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***n*-Alkan-2-one biomarkers as a proxy for palaeoclimate reconstruction in the Mfabeni fen, South Africa**

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Abstract

The sub-tropical Mfabeni fen is the only continuous coastal peat deposit that documents glacial and interglacial palaeoenvironmental conditions since the late Pleistocene (ca. 47 cal kyr BP) in southern Africa. Published bulk geochemical, biomarker and leaf wax $\delta^{13}\text{C}$ data, along with palynology and stratigraphic studies of the Mfabeni peat sequence, renders it an ideal record for testing new palaeoreconstruction proxies. In this study, we aimed to establish the proxy potential of *n*-alkan-2-one (*n*-ket) compounds by tracing their source/origin, post-depositional diagenetic changes and if they preserve a robust palaeoenvironment signal that complements our understanding of palaeoclimatic variations. In the Mfabeni archive the most likely source for *n*-kets is via microbial decarboxylation of *n*+1-alkanoic acids (*n*-FAs) and, to a lesser degree, oxidation of same chain length *n*-alkanes (*n*-alks). The *n*-ket average chain length (ACL_{ket}) and *n*-C₂₃ and C_{25ket} / precursor ratios display a statistical significant negative relationship with the *n*-alk aquatic plant proxy (P_{aq}), suggesting the source of *n*-kets to be submerged aquatic plants during waterlogged conditions that suppressed microbial activity during the ensuing anoxic conditions. Both the mid-chain and long-chain *n*-ket/precursor ratios display predominant water level fluctuation controls, with temperature as a secondary regulator. By comparing the *n*-ket data with published environmental and climate reconstructions from the same core, and geomorphology and palynological studies of the Mfabeni basin, we

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conclude that the *n*-keto acids show promise as a palaeoclimate proxy and can be used in conjunction with other biomarker proxies to reconstruct ancient hydrological changes in sub-tropical peatlands.

Key words: *n*-Alkan-2-ones; sub-tropical peat; palaeoenvironment, Late Pleistocene; South Africa.

1. Introduction

Palaeoclimate proxies have inherent limitations due to difficulties in quantifying geochemical relationships in modern systems and distinguishing between preservation and diagenetic changes after deposition (Sageman and Lyons, 2003). Therefore, it is useful to use a multi-proxy approach to reduce uncertainty in palaeoclimate reconstructions by providing improved prognostic data. Consequently, geochemists continually strive to add new and improved proxies to address these inadequacies and to advance understanding about past climate and environmental change archived in sedimentary records.

n-Alkan-2-ones (*n*-kets) are a relatively novel group of biomarkers compared with the more commonly studied straight chain *n*-alkyl lipids, namely *n*-alkanes (*n*-alks), *n*-alkanoic acids (*n*-FAs) and *n*-alkanols (*n*-als, e.g. Xie et al., 2008). Even though studies have documented *n*-kets in soils (Huang et al., 1996; van Bergen et al., 1998; Bull et al., 2000; Naafs et al., 2004; Bai et al., 2006), lacustrine sediments (Cranwell et al., 1987; Meyers and Ishiwatari, 1993; Wenchuan et al., 1999), peat basins (Lehtonen and Ketola, 1990, 1993) and contemporary plants (Wenchuan et al., 1999; Baas et al., 2000; Hernandez et al., 2001; Nichols and Huang, 2007; Ortiz et al., 2011), their identification is frequently part of a general characterisation of the wider suite of biomarkers. There has been little assessment of their effectiveness as a palaeoenvironmental proxy. To the authors' knowledge, the only studies dedicated to determining proxy potential of *n*-kets are those from the Hani mire, north eastern China (Zheng et al., 2011a) and Hongyuan peatland on the eastern fringes of the Tibetan Plateau (Zheng et al., 2011b), where *n*-ket data were compared with regional geochemical and palynological studies.

Although some peat forming plants and phytoplankton are reported to contain low concentrations of *n*-kets (Lehtonen and Ketola, 1990; Hernandez et al., 2001; Nichols

and Huang, 2007; Ortiz et al., 2011), other studies have reported that the principal origin of these biomarkers in sedimentary environments is either microbial oxidation of the same chain length *n*-alk and/or decarboxylation of the *n*+1 FA (Volkman et al., 1983; Bai et al., 2006; Ortiz et al., 2010, 2011). Furthermore, López-Días et al. (2013) reported that distribution patterns of *n*-alks and *n*-kets in the Roñanzas peat bog did not justify a single source, and they therefore suggested an additional secondary source of *n*-kets derived from bacterial input. Regardless, the predominant sources of these biomarkers appear to be governed by enzymatic microbial activity, which is usually linked to temperature (Schmidt et al., 2011).

Peat accumulates when net primary production (NPP) outstrips organic matter (OM) degradation (Chimner and Ewel, 2005). The relatively high ambient temperatures experienced in sub-tropical peatlands are therefore expected to produce an enhanced rate of OM decay driven by microbial processes. However, anoxic conditions generated by extended waterlogging events retard OM decomposition and result in peat accumulating in sub-tropical regions (Rieley et al., 1996). Consequently, physical peat forming indices, such as TOC concentrations and accumulation rates (Baker et al., 2014) are useful for measuring the proportion of OM stored as peat and for providing insight into the palaeoenvironmental conditions prevalent at the time of sedimentation, which are ultimately controlled by climate (Baker et al., 2014, 2016, 2017).

