Quaternary International xxx (2017) 1–15

Contents lists available at ScienceDirect

Quaternary International

journal homepage: www.elsevier.com/locate/quaint

Late Quaternary relative humidity changes from Mt. Kilimanjaro, based on a coupled ^{2}H-^{18}O biomarker paleohygrometer approach

Johannes Hepp [a, b, *], Roland Zech [c, 1], Kazimierz Rozanski [d], Mario Tuthorn [a, b, 2], Bruno Glaser [b], Markus Greule [e], Frank Keppler [e], Yongsong Huang [c], Wolfgang Zech [f], Michael Zech [a, b, g, 3]

[a] Department of Soil Physics and Chair of Geomorphology, University of Bayreuth, Universitätsstrasse 30, D-95440, Bayreuth, Germany
[b] Institute of Agronomy and Nutritional Sciences, Soil Biogeochemistry, Martin-Luther University Halle-Wittenberg, Von-Seckendorff-Platz 3, D-06120, Halle, Germany
[c] Department of Geological Sciences, Brown University, Providence, RI, 02912, USA
[d] Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059, Kraków, Poland
[e] Institute of Earth Sciences, University of Heidelberg, Im Neuenheimer Feld 236, D-69120, Heidelberg, Germany
[f] Institute of Soil Science and Geography, University of Bayreuth, 95445 Bayreuth, Universitätsstrasse 30, D-95440, Bayreuth, Germany
[g] Institute of Geography, Chair of Landscape- and Geoecology, Technical University of Dresden, Helmholtzstrasse 10, D-01062, Dresden, Germany

ARTICLE INFO

Article history:
Received 6 August 2016
Received in revised form
27 February 2017
Accepted 19 March 2017
Available online xxx

Keywords:
Paleohydrology
Paleosol
Deuterium
Oxygen-18
Leaf water
Evapotranspirative enrichment

ABSTRACT

Our understanding of African paleoclimate/hydrological history is mainly based on lake level and lake sediment studies. It improved during the last decade thanks to emerging stable isotope techniques such as compound-specific deuterium analysis of sedimentary leaf wax biomarkers ($\delta^{2}H_{leaf\text{-}wax}$). Here we present the results from a multi-proxy biomarker study carried out on a ~100 ka loess-like paleosol sequence preserved in the Maundi crater at ~2780 m a.s.l. on the southeastern slopes of Mt. Kilimanjaro in equatorial East Africa.

The Maundi stable isotope records established for hemicellulose-derived sugars, lignin- and pectin-derived methoxyl groups, leaf wax-derived fatty acid and *n*-alkane biomarkers ($\delta^{18}O_{sugars}$, $\delta^{2}H_{methoxyl\ groups}$, $\delta^{2}H_{fatty\text{-}acids}$ and $\delta^{2}H_{n\text{-}alkanes}$, respectively) reveal similar patterns, but also some distinct differences are obvious. The periods from ~70 to 60 ka, the Last Glacial Maximum (LGM) and the Younger Dryas (YD) are characterized by more positive δ values, whereas during the Holocene, and around 30, 39, and 56 ka BP more negative δ values are determined. The application of a 'coupled $\delta^{2}H_{n\text{-}alkane}$-$\delta^{18}O_{sugar}$ paleohygrometer' approach allows us to derive information about Late Quaternary changes of air relative humidity at the Maundi study site. Reconstructed changes of mean day-time relative humidity (RH_D) are in good agreement with pollen results from the study area. Apart from the overall regional moisture availability, the intensification versus weakening of the trade wind inversion, which affects the diurnal montane atmospheric circulation on the slopes of Mt. Kilimanjaro, is suggested as a local factor which may contribute to the observed variability of RH_D at Maundi study site.

The combined usage of $\delta^{2}H_{n\text{-}alkanes}$ and $\delta^{18}O_{sugars}$ allowed us to reconstruct $\delta^{2}H/\delta^{18}O$ of source water utilized by plants in the study area, which is directly linked to local precipitation. The results of this reconstruction caution against a straightforward interpretation of $\delta^{2}H_{leaf\text{-}wax}$ and $\delta^{18}O_{sugars}$ records as proxies for isotopic composition of local precipitation because variable and primarily RH-dependent isotopic evaporative enrichment of leaf water can mask changes of $\delta^{2}H_{prec}/\delta^{18}O_{prec}$ in the past. The biomarker-based $\delta^{2}H/\delta^{18}O_{source\text{-}water}$ records derived for the Maundi site revealed a discernible link with the reconstructed RH_D record; lower RH_D values were generally observed during periods characterized by more negative $\delta^{2}H/\delta^{18}O_{source\text{-}water}$ values, indicating a reverse relationship with the expected precipitation amount. This indicates that the empirical relationship between amount of rainfall and its

