena, caused by various ^{210}Pb activities in the gases that gradually were produced in burning heap material. A significant zoning of the galena crystals is apparent in the autoradiographic images, supporting this explanation. Another possible contributing factor is migration of structure defects and their concentration into insulated clusters with the highest damage (Yashuda et al. 2003; Katoh et al. 2012). This situation is completely different from those observed in materials such as zircon or other metamict minerals studied to date, which are all dielectrics. Galena is a natural semiconductor (Jenkins 2005), so electrons, holes and also lattice defects can migrate very readily.

The chemical compositions of galena samples from Radvanice, Markoušovice and Rybníček are relatively homogeneous and there is only a small concentration of minor elements that has no significant effect on the unit cell parameters of the studied galena. Empirical formulae are: for Markoušovice galena $(Pb_{0.96}Sn_{0.02}Cd_{0.01})_{\Sigma 0.99}(S_{0.97}Se_{0.03})_{\Sigma 1.00}$, Rybníček galena $(Pb_{0.97}Cd_{0.02}Sn_{0.01})_{\Sigma 1.00}(S_{0.94}Se_{0.07})_{\Sigma 1.01}$ and Radvanice galena $(Pb_{1.00}Sn_{0.01})_{\Sigma 1.01}(S_{0.95}Se_{0.03})_{\Sigma\ 0.98}$. Refined unit cell parameter a varies between 5.934(4) Å and 5.9426(5) Å (with corresponding V = 208.97(9) and 209.86(5) Å^3). These are in good agreement with results given by Vávra and Losos (1992), Žáček and Ondruš (1997), and Sejkora et al. (1998a), who studied galena from the Radvanice locality.

Average isotopic ratios of lead from the heap material from the localities Radvanice, Markoušovice and Rybníček are in the range (^{207}Pb/^{206}Pb) from 0.8213 to 0.8466 and (^{208}Pb/^{206}Pb) from 2.0176 to 2.0791. These values correspond well with data of Mihaljevič et al. (2009), where the most general value for Czech coal lies in the range (^{207}Pb/^{206}Pb) from

0.8333 to 0.8403, as well as for the value representing the upper crust with the isotopic ratio ($^{207}Pb/^{206}Pb$) = 0.8333 (Novák et al. 2003). Similar values were measured in galena formed by direct crystallization from gas produced by heap burning at the localities Markoušovice ($^{207}Pb/^{206}Pb$) = 0.8402, Radvanice ($^{207}Pb/^{206}Pb$) = 0.8411, and Rybníček ($^{207}Pb/^{206}Pb$) = 0.8435. The isotopic ratios in coal, burnt rock and galena are considered equal and no fractionation of lead occurs during heap burning, when lead is released from the coal mass into the gases and consequently crystallizes in the form of galena.

IMPLICATIONS

Radiation damage in sulphides has been observed and described for the first time for the case of recently-formed galena from burning heaps of U-rich coal. The high radioactivity of the galena samples is caused by the presence of ^{210}Pb, its decay products (^{210}Bi and ^{210}Po), as well as by secondary radiation, caused by nuclear effects of the interaction of the ^{210}Bi isotope hard β rays with a heavy PbS matrix. ^{210}Pb in galena originates from the uranium-rich coal. This lead isotope incorporates, together with non-radioactive isotopes, during heap burning. Our investigations confirmed that the ^{210}Pb isotope and products of its decay-chain cause strain and metamictization of the galena structure, as shown by PXRD and HRTEM. This leads to formation of micro-deformations, represented by increased strain in the structure, and by local structure degradation leading to an “amorphous” galena. Although galena activities at the time of their formation were similar for all localities studied, their structures are affected differently. Observed micro-strain is thus dependent mainly on the age of the galena, *i.e.* on how long their crystal structures were exposed to radiation. Due to a short half-life of ^{210}Pb (22.3 years), the activity of samples stored in mineral collections decreases rapidly; for our followers they will no-longer be detectable, but the radiation damage of their structures will be recorded.

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Figure captions

Figure 1. Free galena skeletal crystals. Radvanice (Photo: P. Škácha 2014).

Figure 2. A burnt rock with galena. Markoušovice (Photo: P. Škácha 2014).

Figure 3. A burnt rock with galena covered with anglesite. Rybníček (Photo: P. Škácha 2014).

Figure 4. Presence of ^{210}Pb in the γ-spectrum of galena from Radvanice.

Figure 5. An α-spectrum of galena: ^{210}Po is the main emitter, ^{212}Po is also detected as in negligible amount.

