## Kravtsovite, PdAg<sub>2</sub>S, a new mineral from the Noril'sk-Talnakh deposit, Krasnoyarskiy kray, Russia

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Abstract: Kravtsovite, PdAg<sub>2</sub>S, is a new platinum-group mineral discovered in the Komsomolsky mine of the Talnakh deposit, Noril'sk district, Russia. It forms equant inclusions (ranging in size from a few µm to 40-50 µm) in silicates and pyrite, commonly intergrown with vysotskite and Au-Ag alloy in aggregates (100-200 µm across) with telargpalite, cooperite, braggite, vysotskite, sopcheite, stibiopalladinite, sobolevskite, moncheite, kotulskite, malyshevite and insizwaite. Kravtsovite is brittle; it has a metallic lustre and a grey streak. In plane-polarised light, kravtsovite is yellowish white, has strong bireflectance, is strongly pleochroic in shades of slightly vellowish white to bluish grey, and exhibits a strong anisotropy with rotation tints of salmon-pink, orange, pale blue and dark blue-black. It exhibits no internal reflections. Reflectance values in air ( $R_1$ ,  $R_2$  in %) are: 32.2, 38.3 at 470, 31.6, 39.4 at 546, 30.2, 39.8 at 589 and 28.8, 41.1 at 650 nm. Eighteen electron probe microanalyses of kravtsovite give the average composition: Pd 30.53, Ag 60.11, S 8.47, and Se 0.74, total 99.85 wt%, corresponding to the empirical formula  $Pd_{1,03}Ag_{1,99}(S_{0,95}Se_{0,03})_{\Sigma 0.98}$  based on a total of 4 atoms per formula unit (apfu). The average of eight analyses on synthetic kravtsovite is: Pd 30.98, Ag 60.27, and S 8.81, total 100.07 wt%, corresponding to Pd<sub>1.04</sub>Ag<sub>1.99</sub>S<sub>0.98</sub>. The mineral is orthorhombic, space group Cmcm, with a 7.9835(1), b 5.9265(1), c 5.7451(1) Å, V 271.82(1) Å<sup>3</sup> and Z=4. The crystal structure was refined from the powder X-ray-diffraction data of the synthetic analogue. The strongest lines in the X-ray powder diffraction pattern of synthetic kravtsovite [d in Å (I) (hkl)] are: 2.632(51)(021), 2.458(65)(112), 2.4263(71)(310), 2.3305(60)(202), 2.2352(100)(311), 2.1973(48) (221), 2.0619(42)(022), 1.9172(30)(130), 1.3888(42)(240,332), 1.3586(28)(512). The mineral honours V.F. Kravtsov, one of the discoverers of the Talnakh and Oktyabrsk deposits in the Noril'sk district of Russia.

**Key-words:** kravtsovite; new mineral; platinum-group mineral; PdAg<sub>2</sub>S phase; silver palladium sulphide; synthesis; reflectance data; X-ray-diffraction data; crystal structure; Komsomolsky mine; Talnakh deposit; Noril'sk district; Russia.

### 1. Introduction

Kravtsovite, ideally PdAg<sub>2</sub>S, occurs in vein-disseminated pyrite–chalcopyrite–galena ore from the Komsomolsky mine in the Talnakh deposit of the Noril'sk district, Russia. The sample was found at coordinates:  $69^{\circ} 30' 20''$  N and  $88^{\circ} 27' 17''$  E. Subsequently, the mineral was also found in millerite–pyrite–chalcopyrite ore in the same mine (Sluzhenikin, 2011; Sluzhenikin & Mokhov, 2015). A phase with a similar composition has been also observed in mineralized samples from the Marathon deposit in the Coldwell Complex, Ontario (Doreen Ames, personal communication). It is noteworthy that a chemically related mineral, coldwellite (Pd<sub>3</sub>Ag<sub>2</sub>S; McDonald *et al.*, 2015) has recently been discovered in the same mineralized areas. Both mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC IMA) (No. 2016-092). The mineral name kravtsovite is chosen to honour Victor F. Kravtsov (1932–2014) (Виктор Фомич Кравцов), a Russian geologist who was one of the discoverers of the Talnakh and Oktyabr deposits in the Noril'sk camp, Russia. He worked for most of his career as a leading geologist in the Zapadno-Kharaelakh Prospecting Division of the Noril'sk Geological Survey. The holotype (polished section) is deposited at the Department of Earth Sciences of the Natural History Museum, London, UK, catalogue No BM 2016, 150. According to the chemical composition, the mineral should belong to the 2.A group (sulphides) of the Strunz & Nickel (2001) classification.