* Corresponding author. Present address: Chair of Geomorphology, University of Bayreuth, Universitätsstrasse 30, D-95440, Bayreuth, Germany.
E-mail address: johannes-hepp@gmx.de (J. Hepp).
[1] Present address: Institute of Geography, Chair of Physical Geography, Friedrich-Schiller University of Jena, Löbdergraben 32, D-07743 Jena, Germany.
[2] Present address: Thermo Fisher Scientific, Bremen, Germany.
[3] Present address: Institute of Geography, Chair of Landscape- and Geoecology, Technical University of Dresden, Helmholtzstrasse 10, D-01062 Dresden, Germany.

http://dx.doi.org/10.1016/j.quaint.2017.03.059
1040-6182/

isotopic composition, observed nowadays on monthly timescale in the East African region, might not be valid on millennial time scale.

1. Introduction

East Africa and its Late Quaternary climate and vegetation history has received much attention during the last decades. Evidence for dramatic environmental and hydrological changes come from various types of archives, such as ice cores (Thompson et al., 2002) and glacial deposits (Mark and Osmaston, 2008; Shanahan and Zreda, 2000), lake sediments (e.g. Berke et al., 2012; Cockerton et al., 2015; Gasse, 2000; Gasse et al., 2008; Scholz et al., 2007; Street-Perrott et al., 2004; Trauth et al., 2003; Verschuren et al., 2009) and marine sediments (e.g. Schefuß et al., 2011; Tierney and deMenocal, 2013). The equatorial and northern East Africa, as well as the east Saharan region, experienced multiple lake level highstands and humid conditions, especially during the Early Holocene (African Humid Period - AHP). The East African monsoon is responsible for rainy periods in East Africa and is controlled by low-latitude insolation changes occurring on orbital timescales. However, the forcing of the East African monsoon on millennial timescales is still a matter of debate. Evidence for precession forcing, including half-precession effects, have been presented in numerous studies (e.g. Trauth et al., 2003; Verschuren et al., 2009). However, many influencing factors and controlling mechanisms on East African paleoclimate are not yet fully understood. This concerns the teleconnection with high-latitude boundary conditions, for instance during the Younger Dryas period, the possible influence of the Indian Ocean Dipole (IOD) and the El Niño Southern Oscillation (ENSO) phenomena, and the possible influence of a migrating Congo air boundary (Abram et al., 2007; Castañeda et al., 2007; Konecky et al., 2011; Schefuß et al., 2011; Stager et al., 2011; Tierney et al., 2008, 2011). The multitude of possible controls of East African climate in the past stimulate the ongoing research efforts addressing exact timing, abruptness and spatial/temporal variability of East African monsoon precipitation.

During the last decade, the hydrogen isotopic composition of sedimentary leaf waxes ($\delta^2H_{leaf\text{-}wax}$) became a widely used proxy that was also explored in East African paleoclimate/hydrological archives. There are two major assumptions underlying most interpretations of $\delta^2H_{leaf\text{-}wax}$ records originating from this region. First, δ^2H values of leaf waxes extracted from lake sediments reflect the isotopic composition of paleoprecipitation (δ^2H_{prec}) (e.g. Konecky et al., 2011; Tierney et al., 2010, 2011). Second, $\delta^2H_{leaf\text{-}wax}$ records retrieved from sedimentary archives can be interpreted in terms of an 'amount effect', as inferred from modern precipitation in the tropics (e.g. Schefuß et al., 2005, 2011; Tierney et al., 2008; Tierney and deMenocal, 2013).

However, the first assumption may not be as robust as previously thought. For instance, the ^2H content of leaf wax-derived *n*-alkane biomarkers, studied in a modern topsoil climate transect along the southern slopes of Mt. Kilimanjaro, does not follow the expected 'altitude effect' for δ^2H of local precipitation (Zech et al., 2015). The *n*-alkanes were rather found to reflect the isotopic composition of leaf water ($\delta^2H_{leaf\text{-}water}$), as it was previously suggested by Kahmen et al. (2013). Given that ^2H-enrichment of leaf water strongly depends on relative air humidity (Farquhar et al., 2007; Flanagan et al., 1991; Roden et al., 2000), large changes of this parameter may thus mask climatically-driven fluctuations of δ^2H_{prec}.

