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## Reconstruction of anthropogenic activities on the excavations of a fireplace sequence from the Krems-Wachtberg site (Austria) using molecular proxies

Guido Wiesenberg (1) and Ulrich Hambach (2)

(1) Bayreuth University, Dept. for Agroecosystem Research, Bayreuth, Germany (guido.wiesenberg@uni-bayreuth.de), (2) Bayreuth University, Geomorphology Department, Bayreuth, Germany

The well investigated Krems-Wachtberg excavation yielded a broad variety of anthropogenic artefacts and thus enables a proper reconstruction of an ancient settlement of Upper-Palaeolithic age. Despite these artefacts, some questions cannot be answered by sedimentologic and archaeologic approaches. Molecular fossils like lipids including aliphatic hydrocarbons are suitable to improve understanding of e.g. paleoclimatic, pedogenetic, and archaeologic contexts. Especially aliphatic hydrocarbons including straight-chain and branched alkanes yield potential to elucidate biogenic sources of soil and loess organic matter and to assess degradation conditions of primary organic matter. To improve understanding on the terms the fireplaces at the Krems-Wachtberg site are used, aliphatic hydrocarbons are investigated on a set of samples covering several horizons in the context of one fireplace, which was part of the excavation.

Horizons above and below the fireplace as well as the fireplace itself were investigated for lipids. Additionally, reference loess samples from a similar age like the fireplace and a pit filling were investigated. Two replicates were available for most samples except for the pit filling. Two distinct fireplace series have been studies. All samples were extracted for lipids using Soxhlet extraction followed by column chromatography in order to separate the aliphatic hydrocarbon fraction from other lipids. Thereafter, aliphatic hydrocarbons were quantified using gas chromatography.

The total amounts of extractable organic compounds in the whole sample set from the Krems-Wachtberg site were in the range of usual loess deposits and accounted for 30-80 mg kg-1 loess. The largest contents were observed in reference loess samples and decreased within the excavation from fireplaces > sediments covering fireplace > basement of fireplace > pit. The lower the extract yields, the stronger was the degradation of organic matter. In this context, the pit yielded either organic matter that was strongly degraded during rotting process of organic material after burial or incorporation of already strongly degraded organic matter like ash from fireplaces. The basement of the fireplace was exposed to high temperature for the whole usage of the place, resulting in a modification in the structure of the sediments and a degradation of organic matter within the sediments. The material from the fireplace itself probably was not completely burned and thus yielded comparatively large amounts of extractable components. The sediments covering the fireplace were potentially used to extinguish the fire and hence received a thermal alteration of the organic matter within the sediment under oxygen limiting conditions. Hence, the amount of extractable organic compounds can be used to reconstruct the firing process in the Krems-Wachtberg excavation.

The amount of individual aliphatic hydrocarbons parallels the content of all extractable compounds and thus confirms the findings explained above. The aliphatic hydrocarbons reveal typical distribution patterns for grassland vegetation as indicated by a strong predomination of odd long chain alkanes and n-C31 as the most abundant homologue for most samples. Only sediments covering the fireplaces are dominated by n-C29 alkane. The different alkane distribution pattern for these sediments compared to all other samples including reference loess indicates a different biogenic source of the covering sediment than for all other samples. Probably, the covering sediments yield organic matter incorporated under forest or different grassland vegetation than the other sediments.

In this study, several molecular markers have been tested for aliphatic hydrocarbons in order to elucidate their sources and to identify degradation effects responsible for the determined distribution patterns. The ratio of long chain vs. short chain alkanes enables the differentiation of plant-derived organic matter characterized by high ratios (>10) and organic matter derived from microbial biomass or degradation (<10). The reference loess samples were characterized by very high values (>50), which indicates plant biomass as the predominant source of loess organic matter. All other samples were characterized by low values (<10), which is due to degradation effects. Microbial alkanes as second potential source of short chain n-alkanes are not likely as odd homologues did not predominate over even homologues, which is typical for microbial alkanes. Furthermore even alkanes dominated in most samples, which can be related to thermal alteration of organic matter as common in fireplaces. Other degradation markers like n-alkanes vs. isoprenoid alkanes (n-C18/phytane) revealed values between 2-4.5. The fireplace samples were characterized by lowest values whereas the reference samples yielded highest values. Hence degradation increased from loess towards fireplace with an intermediate degradation of most other samples.

Aliphatic hydrocarbon biomarkers like alkanes were found useful to reconstruct degradation intensity in ancient sediments and to elucidate anthropogenic activities like extinguishing of fire. Hence, organic geochemical investigations can be useful techniques to complement standard archaeological techniques.