Fig. 1. Images of kravtsovite (kra) in association with (a) chalcopyrite (ccp) and galena (gn), a polycrystalline kravtsovite grain (from greenish grey to brownish grey) showing strong bireflectance, reflected polarised light, (b) vysotskite (vys), pyrite (py), chalcopyrite (ccp), galena (gn), and aurian silver (back-scattered electron image).

# 2. Appearance, physical and optical properties

Kravtsovite forms small (a few  $\mu$ m to 40–50  $\mu$ m) equant inclusions in silicates (diopside, grossular, chlorite-group minerals) and in pyrite, commonly intergrown with vysotskite and Au-Ag alloy, chalcopyrite, rarely with galena. It is also found in aggregates (100–200  $\mu$ m in size) intergrown with other platinum-group minerals (PGM), such as telargpalite, cooperite, braggite, vysotskite, sopcheite, stibiopalladinite, sobolevskite, moncheite, kotulskite, malyshevite, and insizwaite. The full list of ore minerals in the assemblage contains more than 25 species. Calcite (relics of carbonate host rock and late veinlets), diopside, grossular, apatite, and chlorite-group minerals are among the most common gangue minerals (confirmed by energy-dispersive spectrometry (EDS), diopside was also confirmed by electron-backscatter diffraction, EBSD). The host rock for the disseminated ore minerals is skarn, replacing calcite matrix rock located beneath a basaltic sill. An image of kravtsovite with associated minerals is shown in Fig. 1.

Kravtsovite is opaque with a metallic lustre. The powder of synthetic kravtsovite is grey in colour. Synthetic kravtsovite is brittle. The density calculated on the basis of the empirical formula and cell dimensions of synthetic kravtsovite (Table 1) is 8.73 g/cm<sup>3</sup>. In plane-polarised reflected light, relative to galena, it displays strong pleochroism in shades of slightly yellowish white to a bluish grey, and strong anisotropy with rotation tints of salmon-pink, orange, pale blue and dark blue–black. It exhibits no internal reflections.

Reflectance measurements were made in air relative to a WTiC standard on both natural and synthetic kravtsovite using a J & M TIDAS diode array spectrometer attached to a Zeiss Axiotron microscope. The results are presented in Table 2 and Fig. 2. The reflectance spectra for natural and synthetic kravtsovite are an excellent match bearing in mind that the number of natural grains suitable for measurement was limited and that the measurements were on non-oriented sections, hence the designations  $R_1$  and  $R_2$ . The reason for the rather sharp change of slope in the spectra at around 500 nm is not known, but certainly contributes to the observed strongly pleochroic nature of kravtsovite in plane-polarised reflected light.

#### 3. Chemical composition

Electron probe microanalyses (EPMA) of grains of kravtsovite were performed using the WDA Inca Wave 500 (Oxford Instruments) installed on SEM Lyra 3GM (Tescan), with the following analytical conditions: 15 kV, 12.5 nA, and counting times 30 s (on peak positions) and  $2 \times 15$  s (background on left and right positions). The spectra were collected on PdL $\alpha$ , AgL $\alpha$ , SK $\alpha$ , SeL $\alpha$  lines, with the following standards: pure Se, Pd, Ag, Bi, synthetic PbTe, natural FeS<sub>2</sub>; Pb, Fe, Bi, Te were below detection limit (<0.08–0.10 wt%).

Synthetic kravtsovite was analysed with a CAMECA SX-100 electron probe microanalyser in wavelength-dispersive mode using an electron beam focussed to  $1-2 \mu m$ . Pure elements were used as standards. Contents were quantified on the PdL $\alpha$ , AgL $\alpha$ , and SK $\alpha$  (with an overlap correction on PdL $\beta$ ) with an accelerating voltage of 15 kV, and a beam current of 10 nA measured on a Faraday cup.

