International Journal of Coal Geology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

Radiation- and self-ignition induced alterations of Permian uraniferous coal from the abandoned Novátor mine waste dump (Czech Republic)

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ARTICLE INFO

Article history:
Received 11 April 2016
Received in revised form 13 July 2016
Accepted 3 August 2016
Available online xxxx

Keywords:
Coal wastes
Organic matter
Uranium
Mineralization
Self-heating
Biomarkers

ABSTRACT

The effects of uranium mineralization and self-burning processes on inorganic and organic components of coal have been studied at a waste pile of the former Novátor coal and uranium mine at Bečkov (Intrasudetic Basin, Czech Republic) in order to characterize physical and chemical properties of wastes as a basis for further environmental studies. Unaltered bituminous coal was composed predominantly of vitrinite with random reflectance values between 0.72% and 0.86%, and inertinite, less common liptinite macerals, and a low level of organic solvent-extractable material (0.01–1.33 wt.%). Uranium minerals caused local radioactive alterations in the uranium-enriched coal matrix. The diameter of rounded radiation-induced haloes ranged from 0.35 to 100 μm with higher reflectance (0.84–3.44%) compared with bulk coal. Structural changes in radiation induced altered organic coal matter were characterized by low values of Raman band disorder, fewer aliphatic C—H bonds and higher levels of oxygenated functional groups in micro-infrared spectra. Zones of higher reflectance were also confined to veinlets of epigenetic chalcopyrite, galena, and sphalerite mineralization, oriented perpendicularly to the coal bedding. The methylnaphthalene ratios (MNR) of extracted organic matter correlated with uranium concentrations in individual samples.

In self-ignition-affected samples, the higher reflectance (1.31–1.71%), and values of Raman band disorder mirrored the intensity of burning processes. Organic matter samples located at unburnt- and burnt coal interfaces were composed of a mixture of coal macerals, char and solid bitumens. In the waste heap burning zone, coal and claystone were transformed to "clinkers" composed of plagioclase, pyroxenes, tremolite, hematite, magnetite, anatase, and aluminosilicate glass or to "paralava", formed by porous cordierite and hematite. Organic components in the burnt-out zone were represented by small dense and massive coke particles with reflectance of 4.48%, fusinite with reflectance of 3.05% and rare coke droplets of solid bitumen (R = 1.90%). Only traces of phenanthrene and alkanes were identified in organic extracts of burnt-out rock.

1. Introduction

The coal waste dump of the abandoned Novátor mine (at the Rybníček coal and uranium deposit, Czech Republic) was partly affected by self-burning processes. This enabled us to study and compare unaffected-(unburnt) coal and coal altered by burning processes to various degrees. Moreover, the original coal contained variable amounts of uranium, lead, copper and zinc. Therefore, aside from self-ignition processes, it was possible to study alterations in coal related to uranium and base metal mineralization.

As uranium is a common chemical element associated with coal seams, the effect of α-radiation-induced coal alteration was studied by Dill (1983), Halbach et al. (1984) and Dill et al. (1991). They concluded that radiation-induced alterations are observable by the development of anisotropic haloes surrounding accumulations of uranium minerals (coffinite, uraninite, brannerite or "uranium blacks"). Reflectance within the radiation haloes usually increases from the outer part of the halo towards the inner part, adjacent to the accumulation of uranium minerals. Smieja-Król et al. (2009) found a direct correlation between an increase in the maximum reflectance of carbonaceous materials and the concentration of uranium in the Proterozoic basin in South Africa. An increase in uranium content, from 2.5 wt.% to 15 wt.%, was accompanied by an increase in maximum reflectance from 2% to 7%, corresponding to an increase in the degree of coalification from anthracite to graphite.

The effect of radiation on organic matter (kerogen) and migrabitumens was also studied on uranium deposits in black shales, gold-uranium deposits in conglomerates, non-conforming-type

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http://dx.doi.org/10.1016/j.coal.2016.08.002

Please cite this article as: Sýkorová, I., et al., Radiation- and self-ignition induced alterations of Permian uraniferous coal from the abandoned Novátor mine waste dump (Czech Re..., Int. J. Coal Geol. (2016), http://dx.doi.org/10.1016/j.coal.2016.08.002

uranium or vein-type uranium deposits (Zumberge et al., 1978; Sassen, 1984; Leventhal et al., 1986; Lewan and Buchardt, 1989; Landais, 1993, 1996; Kříbek et al., 1999). In summary, it was concluded that radiation damage can be responsible for an increase in the Rock Eval T_{max} and O/C values, reflectance and aromaticity values, and a decrease in H/C, and Rock Eval Hydrogen Index (HI) values of organic matter. Yields of chloroform extracts also decreased with increased radiation-induced alteration of carbonaceous matter. Micro-infrared analysis clearly shows that radiolysis effects (aliphatic C—H decrease, aromatic C—C increase) are limited to within 100 μm of the boundary of the uraninite grains (Landais, 1996).

Very similar alterations in organic matter as in uranium deposits (i.e. increased thermal maturity, aromatization and decreased H/C ratio) were described in many types of hydrothermal Au-, Pb-, Zn-, Cu- or Hg deposits (for review, see for example Parnell et al., 1993; Glikson and Mastalerz, 2000; Greenwood et al., 2013).

