# Aging of historical charcoals in the environment

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The ubiquitous occurrence of charcoals in the environment has led to an increasing interest in this material. Carbonaceous residues (“black carbon”) rank among the fraction of recalcitrant organic matter in soils. Aging and degradation are relevant processes with respect to the effect on soils and the carbon cycle. Sample sets of prehistorical, historical (Bronze Age, Middle Ages and Modern Period) and recent charcoals were investigated using different methods to reveal changes during the aging process. The influence of the burning technology applied and the type of wood were important factors to be considered in this context. Climatic conditions that affect the aging process as well were not included in the evaluation as all historical samples originated from archeological excavations in the same region of the Eisenerzer Alps (Styria, Austria).
Recent charcoal samples served as a reference for the starting material. They were produced according to a historical technology in a rectangular charcoal hearth. A comprehensive characterization was based on thermal analysis and ATR-FTIR spectroscopy (Leifeld, 2007; Bornemann et al., 2008). Data interpretation was supported by multivariate data analysis.
Due to their characteristic thermal and spectral fingerprint charcoals that were produced for energy supply can be clearly distinguished from other historical charred residues (e.g. from historical fireplaces). Despite the same appearance wood was exposed to lower temperatures and was less affected by pyrolysis. The thermal and spectral patterns still show properties of the wooden input material.
Chemical changes during the aging process are paralleled by a decrease of hydrophobicity which is a main precondition for microbial degradation. Historical charcoals show a mass loss between 90 and 110 °C and the corresponding endothermic reaction of the heat flow that indicate evaporation of absorbed water. This result is confirmed by infrared spectral data and by contact angle measurements. The changing behavior in terms of hygroscopicity is closely related to the transformation of organic matter with time. It is reflected by TG- and DSC-profiles and the relevant spectral regions (1800–1150 $cm^{-1}$). Combustion of aged charcoals occurs at lower temperatures, additionally a decrease of enthalpies is observed. Principal component analyses (PCA) are based on the specific thermal and spectral signatures of historical and recent charcoals. The sample set covers different categories that are potential distinguishing features for the grouping in the PCA, such as age, charcoal burning technology and type of wood. Age plays a major role among the distinguishing factors. Recent charcoals are clearly separated from historical charcoals. Within the set of prehistorical and historical charcoals, samples from the Bronze Age differ from “younger” charcoals that are assigned to the Middle Ages and the Modern Period.
No difference was found between ancient charcoal burning technologies: the charcoal pit, the circular charcoal hearth and the rectangular charcoal hearth. For the sample set originating from the Bronze Age different types of wood used for charcoal production were identified: spruce, fir, maple and beech. The loss of characteristic features that contribute to the differentiation of wood types suggests temperatures >400 °C during the pyrolysis process.
Further cooperation with archeologists will focus on the relation between temperatures for historical charcoal production and duration of the process within the scope of experimental archeology.

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[2] L. Bornemann L., G. Welp, S. Brodowski, A. Rodionov, W. Amelung, *Org. Geochem.* **39** (2008) 1537-1544.