The EPMA data are given in Table 3. The empirical formula (based on 4 atoms) for kravtsovite (average of 18 analyses on 3 grains) is  $Pd_{1.03}Ag_{1.99}(S_{0.95}Se_{0.03})_{\Sigma 0.98}$ , and for synthetic kravtsovite (average of 11 analyses), is  $Pd_{1.04}Ag_{1.99}S_{0.98}$ ; it corresponds to  $PdAg_2S$ .

#### 4. Synthetic analogue

The small size and fine intergrowths of kravtsovite with pyrite, Au-Ag alloy and other minerals listed above prevented its extraction and isolation in an amount

Data collection Radiation type, source	X-ray CoKa		
Generator settings	$40 \mathrm{kV}$ 30 mA		
Range in 2A (°)	10-130		
Step size (°)	0.033		
Crystal data			
Space group	<i>Cmcm</i> (No. 63)		
Unit-cell content	$PdAg_2S, Z=4$		
Unit-cell parameters (Å)	a = 7.9835(1)		
• • • • •	b = 5.9265(1)		
	c = 5.7451(1)		
Unit-cell volume ( $Å^3$ )	271.82(1)		
Rietveld analysis			
No. of reflections	90		
No. of structural parameters	6		
No of. profile parameters	5		
R <sub>Bragg</sub>	0.049		
R <sub>p</sub>	0.023		
R <sub>wp</sub>	0.033		
Weighting scheme	$1/y_{o}$		

Table 1. Data collection and Rietveld analysis of synthetic kravtsovite.

Table 2. Reflectance data for natural and synthetic kravtsovite and coldwellite (McDonald *et al.*, 2015).

sufficient for the relevant crystallographic and structural investigations. Therefore, these investigations were performed on the synthetic analogue  $Pd_{1.04}Ag_{1.99}S_{0.98}$ .

Synthetic  $PdAg_2S$  was prepared using the evacuated silica-glass tube method in the Laboratory of Experimental Mineralogy of the Czech Geological Survey in Prague. Palladium (99.95%), Ag (99.999%) and S (99.999%) were used as starting materials for synthesis. The evacuated tube with its charge was sealed and annealed. After cooling using a cold-water bath, the charge was ground into powder in acetone using an agate mortar, and thoroughly mixed to homogenize. The pulverized charge was sealed in an evacuated silica-glass tube again, and heated at 400 °C for 70 days. The experimental product was rapidly quenched in cold water.

#### 5. X-ray crystallography

The attempts, using various experimental methods (*e.g.*, salt flux) to obtain a single crystal of the phase  $PdAg_2S$  were not successful. Therefore, the crystal structure and unit-cell parameters of synthetic kravtsovite were refined from the powder X-ray diffraction data.

The X-ray diffraction pattern of synthetic  $PdAg_2S$  used for structure determination was collected in Bragg– Brentano geometry on an X'Pert Pro PANalytical diffractometer, equipped with X'Celerator detector and a CoK $\alpha$  radiation source. The data were collected between 10 and 130° 20; a full width at half maximum of 0.107° in 20 was obtained at 30.709° 20, indicating a good crystallinity of the studied sample. For comparison, LaB<sub>6</sub> used as a diffraction standard shows a full width at half maximum of 0.067° at 35.434° 20 in the same configuration of the diffractometer.

$\lambda$ (nm)	Coldwellite	Kravtsovite				
	R (%)	Nat	ural	Synthetic		
		$R_1$ (%)	$R_2$ (%)	$R_1$ (%)	R <sub>2</sub> (%)	
400	40.0	30.6	37.0	32.9	37.5	
420	40.4	31.1	37.5	33.2	38.2	
440	40.9	31.5	38.0	33.5	38.9	
460	41.5	32.0	38.5	33.9	39.6	
470	41.9	32.2	38.8	34.1	39.9	
480	42.1	32.4	39.0	34.3	40.2	
500	42.7	32.5	39.2	34.5	40.6	
520	43.4	32.4	39.2	34.4	40.8	
540	43.9	31.9	39.3	34.0	40.8	
546	44.0	31.6	39.4	33.7	40.8	
560	44.1	31.2	39.5	33.5	40.9	
580	44.1	30.5	39.7	33.0	41.1	
589	44.0	30.2	39.8	32.8	41.3	
600	44.1	29.9	39.9	32.5	41.5	
620	44.2	29.5	40.3	31.9	41.9	
640	44.6	29.0	40.8	31.3	42.4	
650	45.0	28.8	41.1	31.1	42.7	
660	45.2	28.5	41.3	30.8	42.9	
680	45.9	28.2	41.8	30.3	43.3	
700	46.6	27.8	42.3	30.0	43.6	

