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Organic effloresences blooming on an overburning waste dump in Katowice-Welnowiec, Poland

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Since 1996, efflorescences have been formed by hot gases emanating through fissures on the northern slope of a rubbish dump reclaimed with coal wastes at Katowice-Wełnowiec, Upper Silesian Coal Basin, Poland. The aim of this work was to precisely identify the blooming organic phases and to establish the way of their formation. Their identity was determined using optical microscopy, SEM-EDS, XRD, IR, UV-VIS absorption spectroscopy, photoluminescence (PL) and GC-MS. They form monoclinic, translucent, honey-colored needles < 3 mm long. They occur as discrete crystals growing on the surfaces of other crystals or as inclusions in them. Their presence changes the color of white sallamoniac or yellow sulfur to a honey tint.
FTIR reflectance spectra show the characteristic vibrations for acids, esters, amides, methylene group, methyl group and aromatic hydrocarbons. UV-VIS absorption and PL spectra indicate the presence of benzamide and its derivates. Crystals dissolved in DMA prove the presence of several PAH compounds (pyrene and its derivatives, especially benzo(a)pyrene) and of anthracene derivatives (1- and 2- methylanthracene). Photoluminescence synchronic measurements establish the presence of phenanthrene, 9,10-dimethylphenanthrene, 1- and 2-methylanthracene, 9,10-dimethylanthracene, tetraphene, 3-methyltetraphene, 4-methyltetraphene, 5-methyltetraphene, 6-methyltetraphene, benzo(a)-pyrene-3,10-quinone, benzo(a)pyrene, benzo(e)pyrene, 10-methyl-benzo(a)pyrene. GC-MS analysis of DCM extracts revealed the aromatic hydrocarbons: phenanthrene, anthracene, phenylnaphthalene, fluoranthene, and pyrene together with such alkyl derivatives as dimethylnaphthalenes, methylphenanthrenes, and 2-methylanthracene. These compounds are accompanied by light n-alkanes. Their origin from coal-waste organic matter is indicated by comparison with similar occurrences in coal wastes or bituminous coals. However, the main components of the efflorescences are various oxygen- and nitrogen compounds having no obvious relationship to the geochemical composition of coal organic matter, namely, carboxylic acids such as benzoic acid and 3-methylbenzoic acid, aromatic ketones (fluoren-9-one, diphenylmethanone, 9(10H)-anthracenone, 9,10-antraquinone, methyl-9,10-antraquinone, xanthone) and various furane derivatives (dibenzofurane, methyldibenzofuranes, 1,2-dimethylo-naphtho(2,1-b)furane, and benzoxanthenes). Nitrogen compounds include benzamide, phthalimide, and benzoquinoline.
Some of these compounds occur as valid organic mineral phases, e.g., kladnoite is the organic compound phthalimide, ravatite is phenanthrene, and hoelite is 9,10-antraquinone. Semi-quantitative analysis indicate that phthalimide can represent 8-26% of DCM extracts, phenanthrene – 2.5-8.5%, benzamide – 0.1-3.5% and 9,10-antraquinone – 0.03%. Unresolved compounds and/or elemental sulphur (S8) are a large part of many extracts.
As nitrogen compounds, particularly those with amide- and imide functional groups are very minor components of bituminous coals, it can be suggested that phthalimide and benzamide are formed from benzoic acid and phthalic acid at high temperatures in reactions similar to those used to synthetize imides and amides in industry. The presence of benzoic acid (a substrate) and benzamide (a product) confirms this. Moreover, aromatic carboxylic acids, substrates in these reactions, as common products of coal pyrolysis are present in the reaction environment. Phenanthrene can originate directly from coal-waste organic matter or by thermal destruction of its macromolecule.