It is understood that due to the negative effects of burning coal heaps on the environment (toxic fumes, subsidence, wood fires, surface and ground water contamination), much attention has been paid to solid, liquid, as well as gaseous products of coal self-burning (Finkelman, 2004; Pone et al., 2007; Stracher et al., 2011). Organic material resulting from the burning processes of coal heaps and coal seams includes altered coal matter with different reflectance, cracks, reaction rims, devolatilization pores, chars, cokes and expulsed bitumens (tars), which contain many trace elements and organic compounds (Ciesielczuk et al., 2014; Emsbo-Mattingly and Stout, 2011; Misz et al., 2007; Suárez-Ruiz et al., 2012). Organics generated from carbonization cover a broad spectrum of compounds including *n*-alkanes, terpenes, simple aromatic compounds, polycyclic aromatic hydrocarbons, and phenols whose presence is dependent on the original coal material, as well as conditions during the burning processes (Emsbo-Mattingly and Stout, 2011; Misz-Kennan and Fabiańska, 2011; Misz et al., 2007; Querol et al., 2011; Ribeiro et al., 2010; Simoneit et al., 2007; Sýkorová et al., 2010). Less thermally stable compounds, such as lighter alkanes or alkylated naphthalenes and phenanthrenes are destroyed or evaporated in most self-ignition-affected materials. The emissions of aliphatic and aromatic hydrocarbons from coal fires are highly dependent on the rank of coal as well as on the conditions of thermal alteration. Low-rank and partly medium-rank coal would be expected to evolve char and tars, along with CO, CO_2, hydrocarbons and gases, while higher ranked coals would have coke and less tar in the product mix (Beamish and Arisoy, 2007; Emsbo-Mattingly and Stout, 2011; Querol et al., 2011).

The present study examines the composition of mineralized coal matter in a coal waste dump, the distribution and binding of trace elements, particularly of uranium, and characterization of alterations caused by radioactive and self-burning thermal degradation. For this we have used a multi-instrumental geochemical approach, including elemental inductively coupled plasma mass spectrometry (ICP-MS), micro-petrographic (optical microscopy), scanning electron microscopy with X-ray microanalysis (ESEM/EiDX) of mineral matter, infrared and Raman spectroscopies and solvent extraction followed by gas chromatography–mass spectroscopy.

The aim of present study is to contribute to our knowledge of changes that occur in the composition of mineralized coal matter during radiogenic and self-burning thermal degradation of coal waste heap materials using multi-instrumental geochemical and micro-petrographic studies. The results can be used to decipher the history of coal wastes affected by the interplay of several successive processes and to evaluate their possible environmental impacts.

Fig. 1. Location of the abandoned Novátor coal and uranium mine.

2. Geological setting – study area

Coal and uranium were mined in the Upper Paleozoic Intra-Sudetic Basin (ISB) located at the boundary between the Czech Republic and Poland (Fig. 1). The Czech part of the ISB is filled exclusively with continental clastic and volcaniclastic deposits, mostly sub-horizontally bedded. Sedimentation in the basin began in the Upper Viséan and continued with some hiatuses until the Triassic (Fig. 2). The great majority of coal seams (>60) are confined to the Žacléř Formation (Westphalian A-C) or the Odolov Formation (Westphalian D to Stephanian C). Dull banded coals and banded coals sometimes with clay admixture prevail in coal seams of the ISB. Pure lithotypes as bright coals and dull coals are less abundant. In general, they belong to the category of high volatile bituminous coals with V^{daf} 27–44% and vitrinite reflectance (R_r) 0.68–1.2% (Pešek et al., 2010; Opluštil et al., 2013). The major maceral constituent was vitrinite (43–82 vol.%), while liptinite (5–27 vol.%) and inertinite (8–35 vol.%) were less abundant (Pešek et al., 2010). Less important coal seams form a part of the uppermost Stephanian and lowermost Permian formations.

Uranium mineralization in coal seams was confined to several lithostratigraphical units (Fig. 2). The Pětiletka and Lampertice ore showings occurred in the Žacléř Formation, uranium deposits of the Kolektiv ore field in the Svatoňovice Formation, the Stachanov uranium ore field in the Radvanice Formation, and the Rybníček deposit and Chvaleč showing in the uppermost Stephanian and Autunian (Chvaleč Formation; Fig. 2).

At the former Novátor mine (the Rybníček coal and uranium deposit uranium) mineralization was composed of “uranium blacks”, coffinite and uraninite and formed small stratiform lenses from 0.1 to 0.3 m thick (Arapov et al., 1984; Bernard, 1991). Higher uranium contents were found in pyrite-rich, dull or fusinitized coal positions. Uranium was associated with elevated contents of copper (up to 1.8 wt.%) molybdenum (0.6 wt.%), lead (0.5 wt.%) and zinc (up to 0.9 wt.%). Uranium mining took place in the Rybníček deposit (the former Novátor coal and uranium mine at Bečkov) from 1952 to 1957. Roughly 300,000 tons of coal and 40,000 tons of radioactive material were extracted. Uranium contents ranged from 0.008 to 2 wt.%. Spontaneous combustion of coal heaps at the Novátor mine occurred from 1959 to 1962 (Adamec, 2015; Žáček and Skála, 2015). Since 1963 until the present time coal heaps have gradually been overgrown with vegetation, mostly birch trees.

3. Samples and methods

3.1. Samples

Samples of coal and coal claystone were taken from shallow pits, from a depth of 20–40 cm, both in unburnt and burnt parts of the heap. Additional samples were collected from a trench located at the interface between the burnt and unburnt part of the spoil heap. A total of 14 samples (approx. 0.3 kg each) were collected from all types of

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