The details of data collection and basic crystallographic data are given in Table 1. The indexing of the X-ray powder pattern was performed using the DICVOL06 program (Boultif & Louër, 2004). The first 20 lines covering a range from  $21.57^{\circ}$  to  $77.06^{\circ}$  in 20 were indexed on the basis of an orthorhombic cell with the lattice parameters listed in Table 1. The figures of merit for assessing the quality of the solution were  $M_{20}=70$  (de Wolff, 1968) and  $F_{20}=44$  (0.0063; 72) (Smith & Snyder, 1976).

As a next step, a search in the Inorganic Crystal Structure Database (FIZ/NIST 2015) for possible isostructural compounds was performed. The phase Na<sub>2</sub>AuBi (Kim *et al.*, 2010) was subsequently selected since it has the same stoichiometry, similar unit-cell parameters (Na<sub>2</sub>AuBi: 9.44, 7.70, 5.84 Å; PdAg<sub>2</sub>S: 7.98, 5.92, 5.74 Å) and orthorhombic symmetry. Its space group (*Cmcm*) is also consistent with observed extinctions in the powder diffraction data of PdAg<sub>2</sub>S.

Hence, the structure of Na<sub>2</sub>AuBi was used as the initial structural model in the subsequent Rietveld refinement of PdAg<sub>2</sub>S by means of the program FullProf (Rodríguez-Carvajal, 2006). The starting model for PdAg<sub>2</sub>S was obtained from the Na<sub>2</sub>AuBi structure by following the atom replacements Na – Ag, Au – Pd, and Bi – S.

A pseudo-Voigt function was used to generate the shape of the diffraction peaks in the subsequent Rietveld refinement. The background was determined by the linear interpolation between consecutive breakpoints in the pattern. The refined parameters include those describing the peak shape and width, peak asymmetry, unit-cell parameters, three fractional coordinates, preferred orien-



Fig. 2. Reflectance data for kravtsovite compared to synthetic kravtsovite and coldwellite (McDonald *et al.*, 2015), in air.

Table 3. Electron-microprobe analyses of kravtsovite.

wt%	Pd	Ag	S	Se	Total
(n=18)					
Mean	30.53	60.11	8.47	0.74	99.85
Range	29.41-32.11	59.15-62.00	7.98-8.79	0.33-1.12	
Std. dev.	0.78	0.75	0.21	0.22	
Synthetic	sample $(n = 1)$	1)			
Mean	30.98	60.27	8.81		100.07
Range	30.37-31.58	59.73-60.77	8.63-8.99		
Std. dev.	0.43	0.37	0.1		

Table 4. Atomic positions and isotropic displacement parameters for synthetic kravtsovite.

Atom	Wyckoff site	x	У	Ζ	Biso (Å <sup>2</sup> )
Pd Ag	4 <i>a</i> 8g	0 0.3107(1)	0 0.1653(2)	0 1/4	0.88(4) 1.40(3)
S	4c	0	0.3102(9)	1/4	1.24(11)

tation along [100], and isotropic displacement parameters. A total of 18 parameters were refined. Although no distinct cleavage was observed in natural kravtsovite, the correction of preferred orientation significantly improved the Rietveld fit of PdAg<sub>2</sub>S. The weighted profile factor  $R_{wp}$ dropped from 0.043 to 0.033 after its refinement.

The final cycles of refinement converged to the residual factors:  $R_{\text{Bragg}} = 0.049$ ,  $R_{\text{wp}} = 0.033$  and  $R_{\text{p}} = 0.023$ . Crystal structure data are presented in Table 4, Fig. 3 shows the final Rietveld plot. Powder-diffraction data of kravtsovite are presented in Table 5.

#### 6. Structure description

The crystal structure of kravtsovite contains three unique crystallographic sites, one each for Pd, Ag and S. A characteristic feature of the structure are infinite [Pd–S–Pd–



Fig. 3. Observed (circles), calculated (solid lines) and difference Rietveld profiles for synthetic kravtsovite.