The Mfabeni fen, situated on the south-eastern coastline of Africa (Fig. 1), is an exceptional and continuous record of peat accumulation spanning the last ca. 47 cal kyr BP. Such rich sedimentary archives are rare in southern Africa due to the overall dry climate and steep topography of the region. Palynological (Finch and Hill, 2008) and geomorphological (Grundling et al., 2013) studies in the fen have been undertaken, and high-resolution bulk geochemical (Baker et al., 2014), biomarker (Baker et al., 2016) and leaf wax ¹³C isotopic (Baker et al., 2017) investigations have been carried out on the

same core (SL6), making the Mfabeni peat sequence an ideal archive for assessing the climate proxy value of the *n*-keto alcohols during the transition from glacial to postglacial conditions. Because the Mfabeni fen is situated at a relatively low latitude, Finch and Hill (2008) and Baker et al. (2016) both found that the basin experienced subdued temperature fluctuations relative to higher latitudes since the Late Pleistocene. The biomarker (Baker et al., 2016) and leaf wax $\delta^{13}\text{C}$ proxies (Baker et al., 2017) implied that plant OM sources in the Mfabeni were predominantly influenced by water level fluctuation, as opposed to temperature changes in the basin. Ficken et al. (2000) developed the *n*-alk aquatic plant proxy (P_{aq}) on the premise that aquatic plants contributed predominantly mid-chain length (C_{23} and C_{25}) *n*-alks, while emerged and terrestrial plant leaf waxes are dominated by long-chain ($C_{27} - C_{33}$) homologs. Some of these compounds have been proposed as precursors for *n*-keto alcohols and therefore, could help delineate the *n*-keto alcohol sources and ultimately the palaeoenvironmental conditions at times of peat deposition. Additionally, microbial respiration, which is the mechanism by which precursors may be converted to *n*-keto alcohols can be influenced by several factors besides temperature, including OM chemistry and reactivity, soil pH, redox conditions and accessibility to potential decomposers (Schmidt et al., 2011). Considering that Mfabeni basin's geomorphology resulted in hydrology being the dominant control on plant-derived OM sources and rate of microbial alteration (Grundling et al., 2013, Baker et al., 2016, 2017), the bimodal distribution of *n*-keto alcohol homologues, the concentration correlations between *n*-alks, *n*-FAs and *n*-keto alcohols, and the ratios of the respective *n*-keto alcohols/*n*-keto alcohol precursors could help in delineate changes in past water levels, which according to Baker et al. (2016, 2017) can be directly linked to regional precipitation and to a lesser degree ambient air temperatures.

In this study, we explore the relationships between *n*-keto alcohols and published bulk geochemical and biomarker proxies in Mfabeni core SL6 to assess the potential of *n*-keto alcohols

in reconstructing palaeoenvironmental conditions. This assessment will be done by determining their origin, post-depositional alteration, and by corroborating the *n*-keto data with pollen and stratigraphic records from the Mfabeni fen to establish whether or not a climate signal is preserved in these novel compounds.

2. Geographical and geological setting

2.1. Site description

The shallow 350 km² St Lucia Lake dominates the UNESCO World Heritage iSimangaliso Wetland Park situated on the northern shores of Kwazulu-Natal province, South Africa (Fig. 1). On the eastern shores of the lake, the Mfabeni fen lies within an interdunal valley (Botha and Porat, 2007) at ca. 11 m a.s.l. (Finch and Hill, 2008) measuring 10 x 3 km (Clulow et al., 2012; Grundling et al., 2013) and an up to 10.8 m thick sediment record that accumulated along the M8 transect (Fig. 1, Grundling, 2001; Grundling et al., 2013). The fen's hydrology is dominated by groundwater from the Maputaland aquifer, which is structurally controlled by the north-south aligned coastal dune barrier (Grundling et al., 2013; Taylor et al., 2006a; Venter, 2003), and local precipitation. The area is subject to a sub-tropical climate and experiences mainly austral summer rainfall of between 900 and 1200 mm/yr (Grundling, 2001; Taylor et al., 2006b), with the highest amount of precipitation falling on the sand dune coastal barrier, which is the recharge area of the Maputaland aquifer (Kelbe and Rawlins, 1993). This results in seasonal inundation of the Mfabeni basin during the wetter summer months and groundwater level stabilisation just below or near the soil surface during the drier winter months. No correlation was found by Baker (2016) between peat accumulation in the Mfabeni basin, as measured by TOC concentrations and accumulation rate and regional Late Pleistocene sea level reconstructions done by Ramsay and Cooper (2002). Therefore, sea level has not had a major influence on the fen's hydrology, resulting in a unique coastal peat deposit that owes its longevity and

142 continuous accumulation record to the protection against sea level transgressions and
143 the enhanced groundwater transmissibility (Grundling et al., 2013) of the ca. 55 kyr old
144 adjacent coastal dune barrier (Porat and Botha, 2008). The fen forms part of the greater
145 Natal Mire Complex (Fig.1) that extends from southern Mozambique to the south of
146 Richards Bay, Kwazulu-Natal, and was formed via valley infilling within the
147 KwaMbonanbi formation coastal dune depression (Smuts, 1992). The fen vegetation is
148 predominantly herbaceous sedges and grasses (Finch, 2005) that are dominated by
149 *Fimbristylis bivalvis*, *Scleria poiformis*, *Rhynchospora holoschoenoides*, *Rhynchospora*
150 *corymbosa* sedges and *Panicum glandulopaniculatum*, *Ischaemum fasciculatum* grass
151 species (Venter, 2003, Finch and Hill, 2008, Clulow et al., 2012), and the fen is
152 surrounded by Maputaland wooded grassland, coastal dune and fresh water swamp
153 forests (Mucina et al., 2006). Apart from a general Mfabeni plant community study done
154 by Venter (2003), where she broadly classified 11 fen and 3 swamp forest plant
155 communities grouped according to their habitat existing in and around the basin, in-
156 depth records of contemporary Mfabeni plant communities and their lipid
157 characteristics are currently absent in the literature.

