

ENVIRONMENTAL CHANGES IN TANZANIA DURING HOLOCENE: NEW INSIGHTS FROM HYDROXYLATED BIOMARKERS (ABUNDANCE AND ^{13}C)

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Although East African highlands constitute a main freshwater and food source for human population (Williamson et al., 2014), their climatic and environmental susceptibility remains partially understood. This study aims at better documenting the relationships between vegetation and environmental changes within the Rungwe province (South-West Tanzania) along the last 4,000 years. As humid environments such as peatbogs and swamps are especially sensitive to climate change, this study focuses on a swampy area: the maar crater of Kyambangunguru. Previous investigations of a 4m-core collected in the swamp allowed reconstructing past vegetation, temperature and hydrology variations, based on pollen, GDGT and specific alkane δD records, respectively (Coffinet et al., 2018). While *n*-alkane abundance and isotope composition are of little use for reconstructing paleovegetations, hydroxylated biomarkers exhibit higher diagnostic capacities. Particularly, 5-*n*-alkylresorcinols were found to be typical for sedges in East African humid environment (Magill et al., 2016). This study identified and quantified hydroxylated biomarkers to precise paleovegetation variations. Furthermore, in order to determine the photosynthetic status and water stress undergone by sedges, key components of swamp vegetation, stable carbon isotope analyses were performed on purified resorcinols.

After Bligh and Dyer extraction, total lipids were fractionated on column chromatography (silica) and hydroxylated biomarkers were recovered in the intermediate polarity fraction (dichloromethane:acetone, 2:1, v:v). An aliquot of the intermediate polarity fraction was trimethylsilylated prior to gas chromatography-mass spectrometry (GC-MS) for biomarker identification and quantification. Resorcinols were further isolated from the intermediate polarity lipids by semi-preparative high-performance liquid chromatography using a Diol column (Inertsil), according to a protocol adapted from Smittenberg et al. (2002). Specific resorcinol isotope composition was determined by gas chromatography coupled to isotope ratio mass spectrometry via a combustion interface (GC-C-IRMS).

GC-MS analyses revealed that intermediate polarity lipids are dominated by aliphatic series: *n*-alkanoic acids (C_{15} - C_{30} , max. C_{26} , submax C_{16}), *n*-alkan-1-ols (C_{16} - C_{32} , max. C_{28} , submax. C_{16}), *n*-alkan-2-ones (C_{21} - C_{31} , max. C_{29}) and 5-*n*-alkylresorcinols (C_{15} - C_{27} , max. C_{23}). Sterols (β -sistosterol, campesterol, campestanol, stigmasterol, stigmastanol) and pentacyclic triterpenoids (α -amyrin, friedelan-3-one, bishomohopanol) were also detected in substantial amounts. These biomarkers confirm that higher plants constitute the main source of organic matter at the Kyambangunguru site. Nevertheless, quantification of the biomarkers and their distribution patterns (CPI, ACL) along the 4m-core suggested higher microbial contribution during lake phases, in agreement with previous reconstructions (Coffinet et al., 2018). 5-*n*-alkylresorcinols displayed abundances paralleling that of Cyperaceae pollens, validating their use as biomarkers of this sedge family. Lipid analysis of the various Cyperaceae genera developing around the maar crater further demonstrated that plants of the *Cyperus* genus were the main source of resorcinols in the area. Resorcinol specific isotope analyses are under progress. Preliminary results show contrasted $\delta^{13}\text{C}$ values for resorcinols pointing to

different photosynthetic pathways (C_3 and C_4) for *Cyperus* species around the maar crater (Fig. 1). Different isotope patterns according to chain length further suggest that the different *Cyperus* species developing around the crater synthesize different resorcinol chain lengths and/or adapt differently to variations in environmental conditions. Additional GC-C-IRMS analyses of resorcinols isolated from the core and from the vegetation surrounding Kyambangunguru marsh should help in precisizing (1) paleovegetation changes during the Holocene, as well as (2) ecological plasticity of *Cyperus* species.

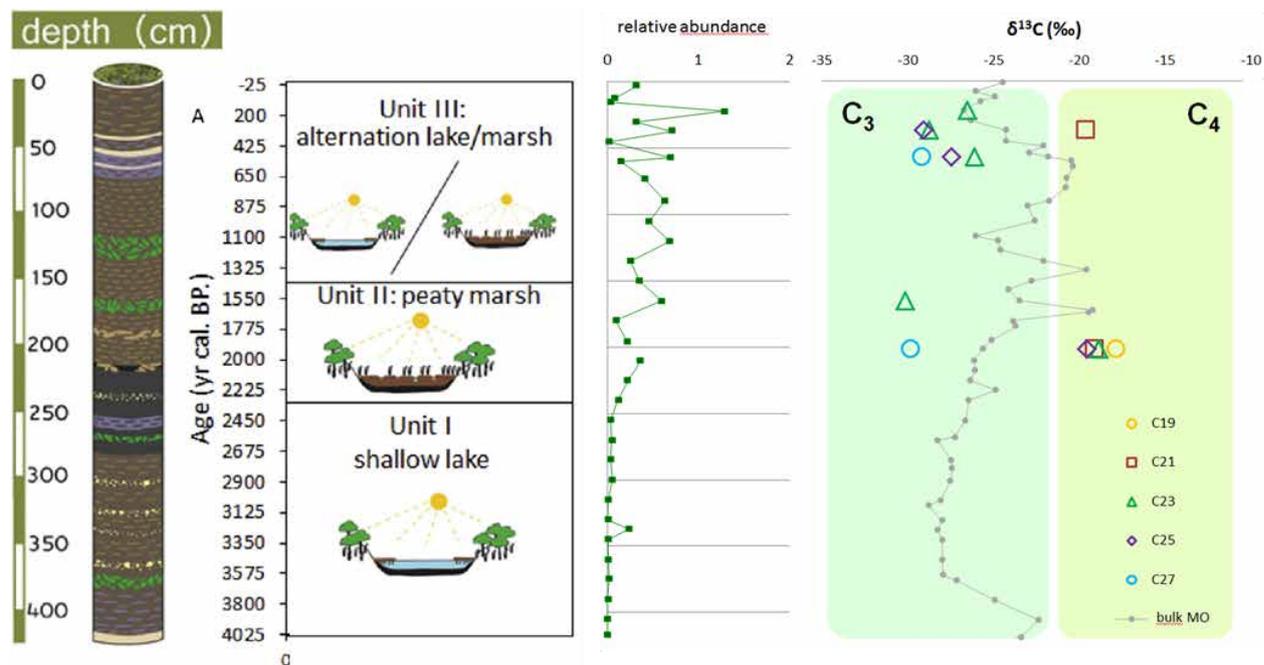


Figure 1 5-n-Alkylresorcinols abundance and specific isotope composition (preliminary results) along the Kyambangunguru core. Lithology and paleoecological reconstruction are from Coffinet et al. (2018).

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