

Analysis of alteration effects of lignite-containing soil samples

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To determine the alteration effects of two lignite-containing soil samples (New Mexico, USA (BH) and North Rhine-Westphalia, Germany (HM)), the organic geochemical composition was analysed before and after an accelerated alteration simulation (continuous storage at $T = 30\text{ °C}/303\text{ K}$) over a period of 3 months using Rock-Eval pyrolysis, analyses of total carbon contents (TOC), and GC-MS. In addition, humic acid (HA) fractions were extracted from all samples and analysed for their chemical composition. In order to determine the organic geochemical composition, extracted organic matter was separated first into asphaltenes and maltenes. The maltene fraction was separated by MPLC and HMPLC into aliphatic/aromatic fractions and in low-polarity, medium-polarity NSO compounds and acids. All fractions were analysed with GC-MS. HAs are complex macromolecules, which are unmeasurable with a standard GC-MS method. Therefore, alkaline CuO oxidation with a microwave system as well as the derivatisation of HA samples were carried out prior measuring with GC-MS to characterise compositional fragments of these HA. In addition, qualitative measurements by FT-IR spectrometry were performed on both, the lignite-containing soil samples and the HA samples, for functional groups characterisation. The TOC content of the two lignite-containing soil samples as well as that of the HAs extracted from them decreases over the period of alteration. Over the same period, the proportion of asphaltenes and maltenes increases in all lignite-containing samples. Within the maltene fraction, the percentage increase in mass is greatest within the low-polarity fraction. Rock-Eval pyrolysis results show an increase in the volatile hydrocarbons contained in both samples at the S1 peak. In samples HM and their extracted HAs, the S2 peak (= hydrocarbons generated by thermal cracking) increases over the alteration period. In sample BH, alteration processes lead to a decrease in the S2 peak over the same period of time. Within the isolated HAs, a decrease in the S1 peak and a slight increase in the S2 peak can be detected. The GC-MS investigation shows a comparable alteration behaviour of the samples. Within the respective maltene fractions, there is an increase of identified compounds within the saturated and aromatic fractions as well as in low and medium polar sub-fractions. While in sample BH the amount of identified compounds of the acid fraction decreases, a further increase is also recognisable in sample HM. Within the alkanes, an increase in long-chain alkanes can be seen in both samples, while the proportion of short-chain compounds decreases during alteration. Interestingly, the amount of CuO products of HAs is slightly higher in fresh samples in comparison to the alteration products. This difference is bigger for HM than for BH samples. Slight differences are also visible in the FT-IR spectra of the samples for some functional groups (e.g., CH groups). The study shows a strong age-related change in the composition of the organic components for both samples. Both samples show an increase in non-oxidised or only slightly oxidised organic components due to ageing processes of the matter present. It is conceivable that these arise from highly complex organic macromolecules of the original substances, which are decomposed by oxidation processes of ageing.