Table 5.	X-ray	powder	diffrac	tion d	lata f	for s	ynthetic	kravtsov	vite
(CoKα ra	diation	). Reflec	tions v	vith in	ntensi	ities	> 2% a	re shown	i.

h	k	l	I <sub>(obs)</sub>	$I_{(calc)}$	$d_{(obs)}$	$d_{(calc)}$
1	1	0	21	19	4.7560	4.7587
1	1	1	9	9	3.6624	3.6648
0	0	2	19	17	2.8708	2.8726
0	2	1	51	41	2.6320	2.6336
1	1	2	65	59	2.4580	2.4592
3	1	0	71	66	2.4263	2.4277
2	2	0	36	31	2.3784	2.3793
2	0	2	60	61	2.3305	2.3316
3	1	1	100	100	2.2352	2.2362
2	2	1	48	47	2.1973	2.1983
0	2	2	42	37	2.0619	2.0625
4	0	0	14	13	1.9953	1.9959
1	3	0	30	26	1.9172	1.9177
2	2	2	4	3	1.8320	1.8324
4	2	0	5	3	1.6553	1.6554
0	2	3	9	9	1.6083	1.6084
3	1	3	25	24	1.5035	1.5036
2	2	3	14	13	1.4923	1.4919
5	1	1	19	18	1.4893	1.4891
0	4	1	14	5	1 / 3/6	1.4347
4	2	2 )	14	12	1.4340	1.4343
2	4	0)	10	8	1 2000	1.3890
3	3	2	42	36	1.3888	1.3886
5	1	2	28	29	1.3586	1.3585
6	0	0	13	13	1.3308	1.3306
0	4	2	9	9	1.3169	1.3168
5	3	0	25	24	1.2420	1.2418
3	1	4	13	13	1.2365	1.2362
5	1	3	9	7	1.2011	1.2009
6	2	1	5	4	1.1878	1.1876
1	3	4	11	12	1.1498	1.1496
5	3	2	5	4	1.1402	1.1399
2	4	3	7	6	1.1246	1.1244
6	2	2	16	14	1.1183	1.1181
7	1	1	6	5	1.0995	1.0993
1	5	2	9	7	1.0856	1.0855
3	5	0	4	3	1.0831	1.0828
2	4	4	7	8	0.9987	0.9985



Fig. 4. (a) Crystal structure of kravtsovite emphasising the zig-zag [Pd–S–Pd–S]<sub> $\infty$ </sub> chains running along the *c*-axis. (b) Detailed view of the coordination environment around Ag atoms connecting the chains via Ag–S and Pd–Ag bonds. The Pd–Pd bonds within chains are indicated by dashed lines.

S]<sub>∞</sub> *zig-zag* chains running along the *c*-axis (Fig. 4a). In these chains, Pd atoms display perfect linear coordination by two S atoms at a distance of 2.332(4) Å, whereas the Pd–S–Pd angles are 75.9°. Palladium atoms also have two close contacts with two neighbouring Pd atoms (2.872 Å) within one chain. There are no Pd–S bonds between neighbouring [Pd–S–Pd–S]<sub>∞</sub> chains. As indicated in Fig. 4b, Ag atoms show a quasi-linear coordination by two S atoms at 2.590(4) Å. Moreover, Ag atoms have two additional short contacts with Pd atoms at 2.877(9) Å. Consequently, each Ag atom connects three [Pd–S–Pd–S]<sub>∞</sub> chains via Ag–S and Ag–Pd bonds. Neglecting the Ag–S and Ag–Pd bonds, the [Pd–S–Pd–S]<sub>∞</sub> chains are isolated from each other.

Kravtsovite is isostructural with the synthetic phases  $A_2AuBi$  (A = Na, K) and  $K_2AuSb$  (Kim *et al.*, 2010). It appears to have a unique crystal structure within the mineralogical system. It is worth noting that there are no kravtsovite analogues within the Ag–Pd–Se and Ag–Pd–Te systems (Vymazalová *et al.*, 2014, 2015).