Figure 1: Location of core SL6 (a) in the Mfabeni fen, iSimangoliso Wetland Park, northern Kwazulu-Natal, South Africa. Location of palynology core (b; Finch and Hill, 2008) and most proximal and deepest stratigraphic transect (M8; Grundling et al. 2013) included for orientation. WRZ = winter rainfall zone; ARZ = all-year rainfall zone; SRZ = summer rainfall zone. Modified from Baker et al. (2017).

2.2. Lithology and age model

Grundling et al., (2013) published a detailed morphology of the Mfabeni peat basin where they classified up to five distinctive peat packages, evident in transect M8 (Fig. 1) that are occasionally interspersed with thin sandy layers, found mainly in the eastern part of the basin. They suggested the sand packages are of aeolian origin because evidence of fluvial input into the basin is absent. The 810cm SL6 core was extracted from the deepest part of the Mfabeni fen (28.15021°S ; 32.52508°E) in consecutive drives using a Russian peat corer with a sampling barrel measuring 5 cm x 50 cm. It was catalogued in the field, the lithology described and sliced into 1-2 cm intervals in the laboratory and then freeze-dried in preparation for geochemical analyses. The core

174 consists of 7 distinctive lithological packages that represent varying depositional
 175 regimes (Fig. 2).

Not to Scale

Figure 2: Core SL6 stratigraphic profile with approximate boundary ages. From Baker et al. (2014).

Nine selected bulk peat samples (at 10, 109, 209, 309, 405, 510, 609, 709 and 805 cm) were ¹⁴C radiocarbon dated and calibrated using the northern hemisphere terrestrial calibration curve IntCal09, with a southern hemisphere offset of 40 ±20 ¹⁴C yr. Age values were adjusted using the age-depth Bacon modelling software (Blaauw and Christeny, 2011). For more details see Baker et al. (2014) and references therein.

3. Methodology

A modified lipid extraction was done according to Wakeham et al. (2002) on 36 selected core intervals that were analysed for *n*-alks, *n*-FAs and *n*-alcs (see Baker et al., 2016 and references therein) and *n*-kets. 2g Freeze-dried sediment samples were extracted in a Dionex automated solvent extractor with dichloromethane (DCM)/MeOH (9:1 v/v). An aliquot of the total lipid extract (TLE) was saponified with 0.5N KOH (in MeOH) at 100 °C for 2 hr; then 5% NaCl was added and the mixture agitated and washed with hexane to separate the neutral (TLE-N) and acidic (TLE-A) fractions. The TLE-N fraction was introduced into a silica gel column and the *n*-alk (F1) fraction eluted with 10 ml hexane and then 5 ml of 25%

199 toluene/75% hexane. The *n*-alc and *n*-ket (F2) fraction was eluted by introducing 5 ml

aliquots of increasing proportions of EtOAc in hexane (5%:95%; 10%:90%;15%:85% and 20%:80%). The condensed F2 fraction was then derivatized with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and pyridine at 70 °C for 2 hr. The TLE-A fraction was acidified using 6N HCL, extracted in hexane and methylated with BF₃ in methanol to isolate the methyl ester bound FAs. The samples were injected via splitless mode into an Agilent 6890 gas chromatograph (GC) interfaced to a 5973 MSD mass spectrometer (MS) with a DB-5 (5% phenyl, 95% dimethyl polysiloxane) fused silica column (30 m x 0.25 mm i.d. x 0.25 µm film thickness). See Baker et al. (2016) for GC and MS operating parameters. Biomarker concentrations are reported in ng/mg TOC.

4. Results and discussion

4.1. Interpreting biomarker trends

While Nichols and Huang (2007) found evidence of *n*-kets only in modern peatland *Sphagnum* species sampled across the Midwest and New York state in north America, Ortiz et al. (2011) recorded low concentrations of *n*-kets in both *Sphagnum* (maximized at C₂₃) and other peat forming plants in the Roñanzas bog. They documented high molecular weight *n*-ket homologues in terrestrial plants, more specifically sedge and grass species with predominant C₂₇ and C₃₁ *n*-alks, C₂₉ and C₃₁ *n*-kets and C₂₂ and C₂₄ *n*-FAs, respectively. In the Mfabeni record, the *n*-ket homologues display predominant bimodal distributions (Fig. 3) with a prevalence for both mid- and long-chain compounds with odd / even predominances, and maxima dominated by *n*-C₃₃ (30%) and *n*-C₂₃ (43%). Both *n*-ket/FA and *n*-ket/alk precursor ratios exhibited varying degrees of similarity between different chain lengths (e.g. *n*-C₂₅ket / C₂₅alk and C₂₇ket / C₂₇alk) and precursor combinations (e.g. *n*-C₂₅ket / C₂₆FA and C₂₅ket / C₂₅alk, Table 1). The *n*-C₂₅ to *n*-C₂₉ odd ket/FA precursor ratios range between 5.0 x 10⁻⁴ and 6.4 x 10⁻², whereas *n*-C₃₁ket/*n*-C₃₂FA precursor ratio display a minimum of 1.3 x 10⁻² (ca. 39.5 cal kyr BP) and

