

## MONOSACCHARIDES FROM THE MIOCENE LIGNITE AS A PRODUCT OF OLIGO- AND POLYSACCHARIDE DECOMPOSITION

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### Introduction

Monosaccharides (simple carbohydrates, sugars) have been studied quite rarely due to their high polarity and uniqueness of occurrence in rock sequences. The studies conducted on this compound group in the 60's and earlier indicating the presence of monosaccharides in Precambrian, Paleozoic (from the Cambrian) and younger rocks. However, the high polarity of saccharides and their easy solubility in water, and thus the ability to migrate in rock sequences, cast doubt on the results reported. Furthermore, the analytical methodology of that time could not enable a clear identification of mono- and disaccharides. Moers et al. (1994) provided much more advanced research and identified monosaccharides in sedimentary rocks from the Jurassic to the Neogene. In later studies, the presence of monosaccharides was reported repeatedly in peats (e.g. Disnar et al., 2008), Holocene marine sediments (Hernes et al., 1996), and less commonly in Miocene brown coals (Fabbri et al., 2009), but no studies have been conducted on the presence of sugars (nor anhydrosugars) in older rocks. Here we present the occurrence and distribution of monosaccharides from the Cenozoic lignite from Poland (Konin area) and Bulgaria (Chukurovo).

### Results

TMS-derivatives of monosaccharide were identified in polar fraction and total extract of Miocene lignites using GC-MS method. Mass spectra and retention times of identified monosaccharides were compared with internal standards. All analyzed brown coals contain  $\alpha$ - and  $\beta$ -glucose which seems to be the most common (and possibly most stable) carbohydrate in fossil fuels (see Fabbri et al., 2009). Chukurovo lignite contain in addition:  $\alpha$ - and  $\beta$ -L-arabinose (second abundant) and  $\alpha$ - and  $\beta$ -D-xylose monosaccharide. Detritic coals from Konin area characterized by distinctive domination of  $\alpha$ - and  $\beta$ -D-fructofuranose whereas fossil wood sample from Konin contain  $\alpha$ - and  $\beta$ -L-arabinose,  $\alpha$ - and  $\beta$ -L-arabinofuranose, minor  $\alpha$ - and  $\beta$ -D-fructofuranose and sugar alcohols: erythritol and xylitol. Low abundances of levoglucosan, anhydrosaccharide, oxidation product of cellulose were also detected. The fossilization potentials of monosaccharides is still not fully known. Favorable conditions in peats and lignites may aid their preservation over millions of years (e.g. Moers et al., 1990; Fabbri et al., 2009), and perhaps even tens or hundreds of millions of years. The most possible origin of monosaccharide compounds is depolymerization of hemicellulose and cellulose, but we cannot exclude the possibility of oligosaccharide decay during diagenesis.

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## **References**

- Disnar, J.-R., Jacob, J., Morched-Issa, M., Lottier, N., Arnaud, F., 2008. Assessment of peat quality by molecular and bulk geochemical analysis: Application to the Holocene record of the Chautagne marsh (Haute Savoie, France). *Chemical Geology* 254, 101–112.
- Fabbri, D., Torri, Ch., Simoneit, B.R.T., Marynowski, L., Rushdi, A.I., Fabiańska, M.J., 2009. Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene lignites. *Atmospheric Environment* 43, 2286–2295.
- Hernes, P.J., Hedges, J.I., Peterson, M.L., Wakeham, S.G., Lee, C., 1996. Neutral carbohydrate geochemistry of particulate material in the central equatorial Pacific. *Deep Sea Research Part II: Topical Studies in Oceanography* 43, 1181–1204.
- Moers, M.E.C., Baas, M., Boon, J.J., de Leeuw, J.W., 1990. Molecular characterization of total organic matter and carbohydrates in peat samples from a cypress swamp by pyrolysis-mass spectrometry and wet-chemical methods. *Biogeochemistry* 11, 251–277.
- Moers, M.E.C., de Leeuw, J.W., Baas, M. 1994. Origin and diagenesis of carbohydrates in ancient sediments. *Organic Geochemistry* 21, 1093–1106.