The *zig–zag*  $[Pd–S–Pd–S]_{\infty}$  chains found in the kravtsovite structure strongly resemble the  $[O–Hg–O–Hg]_{\infty}$  chains observed in the crystal structure of montroydite (HgO) (Aurivillius, 1964; Kim *et al.*, 2010). A chemically related mineral, coldwellite (Pd<sub>3</sub>Ag<sub>2</sub>S) adopts a β-Mn-like structure (McDonald *et al.*, 2015). In its structure, Ag atoms are octahedrally coordinated by three Ag and Pd atoms, whereas Ag atoms in kravtsovite are tetrahedrally coordinated by 2 S and 2 Pd atoms. Also the characteristic isolated [Pd–S–Pd–S]<sub>∞</sub> chains found in the kravtsovite structure are missing in the coldwellite structure.

# 7. Structural identity of kravtsovite with synthetic PdAg<sub>2</sub>S

The structural identity of the natural kravtsovite with the structural model proposed for the synthetic PdAg<sub>2</sub>S was confirmed by electron back-scattering diffraction (EBSD) measurements on the natural sample.

A TESCAN Lyra 3 GMH and a Mira 3 scanning electron microscope combined with Oxford Instruments X-Max80 (EDS), NordlysMax3 (EBSD) and Inca Wave500 (WDS) detectors were used for the measurements. Preparation with colloidal silica was not successful for kravtsovite.



Fig. 5. EBSD image of natural kravtsovite; left: primary EBSP; right: the EBSP, indexed with solution overlain.

Therefore, we used ion milling with a focused ion beam (FIB) to prepare a part of a small natural kravtsovite grain for EBSD. The area in a polished section chosen for milling was locally coated with a Pt layer using a GIS system. The sample was then tilted to approximately  $7^{\circ}$ with respect to the ion beam. The Pt layer was also used as a marker to find an area for milling on a highly inclined sample surface. A Ga-ion beam at 5 kV was used to polish an area of a small kravtsovite grain. The EBSD patterns (EBSPs) were collected and processed using a proprietary computer program AztecHKL (Oxford Instruments). The centres of twelve Kikuchi bands were automatically detected using the Hough transform routine with a resolution of 60. The solid angles calculated from the patterns were compared with our structural model for the synthetic PdAg<sub>2</sub>S synthetic phase. The EBSD patterns (also known as Kikuchi patterns) obtained from the natural material (eight measurements on different grains of natural kravtsovite) were found to match the patterns generated from our structural model for the synthetic PdAg<sub>2</sub>S (Fig. 5). The values of the mean angular deviation (MAD, *i.e.*, goodness of fit of the solution) between the calculated and measured Kikuchi bands range between 0.36° and  $0.42^{\circ}$ . These values reveal a very good match; as long as values of mean angular deviation are less than 1°, they are considered as indicators of an acceptable fit.

Based on the EBSD patterns, chemical identity and optical properties, the identity of the natural and synthetic materials was confirmed and, consequently, the use of the synthetic phase for the complete characterization of kravtsovite was legitimate.

#### 8. Implications

Kravtsovite was found in vein-disseminated pyritechalcopyrite-galena ores, which occur in the outermost part of vein-disseminated ores where Ni-bearing minerals are completely absent. Palladium and Pt sulphides do not contain Ni. The ores are particularly rich in galena, in the same proportion as pyrite and chalcopyrite, and relatively rich in Pt-, Pd-, Ag- and Au-bearing minerals. Gold and Ag form alloys as well as sulphides, selenides, sulphoarsenides, and telluro-sulphoarsenides. Such minerals must have been formed during the hydrothermal stage of ore formation. The formation of kravtsovite at lower temperature is also supported by our experimental study in the Ag–Pd–S system (in prep.), showing that PdAg<sub>2</sub>S is not stable at  $\geq$ 550 °C. It is worth noting that kravtsovite and coldwellite coexist at 400 °C. Therefore, both minerals can be observed in nature in stable assemblages.

Acknowledgements: This paper is dedicated to the memory of Dr. Zdenek Johan who was involved in the description of over 30 new mineral species and significantly contributed to our knowledge of PGE mineralogy. The authors acknowledge Ulf Hålenius, Chairman of the CNMNC, and the Commission members, as well as two anonymous reviewers for helpful comments. The editorial handling of guest editor Vojtěch Ettler and chief editor Reto Gieré are also acknowledged. This work was supported by the Russian Science Foundation (grant no. 14-07-00693) at the IGEM RAS and by the internal project No. 331400 from the Czech Geological Survey.

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Received 18 January 2017 Modified version received 10 March 2017 Accepted 27 March 2017