226 a maximum 0.5 (ca. 8.0 cal kyr BP; Fig. 4). In contrast, the C₂₃ and C₂₅ ket/alk
227 precursor ratios range between 2.9×10^{-4} (ca. 0.0 cal kyr BP) and 0.3 (ca. 1.5 cal kyr BP),
228 while $n\text{-C}_{31}\text{ket} / n\text{-C}_{31}\text{alk}$ display a maximum of 0.2 (ca. 8.0 cal kyr BP) and a minimum
229 of 2.0×10^{-3} (0.0 cal kyr BP; Fig. 4). The n -ket average chain length values (ACL_{ket}; Fig.
230 4) have a variable distribution, maximising at 31.7 (ca. 27.4 cal kyr BP) and minimizing
231 at 23.0 (ca. 14.8 cal kyr BP).

Figure 3: *n*-alkan-2-one distributions ($m/z = 59$) of selected peat intervals from the Mfabeni fen. Depth, *n*-alkane aquatic plant ratio (P_{aq}), TOC concentrations and age (cal kyr BP) of sample included for comparison.

Figure 4. *n*-Alkan-2-one and precursor *n*-alkane and *n*-alkanoic acid proxy comparisons in core SL6. (a) %TOC; Baker et al. (2014), (b) aquatic *n*-alkane proxy (P_{aq} ; Baker et al., 2016), (c) *n*-alkan-2-one average chain length (ACL_{ket}), (d) C_{23} and C_{25} *n*-alkan-2-one/*n*-alkane precursor ratios, (e) C_{31} *n*-alkane-2-one/*n*-alkane and *n*-alkanoic acid precursor ratios, (f) n - C_{25} , C_{27} and C_{29} /*n*-alkanoic acid precursor ratios. H1 – 5. Heinrich events (dates from Hemming, 2004); A1 and A2. Antarctic warming events (Blunier et al., 1998;

Stocker, 2000); Last Glacial Maximum (LGM); Antarctic cold reversal (ACR); Younger Dryas (YD); Holocene (Hol).

Table 1: Statistical relations between biomarker concentrations and proxy ratios in Core SL6. (One tail test; P, probability level; df, degrees of freedom; *n*-alkane, *n*-alkanoic acid and *n*-alkanol data previously published by Baker et al., 2016).

	Alk ng/mg TOC vs FA ng/mg TOC	FA ng/mg TOC vs Alc ng/mg TOC	Alk ng/mg TOC vs Ket ng/mg TOC	FA ng/mg TOC vs Ket ng/mg TOC
r	0,56	0,41	0,28	0,44
P=0.01	Sig	Sig		Sig
P=0.05	Sig	Sig	Sig	Sig
	df=34	df=34	df=34	df=34

	<i>n</i> -C ₂₃ ket / <i>n</i> -C ₂₃ alk vs vs <i>n</i> -C ₂₃ ket / <i>n</i> -C ₂₄ FA	<i>n</i> -C ₂₅ ket / <i>n</i> -C ₂₅ alk vs vs <i>n</i> -C ₂₅ ket / <i>n</i> -C ₂₆ FA	<i>n</i> -C ₂₇ ket / <i>n</i> -C ₂₇ alk vs vs <i>n</i> -C ₂₇ ket / <i>n</i> -C ₂₈ FA	<i>n</i> -C ₂₉ ket / <i>n</i> -C ₂₉ alk vs vs <i>n</i> -C ₂₉ ket / <i>n</i> -C ₃₀ FA
r	0,61	0,86	0,49	0,38
P=0.01	Sig	Sig	Sig	
P=0.05	Sig	Sig	Sig	Sig
	df=34	df=34	df=34	df=34

	<i>n</i> -C ₃₁ ket / <i>n</i> -C ₃₁ alk vs vs <i>n</i> -C ₃₁ ket / <i>n</i> -C ₃₂ FA	ACL _{ket} vs P _{aq}	<i>n</i> -C ₂₃ ket/ <i>n</i> -C ₂₃ alk vs vs P _{aq}	<i>n</i> -C ₂₅ ket/ <i>n</i> -C ₂₅ alk vs vs P _{aq}
r	0,82	-0,43	-0,43	-0,40
P=0.01	Sig	Sig	Sig	Sig
P=0.05	Sig	Sig	Sig	Sig
	df=34	df=34	df=34	df=34

