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Formation of mineral phases in the coals as a result of microbial activity

Образуване на минерални фази във въглищата в резултат на микробиална дейност

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Introduction

This work presents the SEM and X-ray studies on the changes, observed during preservation/storage of coal samples (Berovo and Bitola lignite, Macedonia; Pernik subbituminous coal and Sozopol lignite, Bulgaria). Bacteria had been established during testing the newly formed mineralization.

Newly formed mineralization in environment with free/limited atmospheric air access

The following exogenic minerals were found: gypsum (dominant), K-jarosite, Fe-, Mg- and Na-sulphates. The gypsum is represented by prolonged prismatic crystals (up to 200 µm) in Berovo coal and by thick plate crystals (up to 50 µm), plate crystals (8x12 µm) and rounded crystals in Pernik coal. The Na-sulphate is observed under the form of lamella particles with a size of 5 µm (Bitola coal). The jarosite is present under the form of pyramid crystals with a size up to 15 µm or their aggregates (Berovo coal). The jarosite associates with gypsum and is of later genesis. The jarosite crystals are observed upon the gypsum surface. The Mg-sulphat is established among the common exogenic mineralization (Berovo coal). Microorganisms were established among sulphate minerals and the organic matter. Among the microorganisms observed those of cocci morphology dominant; rarer are of bacilli ones. Both kinds are met as single individual or connected into chains. Coccoids are characterized by forming very long chains and variable-sized clusters. Microprobe analyses find sulphur in some of them. The waste product of the bacterial activity can be described as a solid solution or a mixture, where S, H, O, Ca, Fe, Mg, Na, Mn, N (?), disintegrated organic compounds (?) and moisture are present. Subsequently, from that meta-stabile complex crystallite nuclei are formed and sulphate phases crystallize. Often the bacteria are in intimate adjacency with newly formed gypsum crystals so it may be suggested that they promote crystal growth. Microbial oxidation of pyrite was not observed directly, yet in Berovo coal an exogenic rust-coloured mineralization was found. By means of SEM the presence of gypsum, jarosite and iron oxides/hydroxides was observed. The oxides/hydroxides look like chains and clusters of spherical grains sized 1 µm, so they may be bacteria or bacterial products. Other bacteria specie (sized 2 µm) is observed, where the capsule and cell can be recognized. The latter form clusters made by cocci and diplococci. A symbiosis may be exists between both bacterial species (sulphur- and iron bacteria?). In Pernik coal a fragment with mosaic surface was found that has been most probably the result of a mineralization of a bacterial colony. Fe and S were found in its composition – it is probably Fe-sulphate.

Traces of microbial activity in environment with free/limited access of atmospheric air

Sozopol coal was studied through samples that have been collected 27 years ago from the bottom of Black Sea. X-ray analysis of the fresh samples had shown pyrite and elemental sulphur. The present study found iron sulphates and pyrite. SEM observations found elemental sulphur and gypsum (?). The sulphur is represented by a lens sized 1.5x2 mm. On the lens surface many holes with smooth walls and a diameter of ca. 1.6 µm were observed, as well as elongated grooves with rounded ends. Most probably these are traces from microbial activities. Also many aggregates built by densely ordered zigzag-shaped filaments and rosette-shaped concretions were observed. Filaments' thickness varies from 1.1 μm to 4.4 μm. These formations are built of gypsum. They may also be assumed to have a biogenic origin. The differences in mineral composition of fresh and stored coal and the presence of biogenic traces sized in microns can suggest a presence and activity of sulphur- and iron-oxidizing microorganisms.

Exogenic microbial activity in an environment without access to atmospheric air

Two samples from Berovo coals are of peculiar interest, because they reflect particular stages of framboidal pyrite formation. The first sample is presented by vitrain lenses. They have been stored separately in a small firmly closed plastic bag. The lenses were dull, brown to dark brown pieces without visible mineralization. The present investigation was found a whitish mineralizsation, which forms stripes. The vitrain itself has become bright and almost black. The SEM study was found a characteristic striped pattern, as formed by framboidal pyrite, which fills or covers cracks in vitrain at several places. A more detailed observation of some framboids shows that they are skeletal formations, built most probably by closely ordered Sulphur (?) bacteria. Bacterial capsules and cells can be recognized. According to their morphology the presence of cocci and diplococci can be suggested. Adjacent to the framboids, among the organic matter, spherical bodies were found too, with light grey to white colour, sized 1.2 μm to 1.7 μm. According to their way of grouping characteristic of coccus (cocci, diplococci, tetrad, streptococci, and staphylococci) and their micron size they can also be assumed to be Iron (?) bacteria. Based on the observations performed, it can be supposed that in this case framboidal pyrite was formed as a result of a symbiosis of iron-reducing and/or iron-containing and sulphate/sulphate-reducing bacteria. It could be suggested that Fe-bacteria could independently form pyrite using ions from the organic matter or from the solution. Most probably this would reflect on the morphology of the pyrite.

X-ray analyses found a prevailing pyrite presence and quartz traces in the vitrain sample. The second sample presents a matrix coal and a lens of white mineralization. This coal piece has been stored in the same way and for the same time period (two years) as the first sample. During the present study no alteration of the sample was found macroscopically. SEM study of the white mineralization revealed it as a lens of framboidal pyrite. The lens also covers shrinking cracks in the organic matter. The framboids look like covered by a fine film and the separate grains come up through it. This is most likely a case of partial oxidation of pyrite or its substitution by greigite. Among the framboids, fine filaments are observed formed most likely by bacteria. Multitude spherical and disk-shaped bodies firmly attached to the framboids' surface make particular impression. Most likely these are also bacteria sized 3–4 to 9–10 μm. Microprobe studies provide data on variations in the framboids' composition. It varies from a composition near to that of pyrite to greigite-like one. Both analyses record Zn presence (below 1%). Near the lens among the organic matter many bacteria sized ca. 11 μm are observed. The observed facts are hard to interpret and it can be supposed that a bacterial framboids' finishing or bacterial substitution of pyrite by greigite occurs. X-ray analyses found in the sample a prevailing presence of pyrite and quartz, traces of gypsum and rozenite (?).

Conclusions

The present observations and studies confirm the presence of bacterial species (cocci, bacilli, filaments, and spirilla?) in coal of different rank and their participation in several processes, part of which form the basis of the sulphur cycle. By their activity of extracting carbon from organic compounds bacteria disintegrate organic matter. In this way more fresh and non-oxidized coal surface emerges. This surface may prove very reactive at a certain moment and become a reason of coal self-ignition. It is possible that some bacteria could be used for coal preparation (desulphurization and de-calcination), mainly for the reason that they are typical of coal. The phases formed by their waste products crystallize most likely according to the relative activity of the metals: gypsum (Ca) → Na, Mg, Mn sulphates → jarosite (Fe) and are related to the elements' content as well as to their form of presence. It can be supposed that one possibility of framboidal pyrite formation may be symbiosis between bacteria. Similar symbiosis is proposed by sulphates formation too. Both observations indicate a possible presence of facultative bacteria.

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