Figure 6. Autoradiography of galena. a) polished section scan, b) SEM/EDS images, c) α particle tracks on autoradiography.

Figure 7. A comparison of activity of ^{210}Pb in galena samples from Radvanice, Markoušovice and Rybníček at the time of measurements (year 2014) and at the time of formation (crystallisation).

Figure 8. Modified Williamson-Hall plot showing the micro-strain in crystal structure of studied galena based on PXRD data.

Figure 9. HRTEM images showing structural damage caused by radiation emitted by ^{210}Pb in galena crystals. Different stages of metamictization are observed within one crystal. 1a), 1b), 1c) – well crystalline galena from Příbram (reference sample of fully crystalline galena); 2a), 2b), 2c) – crystalline stage in galena from Radvanice; 3a), 3b), 3c) – polycrystalline stage in galena from Radvanice; 4a), 4b), 4c) – metamict stage in galena from Radvanice.

Figure 1

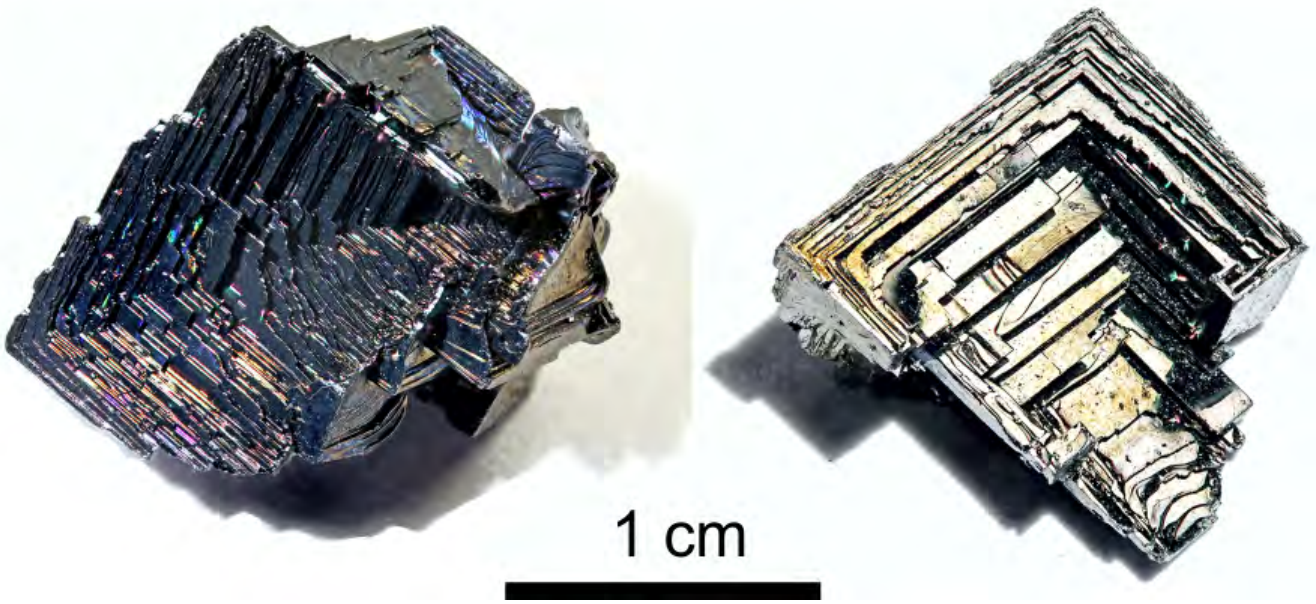


Figure 2

Figure 3

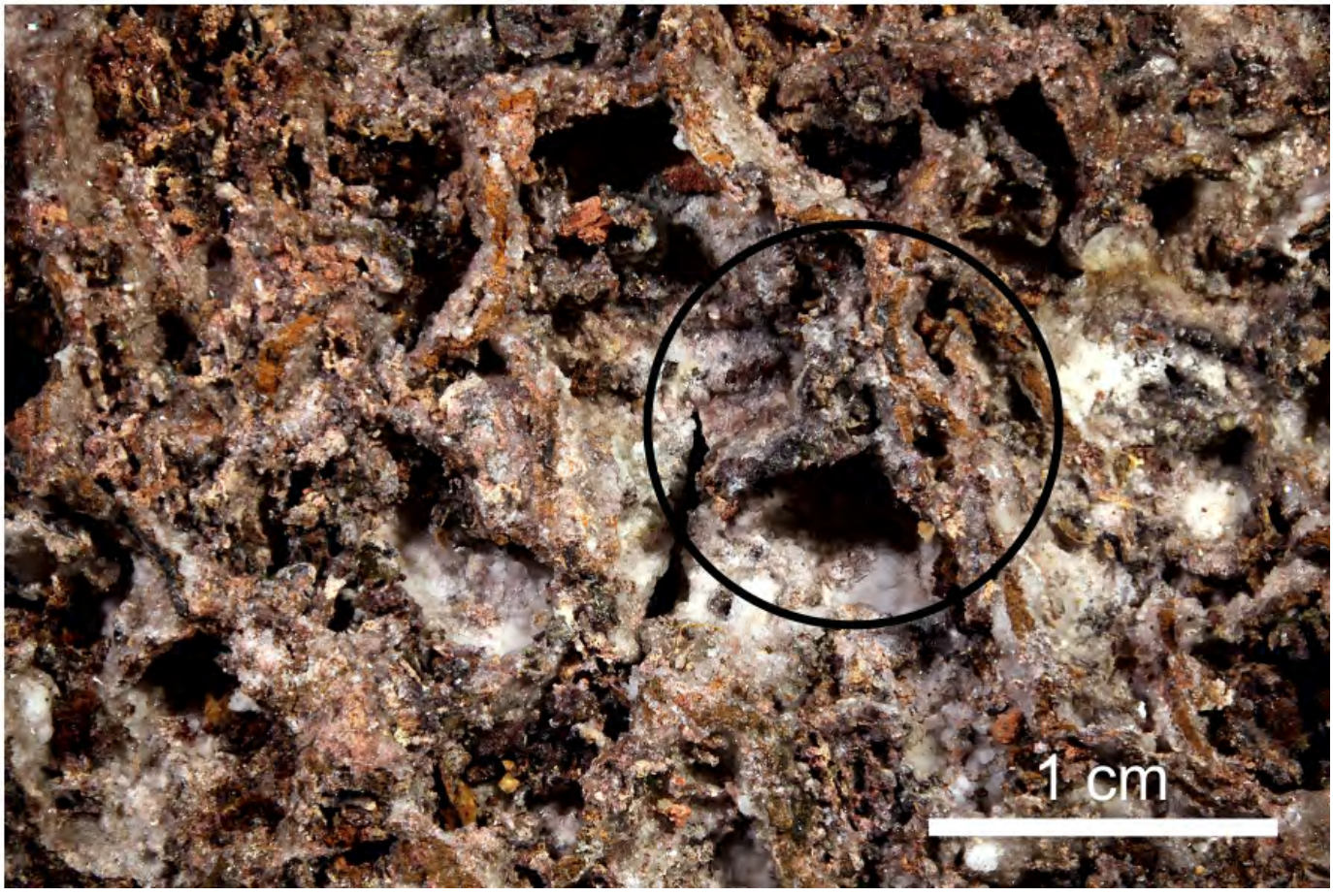


Figure 4

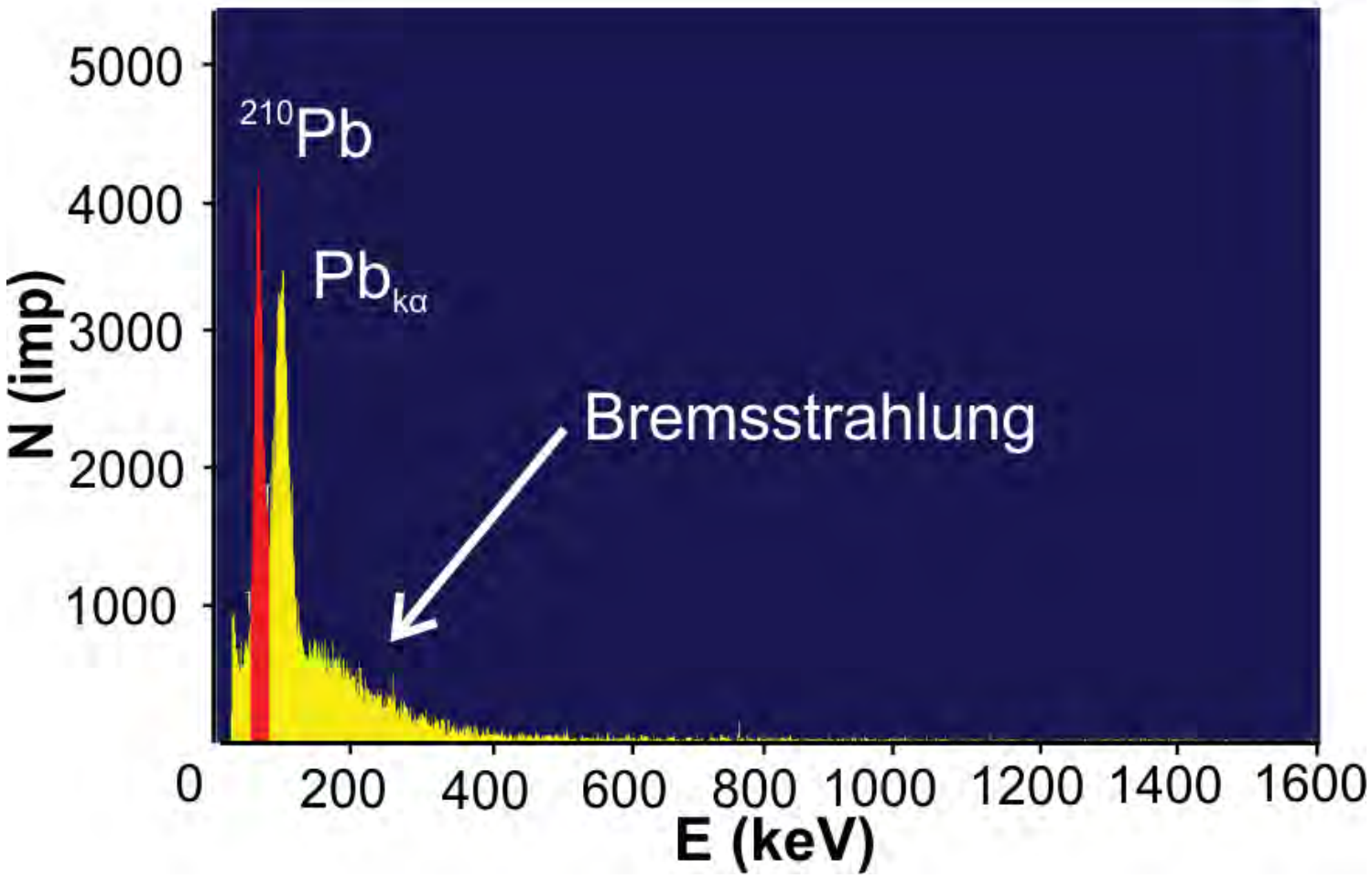

5000
4000
3000
2000
1000
N (imp)
^{210}Pb
Pb$_{k\alpha}$
Bremsstrahlung
0
200
400
600
800
1000
1200
1400
1600
E (keV)