When comparing the trends for total concentrations of *n*-kets in core SL6 (Table 1) with *n*-alks, *n*-FAs and *n*-alcs published by Baker et al. (2016), *n*-alks vs. *n*-FAs ($r = 0.56$, $P = 0.01$, $df = 34$) and *n*-FAs vs. *n*-alcs ($r = 0.41$, $P = 0.01$, $df = 34$) show significant positive correlations. These statistical relations suggest that *n*-alks, *n*-FAs and *n*-alcs share a common source (i.e. plant-derived OM). However, Baker et al. (2016) did conclude that a proportion of the *n*-FAs in core SL6 could have been derived from secondary microbial origin via the conversion of primary plant acids produced by OM decomposers. *n*-Alks and *n*-FAs display lower r values but still significant positive correlations with *n*-kets ($r = 0.28$, $P = 0.05$, $df = 34$ and $r = 0.44$, $P = 0.01$, $df = 34$, respectively), implying the *n*-

kets in the Mfabeni fen are more likely a product of microbial reworking of their $n+1$ -FA precursors and to a lesser extent, from n -alks, in view of the more recalcitrant nature of the latter (Meyers and Ishiwatari, 1993). This possibility is consistent with the origin of these compounds proposed by Zheng et al. (2011b) for the Hongyuan peat basin, which is under the influence of both the East Asian and Indian summer monsoon systems and so subject to fluctuating precipitation levels, similar to the Mfabeni fen (Baker et al., 2014, 2016). The correlation coefficients for n -kets vs. n -alks ($r = 0.28$) and n -kets vs. n -FAs ($r = 0.44$) are however relatively low, suggesting an additional process contributed to the origins of the Mfabeni n -kets. As reported by Ortiz et al. (2011), terrestrial peat forming plants in the Roñanzas bog contain low concentrations of long chain n -kets, leading us to consider that direct input from vegetation, although at lower concentrations than microbial sources, could also be a source for high molecular weight n -ket homologues (Fig. 3) found in the Mfabeni peat record. Consistent with this hypothesis, graminoids, the dominant plant species found in the basin today, are characterised by predominant C_{29} to C_{35} lipid homologues (Jaffé et al., 2001; Mead et al., 2005). On analysis of the homologue distributions in conjunction with the biomarker proxies, the samples with a strong bimodal C_{23} and C_{33} distribution display emerged / mixed source P_{aq} values (Fig. 3c, $P_{aq} = 0.23$), while the other two end members exhibit maxima at C_{33} with a P_{aq} value indicating a terrestrial source ($P_{aq} = 0.13$, Fig 3a) or C_{23} with an aquatic plant signature ($P_{aq} = 0.39$, Fig 3b). This analysis confirms the source of n -kets in the Mfabeni record is governed by the input of plant lipids, either via direct input or conversion of primary lipids by microbial organisms. Besides the relatively low direct input of n -kets from peat forming plants (Nichols and Huang, 2007, Ortiz et al., 2011), the inference for the dominant source of the Mfabeni n -kets from microbial alteration of n -alks and n -FAs is further supported by significant positive trends between the n -kets and their corresponding n -alk and $n+1$ -FA precursor ratios (Fig. 4; Table 1).

285 Because the dominant control on peat accumulation in the sub-tropics is the extent of
 286 waterlogging events (Couwenberg et al., 2010), we surmise that, during times of
 287 increased waterlogging in the fen, the dominant sources of C₂₃ and C₂₅ *n*-kets were
 288 aquatic plant *n*-alk and *n*-FA precursors. However, the *n*-C₂₃ket/alk and *n*-C₂₅ket/alk
 289 ratios display significant negative correlations ($r = -0.34$, $P = 0.01$, $df = 34$ and $r = -0.40$,
 290 respectively) with the *n*-alk aquatic plant proxy (P_{aq} ; Fig. 4, Table 1), suggesting an
 291 additional process that controlled the formation of *n*-kets from their *n*-alk and *n*-FA
 292 precursors. Therefore, we surmise that due to the limited oxygen availability during
 293 extensive waterlogging events, microbial conversion of the precursor *n*-alks and *n*-FAs to
 294 *n*-kets was retarded (Bardgett et al., 2008), which would result in a negative statistical
 295 relation between *n*-C₂₃ and *n*-C₂₅ ket/ alk and P_{aq} proxies. Consistent with this
 296 hypothesis, the ACL_{ket} values (Fig. 4, Table 1) also show a negative correlation with P_{aq}
 297 ($r = -0.43$, $P = 0.01$, $df = 34$), reinforcing the idea that when aquatic plant input
 298 increased due to increased water level in the basin, the predominant *n*-alks available for
 299 conversion to their corresponding *n*-kets were those of mid-chain length compounds
 300 prevalent in aquatic plants (Ficken et al., 2000; Baker et al., 2016), albeit at a slower
 301 rate due to anoxic conditions. Zheng et al. (2011a) concluded the higher ACL_{ket} values
 302 recorded drier periods in the Hani mire, which they inferred from elevated ACL_{ket} and
 303 ACL_{alk} values for peat sequences devoid of *Sphagnum* fossil spores that represented
 304 lower water levels in the Hani basin. During periods of decreased water levels in the
 305 Mfabeni, the plant communities would have been dominated by emerged (sedges) and
 306 terrestrial (grasses) plants that are characterised by long-chain lipids (C₂₇ – C₃₃; Meyers
 307 and Ishiwatari, 1993) and therefore, C₂₉ket / C₃₀FAs, C₃₁ket / C₃₂FAs and
 308 C₃₁ket/C₃₁alks ratios (Fig. 4), are expected to be the most indicative proxies during these
 309 periods. The palaeoenvironmental controls on the long chain ket/alk precursor ratios (*n*-
 310 C₂₇ to *n*-C₃₁) is less clear as they do not exhibit correlations with the OM sources or bulk