The second assumption is based on the observation that for present-day climate monthly means of δ^2H_{prec} ($\delta^{18}O_{prec}$) values in the tropics are inversely correlated with the precipitation amount collected at a given site (e.g. Rozanski et al., 1993). This is also true for East Africa (Rozanski et al., 1996). However, on an inter-annual basis, which is the relevant timescale for (paleo-)climatic considerations, such correlation is very poor or not-existent, at least for the East African region (Rozanski et al., 1996), and validation of a long-term 'amount effect' is in fact lacking for this area. Alternatively, Konecky et al. (2011) suggested that moisture source and transport history dominated the $\delta^2H_{leaf\text{-}wax}$ record at Lake Malawi, whereas rainfall amount played a secondary role.

In order to overcome ambiguities associated with the interpretations of $\delta^2H_{leaf\text{-}wax}$ records, Zech et al. (2013) suggested a coupled $\delta^2H_{n\text{-}alkane}$-$\delta^{18}O_{sugar}$ biomarker approach, where $\delta^{18}O_{sugar}$ is determined by compound-specific $\delta^{18}O$-analyses of the hemicellulose-derived sugar biomarkers, such as arabinose, fucose, xylose and rhamnose (Zech and Glaser, 2009). This coupled approach opens up new possibilities: (i) in combination with known biosynthetic fractionation factors (ε_{bio}) it enables the reconstruction of the isotopic composition of leaf water [$\delta^2H_{leaf\text{-}water} = \delta^2H_{leaf\text{-}wax} - \varepsilon_{bio}$ (*n*-alkanes); $\delta^{18}O_{leaf\text{-}water} = \delta^{18}O_{sugars} - \varepsilon_{bio}$ (sugars)]. (ii) The evapotranspirative ^2H and ^{18}O enrichment of leaf water – characterized by the deuterium-excess of leaf water – can be used to quantify relative humidity of the local atmosphere for the periods when stomata are open and the transpiration process is in operation. Relative air humidity appears to be a decisive factor controlling the extent of this isotope enrichment. Finally, (iii) the intersect of the local leaf water evaporation line (LLEL) with the local meteoric water line (LMWL) can be used to reconstruct δ^2H/$\delta^{18}O$ source water values more robustly than previously done, based on $\delta^2H_{leaf\text{-}wax}$ records alone. Recently, Tuthorn et al. (2015) validated this coupled δ^2H-$\delta^{18}O$ biomarker approach by applying it to an Argentinean climate topsoil transect. Their findings corroborate that the 'coupled $\delta^2H_{n\text{-}alkane}$-$\delta^{18}O_{sugar}$ paleohygrometer' is a promising proxy for reconstructing day-time relative humidity of local atmosphere (RH_D).

The aim of this study was (i) to establish a multi-proxy stable isotope biomarker record spanning the last ~ 100 ka by investigating a loess-like paleosol sequence from the Maundi crater situated on the southeastern slopes of Mt. Kilimanjaro, equatorial East Africa, (ii) to compare the Maundi $\delta^2H_{n\text{-}alkane}$ record with the δ^2H records of fatty acids and lignin-/pectin-derived methoxyl groups ($\delta^2H_{fatty\text{-}acid}$ and $\delta^2H_{methoxyl}$, respectively) as well as with published δ^2H biomarker records from East African lakes, (iii) to reconstruct the past history of the RH_D at the Maundi study site using the 'coupled $\delta^2H_{n\text{-}alkane}$-$\delta^{18}O_{sugar}$ paleohygrometer', and (iv) to reconstruct and interpret the δ^2H/$\delta^{18}O_{source\ water}$ record for the Maundi loess-like paleosol sequence in terms of paleoclimate.

2. Materials and methods

2.1. Study area – the Maundi crater

A detailed description of the study area, as well as an age-depth model of the Maundi loess-like paleosol sequence, were previously presented by Schüler et al. (2012). In brief, Maundi is an ancient volcanic crater of ~60 m diameter and 20–30 m depth that is located on the southeastern slopes of Mt. Kilimanjaro at ~2780 m