Figure 5

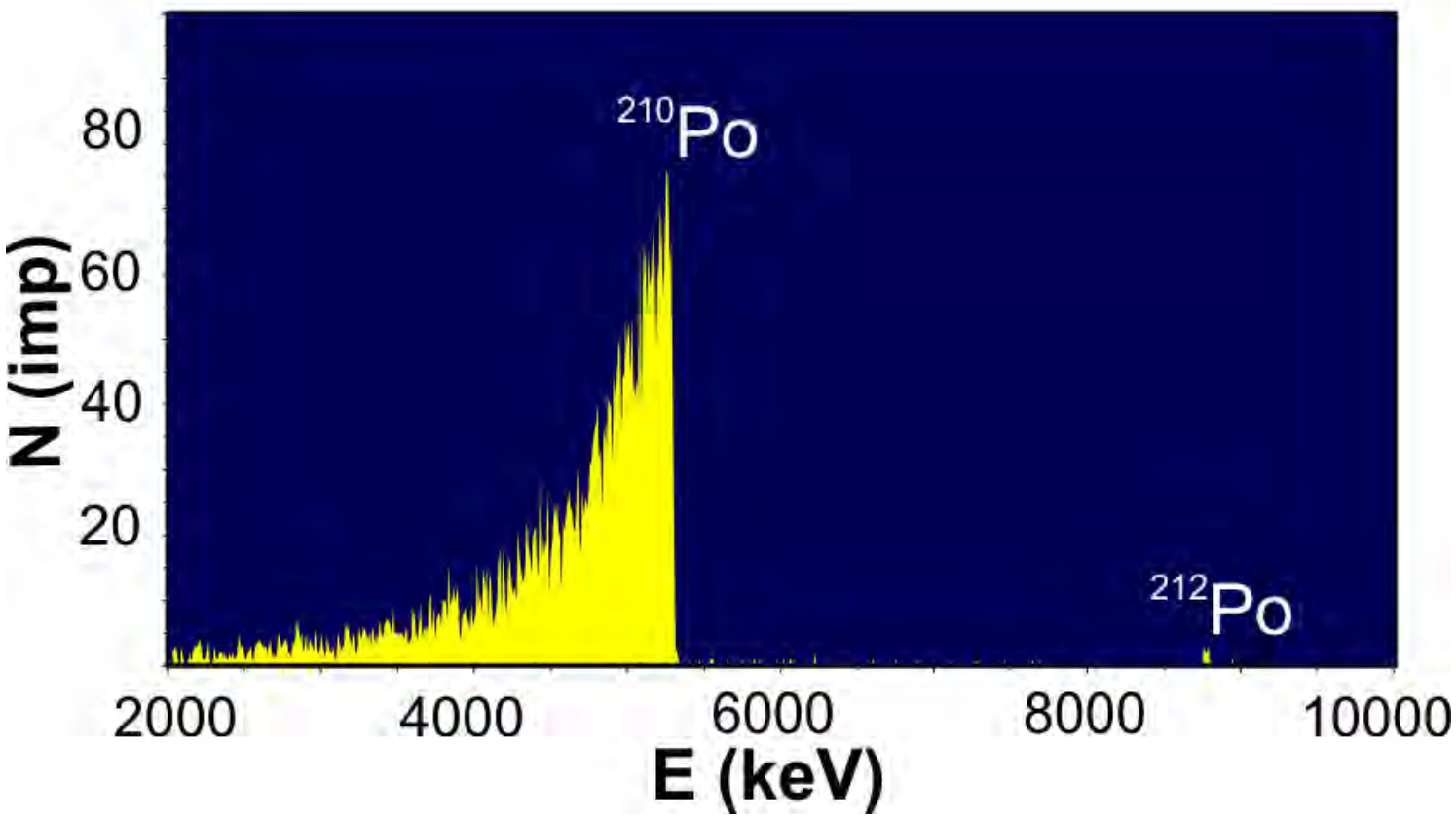


Figure 6

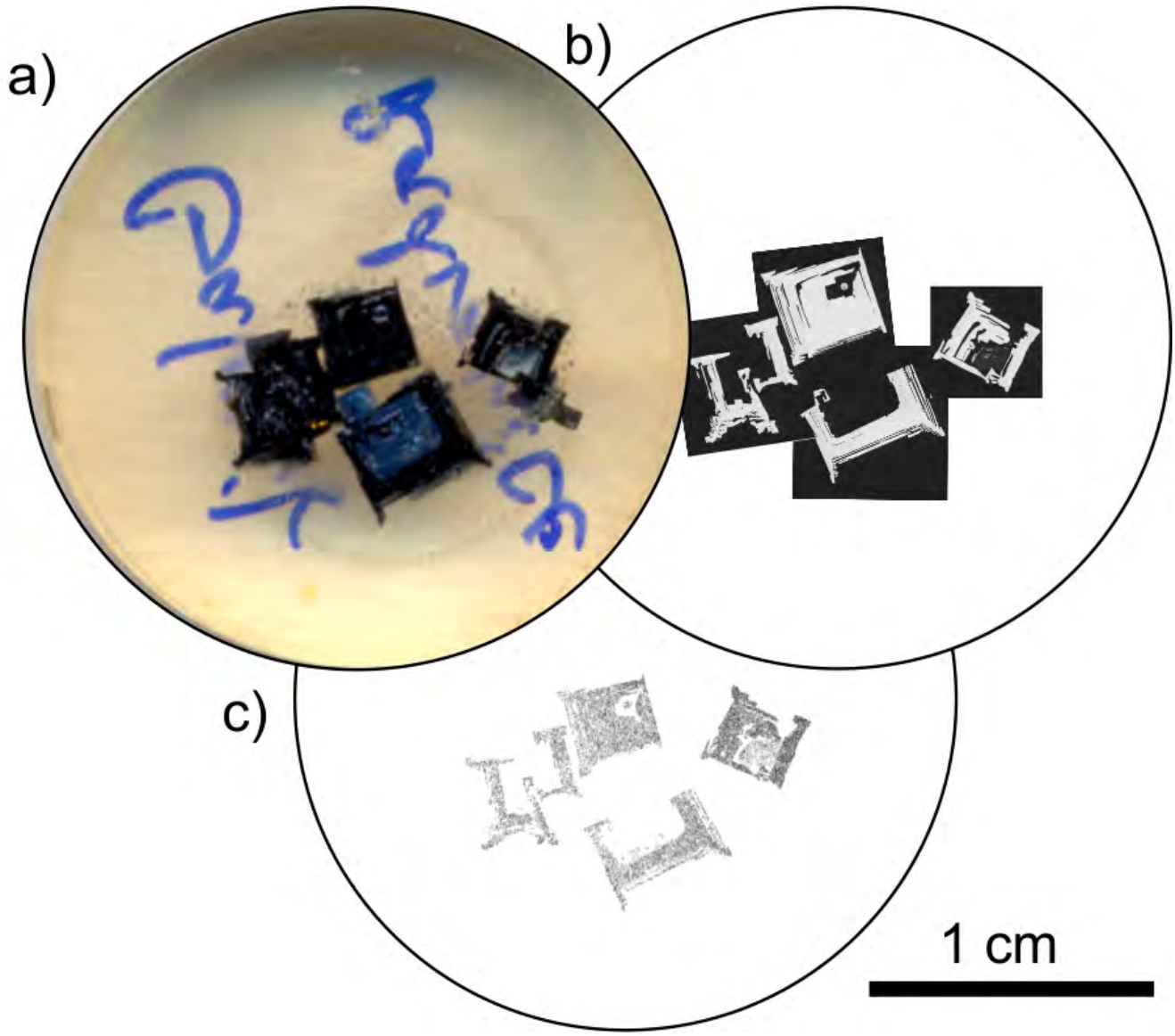