geochemical proxies discussed by Baker et al. (2014, 2016). Nonetheless, they do trend similarly to the mid-chain length ket/alk ratios (n -C₂₃ ket/alk and n -C₂₅ ket/alk; Table 1), and since we have established that low n -C₂₃ and n -C₂₅ket / precursor values were due to increased waterlogging and slowdown in microbial activity as a result of the ensuing anoxic conditions in the basin, it leads us to infer that the longer chained n -kets / precursor ratios were also primarily influenced by water level fluctuation in the Mfabeni record. This assumption is corroborated by the biomarker study in Baker et al. (2016), that concluded plant physiology in the peat basin was dominated by water level fluctuations. On the other hand, Baker et al. (2016) found that even though relatively subdued temperature changes were experienced in the Mfabeni fen, relative to higher latitudes (Finch and Hill, 2008), the sat/unsat_{FA} microbial activity proxy in Core SL6 exhibited a temperature influence. This finding leads us to consider that, even though the n -ket proxies appear to be influenced predominantly by water level in the basin, when temperature fluctuated to extreme levels relative to the average conditions in the Mfabeni basin, the n -ket ratio could also have been influenced by temperature. Consequently, we use the n -ket suite of proxies to directly link higher n -ket/ n -alk or n -FA precursor ratios to decreased waterlogging in the fen, which points to elevated microbial oxidation of OM occurring in the corresponding peat layer, and vice versa, with temperature as a secondary control.

4.2. Mid-chain n -ket / precursor proxies

During periods of greater waterlogging as indicated by >0.4 P_{aq} and elevated TOC concentration (Fig. 4), we argue that the predominant input of n -alks (and n -FAs) would have been mid-chain length monomers from submerged plants, and consequently the n -C₂₃ket/ n -C₂₃alk and n -C₂₅ket/ n -C₂₅alk ratios would be the best indicator of palaeoenvironmental conditions during these periods. The negative correlation between P_{aq} and mid-chain n -ket / precursor ratios suggest a slowdown in microbial reworking of

aquatic plant *n*-alks and *n*-FAs due to anoxic conditions during protracted waterlogging events. For example, during the A2 warming event (ca. 44.5 cal kyr BP and Heinrich 5; H5) the Mfabeni proxies record a period of increased water level in the basin (high %TOC, Fig. 4) with a dominant submerged macrophyte population ($> 0.4 P_{aq}$; Fig. 4) and a replacement of C_3 riparian/swamp forests by C_4 wetland sedge with aquatic vegetation (Fig. 5) because of increased regional precipitation and warmer temperatures (Baker et al., 2017). Similarly, after 30.6 cal kyr BP, TOC concentration steadily increases, with a shift to higher, albeit fluctuating proportions (Fig. 4) of aquatic plant input, increased sat/unsat_{FA} and CPI_{FA} values (Fig. 5, Baker et al., 2016), signalling elevated precipitation and warmer temperatures. However, the *n*-C₂₃ket and *n*-C₂₅ ket/alk ratios remained relatively low but stable (Fig. 4), reinforcing the notion of an overall increased waterlogging that preserved the *n*-alk OM source derived from a predominantly aquatic plant input. Between ca. 26 and 23 cal kyr BP, the P_{aq} values record a dominant aquatic plant signal (> 0.60), concordant with elevated TOC concentration, but subdued *n*-C₂₃, *n*-C₂₅ ket/alk ratios, and decreased *n*-C₂₅ket /*n*-C₂₆FA ratios (Fig. 4). These trends suggest a period of high moisture availability coeval with lower temperatures that prevailed at the time of deposition. This interpretation is supported by the sat/unsat_{FA} proxy (Fig. 5) that displays below average values, which Baker et al. (2016) inferred as evidence of a period of relatively cool and moist conditions.

356

357 Figure 5: Biomarker and leaf wax $\delta^{13}\text{C}$ proxies from the Mfabeni record. (a) TOC concentrations (Baker et
 358 al., 2014), (b) n -alkane average chain lengths (ACL_{alk} , Baker et al., 2016), (c) n -alkanoic acid carbon
 359 chain lengths (CPI_{FA} , Baker et al., 2016), (d) n -alkanoic acid saturated / unsaturated chains ($\text{sat/unsat}_{\text{FA}}$, Baker et
 360 al., 2016), (e) compound specific leaf wax $\delta^{13}\text{C}$ isotopes (Baker et al., 2017).

At the start of the deglacial period (ca. 19 – 10.5 cal kyr BP), TOC concentration remains low until ca. 16.7 cal kyr BP. Thereafter, the biomarker proxies record an increase in aquatic plant input (P_{aq}) and an overall increase in TOC (Fig. 4), but low microbial activity (sat/unsat_{FA} and CPI_{FA} remain relatively high, Fig. 5, Baker et al., 2016) up to the early Holocene. Baker et al. (2016) deduced that this was due to a steady increase in water waterlogging within the peat basin, but stagnant ambient air temperature during deglaciation. This interpretation is supported by the n -C₂₅ket, n -C₂₃ket/alk and n -C₂₅ket/ n -C₂₆FA ratios, that show low values throughout the deglacial period, suggesting slow microbial activity due to overall increased water level and low ambient air temperature.