Figure 7

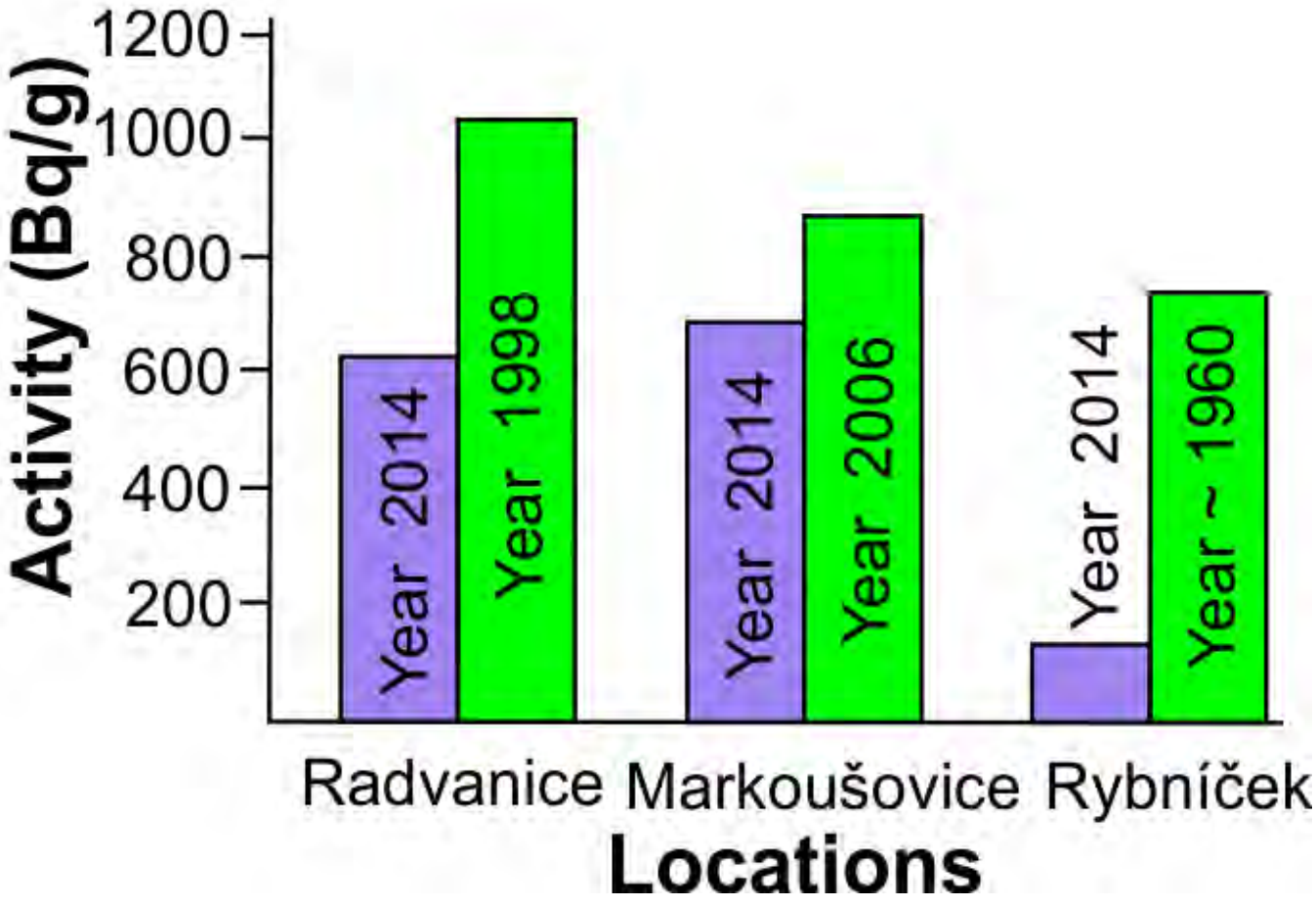

Activity (Bq/g)
1200
1000
800
600
400
200
Year 2014
Year 1998
Year 2014
Year 2006
Year 2014
Year ~ 1960
Radvanice
Markoušovice
Rybníček
Locations