During the early Holocene, core SL6 recorded a predominant submerged macrophyte input ($> 0.4 P_{aq}$), with low n -C₂₃ and n -C₂₅ket/alk proxy values until ca. 7.1 cal kyr BP (Fig. 4), suggesting a cool and moist early Holocene epoch. The biomarker study of the core similarly displayed subdued CPI_{FA} and ACL_{alc} ratios (Fig. 5), concordant with elevated TOC concentration (Baker et al., 2016), reinforcing the cool and moist conditions implied by the n -ket proxies. At ca. 2.2 cal kyr BP, an abrupt increase in P_{aq} values occurs, corresponding to a decrease in n -C₂₃ket and n -C₂₅ket/alk (Fig. 4), increased sat/unsat_{FA}, and decreases in ACL_{alk} values (Fig. 5), which Baker et al. (2016) concluded was due to a rapid increase in water level, aquatic plant input, and elevated air temperature. This period of increased waterlogging suggested by the biomarker proxies could arguably have resulted in a protracted anoxic horizon that led to a significant decrease in microbial alteration of mid-chain aquatic plant n-alks, recorded by the ensuing large decline in n -C₂₃ket/alk and to a lesser degree n -C₂₅ket/alk.

4.3. Long-chain n -ket / precursor proxies

Under dry conditions with decreased waterlogging when emerged and terrestrial plants proliferated, the most indicative palaeoenvironment proxies are likely to be the long chain *n*-kets / precursor ratios. During the H4 (ca. 38 cal kyr BP) and A1 (ca. 37 cal kyr BP) events, a transition to C₃ arboreal forests occurred because of decreased water levels in the basin (Fig. 5, Baker et al., 2017). This change was recorded by a terrestrial/emersed OM plant signature ($< 0.2 P_{aq}$) that was coeval with decreased %TOC (Fig. 4), suggesting dry conditions in the basin. Because of the dominance of long-chain lipids in terrestrial and emersed plants, the significant increase in both the *n*-C₃₁ ket/alk and *n*-C₃₁ ket/FA proxies (Fig. 4) during and after the A1 event implies an increase in production of long-chain *n*-kets from their corresponding precursors during this period of decreased water level, and poor preservation of organic matter. The %TOC signal subsequently decreases to the core minimum (4.5%; 30.6 cal kyr BP; H3; Baker et al., 2014) that coincides with an increase in sandy peat deposition and low sat/unsat_{FA} (Fig. 5, Baker et al., 2016), with depressed *n*-C₃₁ ket/alk and *n*-C₃₁ ket/FA values (Fig. 4) up to ca. 30.6 cal kyr BP, signifying cool and dry conditions.

During the peak of the Last Glacial Maximum (LGM, ca. 23 - 19 cal kyr BP) the Mfabeni archive recorded a change to C₃ temperate grasslands (Fig. 5) and an exclusion of wetland aquatic plants (Baker et al., 2017), concordant with a sharp decline in TOC concentration (Fig. 4) and below average sat/unsat_{FA} values (Fig. 5, Baker et al., 2016), implying minimal waterlogging and a shift to cool and dry glacial conditions. Following the LGM, the deglacial period representing the transition from full glacial to interglacial conditions of the Holocene saw a gradual increase in temperatures and water levels. However, Baker et al. (2016) found that the Antarctic Cold Reversal (ACR; ca. 14.5 – 12.9 cal kyr BP) encouraged an increase in emersed and terrestrial plant input (decreased P_{aq}) in response to a brief period of dry conditions. The *n*-ket proxies support

this implication of drier ACR conditions by exhibiting a discernible increase in n - C_{27} ket/ n - C_{28} FA and n - C_{29} ket/ n - C_{30} FA ratios (Fig. 4).

During the Holocene Altithermal (at 8.7 al kyr BP), the sat/unsat_{FA} proxy increases sharply (Fig. 5, Baker et al., 2016), coinciding with an increase in n - C_{31} ket/FA and n - C_{31} ket/alk and a drop in P_{aq} (Fig. 4), suggesting elevated temperatures and inputs from emersed plants. Thereafter, a dry event is recorded at ca. 7.1 cal kyr BP, whereby TOC concentration decreases to its lowest level during the Holocene (19.2%; Baker et al., 2014). Subsequently, the proxy for OM source record a predominant terrestrial/emersed plant origin ($P_{aq} < 0.15$; Fig. 4) indicated by elevated but fluctuating mid- and long-chain n -ket/alk, n -ket/FA ratios (Fig. 4) and increased sat/unsat_{FA} values until 2.2 cal kyr BP (Fig. 5, Baker et al., 2016). These trends suggest decreased water levels, but elevated temperature. Baker et al. (2016) concluded that the warmer post-glacial conditions during the mid-Holocene resulted in higher NPP of vascular plant growth in the basin that resulted in peat accumulating without the usual permanent waterlogging owing to high sedimentation rates and more recalcitrant OM sources.

After the brief period of waterlogging at ca. 2.2 cal kyr BP, core SL6 recorded an increase in the proportions of OM input from emersed and terrestrial plants and a decrease of input from aquatic plants ($0.3 - 0.06 P_{aq}$; Fig. 4). This source change was also indicated by low long-chain ket/FA and ket/alk ratios and fluctuating TOC concentration (Fig. 4). These changes signify an overall drying trend with fluctuating precipitation (Baker et al., 2017) that has persisted until today. This inference is supported by a transition to grassland dominated habitats recorded in the Mfabeni by Finch and Hill (2008) after ca. 2.2 k cal yr BP.