Figure 8

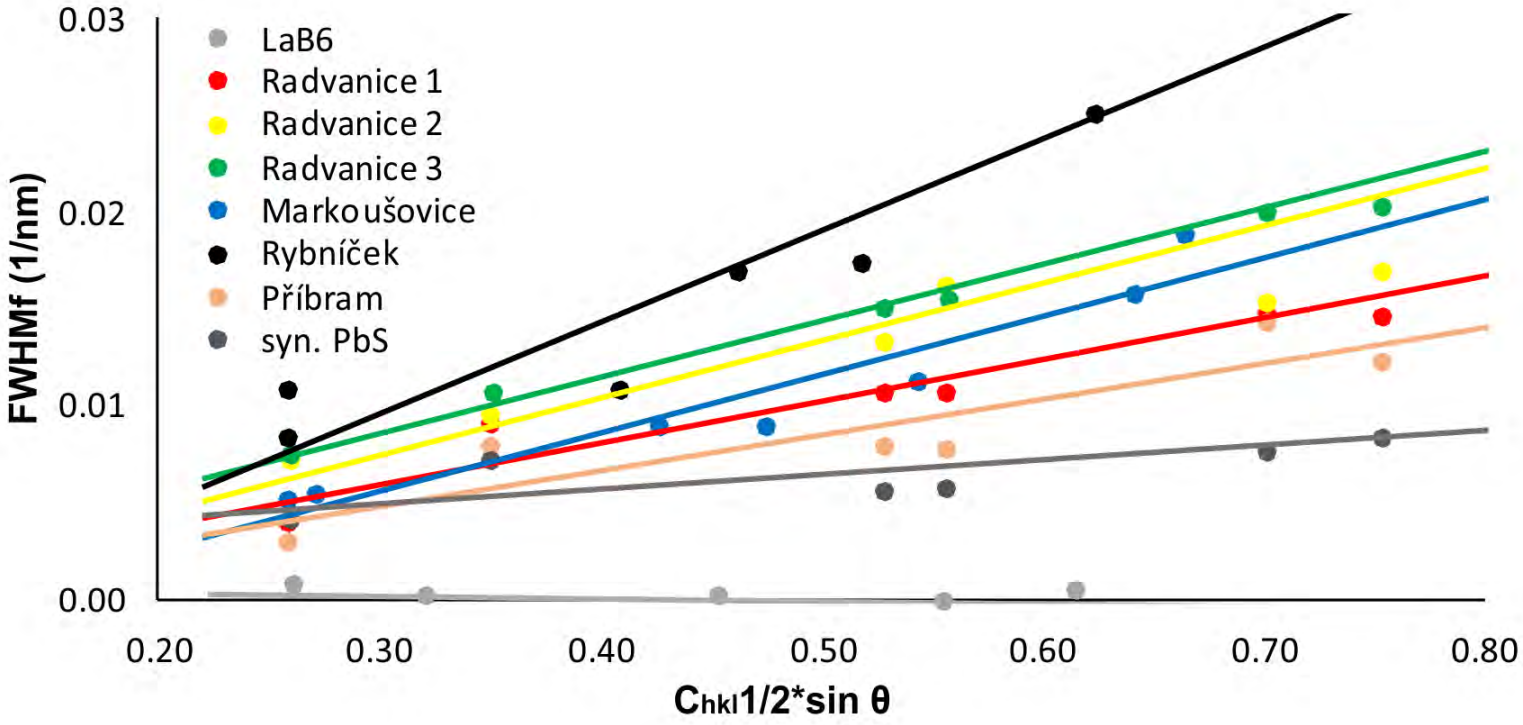
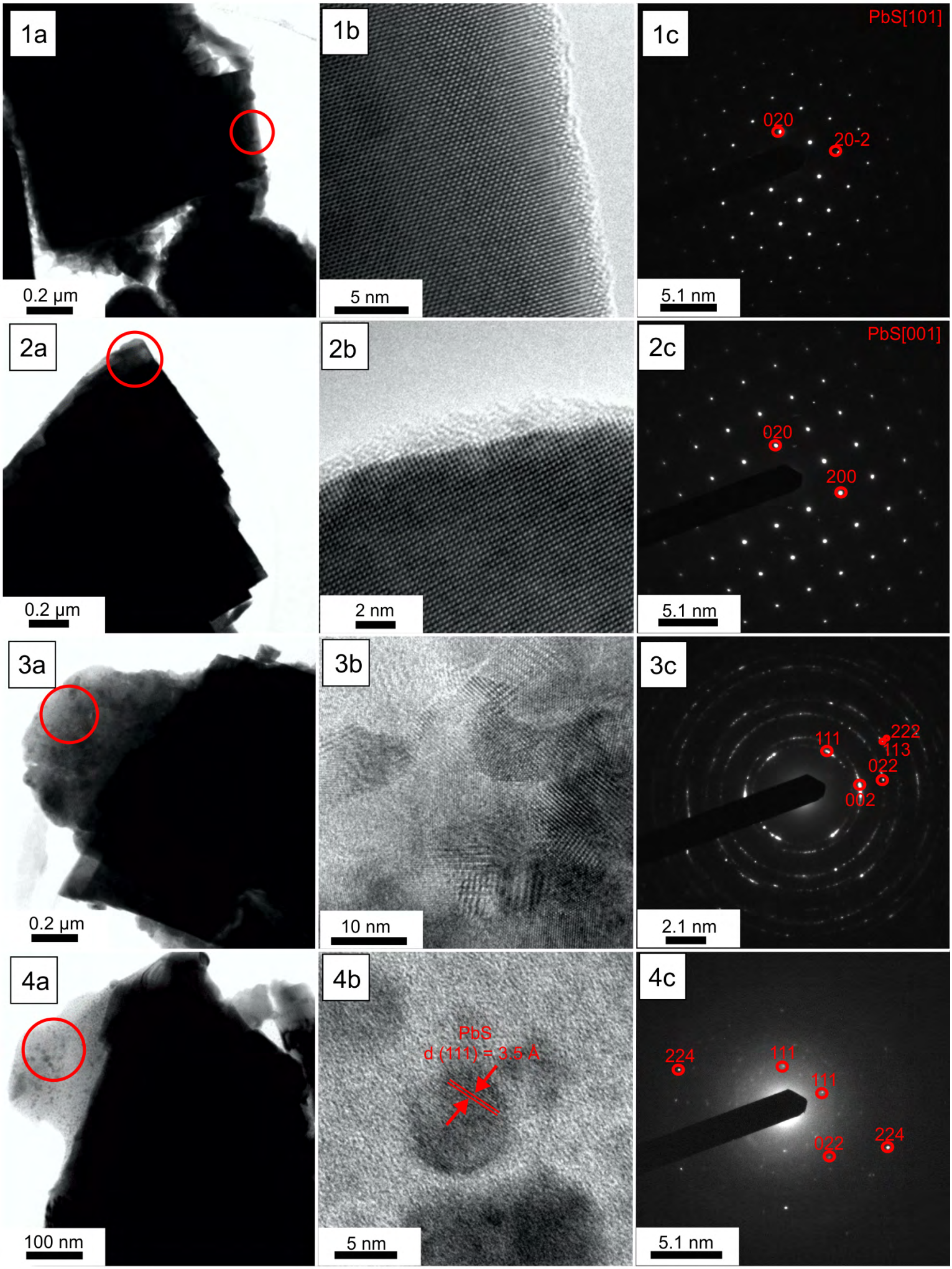

0.03
0.02
0.01
0.00
FWHMf (1/nm)
LaB6
Radvanice 1
Radvanice 2
Radvanice 3
Markoušovice
Rybníček
Příbram
syn. PbS
0.20
0.30
0.40
0.50
0.60
0.70
0.80
Chkl1/2*sin θ

Figure 9


1a
0.2 µm
1b
5 nm
1c
PbS[101]
020
20-2
5.1 nm
2a
0.2 µm
2b
2 nm
2c
PbS[001]
020
200
5.1 nm
3a
0.2 µm
3b
10 nm
3c
111
222
113
022
002
2.1 nm
4a
100 nm
4b
PbS
d (111) = 3.5 Å
5 nm
4c
224
111
111
022
224
5.1 nm