4.4. The ACL_{ket} proxy

Because fluctuations in basin hydrology can cause changes in plant assemblages that produce distinctive leaf wax lipids (Cranwell, 1974, Schwark et al., 2002), the ACL biomarker proxy has been used to delineate available moisture in peat deposits (Schefuß et al., 2003, Zhou et al., 2005, 2010, Baker et al., 2016). ACL_{ket} values in core SL6 correlate negatively with P_{aq} (Table 1, Fig. 4), suggesting the mid-chain aquatic plant *n*-alk precursors were the predominant source of *n*-kets during periods of high water levels. Alternatively, when water levels were lower and emerged /terrestrial plants proliferated, elevated ACL_{ket} values recorded drier conditions.

For instance, during the LGM and early deglacial period (ca. 23 – 15 cal kyr BP), Baker et al. (2017) reported biomarker evidence for dominance of C_3 temperate grasslands in the Mfabeni basin to the exclusion of wetland aquatic plants, concordant with a sharp decline in TOC concentration (Baker et al., 2014) and below average sat/unsat_{FA} values (Fig. 5, Baker et al., 2016). These parameters imply minimal waterlogging and a shift towards dry glacial conditions. Consistent with this, the ACL_{ket} values exhibited a sharp increase during the same period, supporting the implied change to dominant terrigenous plant input (Fig. 4).

Alternatively, under interglacial conditions during the mid-Holocene (ca. 6.5 – 2.5 cal kyr BP) directly after the ca. 7.1 cal kyr BP drying event, where TOC concentration drops to its lowest level during the Holocene (19.2%; Baker et al., 2014), the sat/unsat_{FA} proxy exhibits a sharp increase (Fig. 5, Baker et al., 2016), corresponding to a drop in P_{aq} , and an increase in %TOC and ACL_{ket} (Fig. 4). The OM source proxies agree with this observation by recording a predominant terrestrial/emersed plant origin ($P_{aq} < 0.15$; $ACL_{ket} > 28$); correlating to elevated but fluctuating mid- and long-chain *n*-ket/alk and *n*-ket/FA ratios (Fig. 4). These observations are opposite to what was been previously recorded under glacial conditions in the Mfabeni peat archive, where elevated TOC concentrations indicated elevated water levels, as they coincide with increased aquatic

plant inputs and lower ACL_{ket} (Fig. 4). However, as discussed in section 4.3, Baker et al. (2016), reported an opposite trend between the n -alk carbon preference index (CPI_{alk}) and TOC concentration during the Holocene (Fig. 5). They suggested the high sedimentation rates which accompanied the elevated NPP that was confirmed by the relatively high C accumulation rates reported by Baker et al. (2014) played a dominant role in peat accumulation, as opposed to waterlogging in the Mfabeni basin during this period in Holocene.

4.5. n -ket palaeoproxy potential

We argue that the changes in peat plant communities that were driven by fluctuating palaeoenvironmental conditions in the Mfabeni basin dictated the dominant chain length n -alks and n -FAs available for microbial alteration into the n -kets found in the sediment record and therefore, can serve as an OM source proxy. Additionally, since the mid- and long-chain n -ket/precursor ratios both exhibited a negative relation with the P_{aq} proxy, we concluded that the mid- and long-chain n -ket/precursor ratios are a good indicator of microbial activity during times of aquatic or emersed / terrestrial plant proliferation, each thriving in different palaeohabitats. The opposite trends between the P_{aq} and ACL_{ket} proxy (Table 1) proved to be a useful additional tool to delineate OM sources and palaeohydrology. In addition, ACL_{ket} , can be also be used to reconstruct changes in palaeohydrology and biomarker sources, most appropriately in the Mfabeni fen, where water level fluctuations dominated peat formation under glacial conditions, while high sedimentation rates and recalcitrant OM sources dictated C accumulation during much of the Holocene.

By investigating the trends between established Mfabeni bulk geochemical, biomarker and leaf wax ^{13}C isotope data with those of the novel n -ket ratios, we find that there is a

definite potential for these biomarkers to be used as proxies for interpreting palaeoenvironmental conditions. Not only do they seem to indicate the source/precursor relations, but they also give us more insight into OM remineralisation after deposition. Coupled with a good understanding of peat accumulation dynamics, they have shown to be good indicators in the Mfabeni record for delineating palaeoenvironmental conditions with greater confidence within a multiproxy approach.

5. Conclusions

Our study shows that *n*-ket biomarker compounds have good potential as a palaeoenvironmental proxy for interpreting past climatic conditions. Their predominant origin was established to be via microbial metabolic alterations of primary *n*-alk and *n*-FA compounds derived from higher plants. Because the Mfabeni fen falls within a subtropical climate, peat accumulation is predominantly controlled by waterlogging events, with temperature playing a secondary role. Consequently, we conclude that the *n*-ket proxies respond predominantly to change in precipitation, with temperature being of secondary importance. By comparing the *n*-ket proxies with published bulk geochemical, *n*-alk, *n*-FA, and *n*-alc biomarker proxies and leaf wax $\delta^{13}\text{C}$ data in conjunction with other climate archives, we established that the *n*-ket biomarkers are sensitive to similar environmental/climatic fluctuations in the Mfabeni fen. However, further research is required to establish the full potential of *n*-ket climate proxies in diverse palaeoclimate archives to assist in clarifying the dominant controls of this ubiquitous biomarker at different latitudes. Our research has reiterated the importance of employing a multi-proxy approach to resolve inconsistencies between proxies when attempting to delineate palaeoenvironmental conditions from sedimentary archives.

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