Palaeogeography, Palaeoclimatology, Palaeoecology 459 (2016) 495–507

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

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

Interpreting vegetation change in tropical arid ecosystems from sediment molecular fossils and their stable isotope compositions: A baseline study from the Pilbara region of northwest Australia

Alexandra Rouillard [a,*], Paul F. Greenwood [a,b,c], Kliti Grice [c], Grzegorz Skrzypek [a], Shawan Dogramaci [d], Chris Turney [e], Pauline F. Grierson [a]

[a] West Australian Biogeochemistry Centre and Ecosystems Research Group, School of Plant Biology, The University of Western Australia (UWA), Crawley, WA, Australia
[b] Centre for Exploration Targeting, School of Earth and Environment, UWA, Australia
[c] Western Australia Organic and Isotope Geochemistry Centre and John de Laeter Centre, The Institute for Geoscience Research, Department of Chemistry, Curtin University, Perth, WA, Australia
[d] Rio Tinto Iron Ore, Perth, WA, Australia
[e] Climate Change Research Centre, University of New South Wales (UNSW), Sydney, NSW, Australia

A R T I C L E I N F O

Article history:
Received 6 March 2016
Received in revised form 8 July 2016
Accepted 19 July 2016
Available online 20 July 2016

Keywords:
Biomarkers
CSIA $\delta^{13}C$
n-Alkanes
Organic matter
Pilbara
Triodia

A B S T R A C T

Detection of source diagnostic molecular fossils (biomarkers) within sediments can provide valuable insights into the vegetation and climates of past environments. However, hot and arid regions offer particularly challenging interpretive frameworks for reconstructions because baseline data are scarce, organic matter is generally very low and in the inland tropics in particular, sediments are also often subject to flooding and drought. Here, we investigated whether biomarkers and compound-specific $\delta^{13}C$ values could be extracted from a late Holocene sediment record from the Fortescue Marsh (Pilbara, northwest Australia) to allow interpretation of past catchment vegetation and hydroclimate. The low total carbon (TC) content (<1.4%) was a major challenge for the molecular analyses over the ~2000 years old sequence. Nevertheless, they revealed that the dominant hydrocarbon features (e.g., long chain *n*-alkanes) indicative of terrestrial plants (e.g., C_4 grasses; riparian and other C_3 plants) encompassed the last ~1300 yrs and that low abundance of products from aquatic sources (e.g., *n*-C_{17}) were detected in the uppermost sediments only when permanently inundated conditions prevailed (recent decades). Similarly, the lower $\delta^{13}C$ values (i.e., a difference of −2.3‰) of long chain *n*-alkanes in upper sediments reflected a vegetation response to the emergence of wetter conditions through the late Holocene in the region. Based on the diverging dominant source contributions obtained from the molecular distributions and arid based Bayesian mixing model ($\delta^{13}C$ of *n*-$C_{27–33}$ alkanes) results, less arid conditions may have favoured the input of ^{13}C depleted *n*-alkanes from the *Eucalyptus* (C_3) dominant riparian vegetation. The deepest sediments (<700 CE) however, had a TC content of <0.4%, and no organic compounds were detected, consistent with local and regional records of hyperarid conditions. These results demonstrate that *n*-alkanes can provide a molecular and stable isotopic fingerprint of important - and perhaps underappreciated - ecological processes in modern tropical arid environments for future paleoclimate investigations.

1. Introduction

Lake sediment records can extend temporal scales of hydrologic reconstruction to millennial and longer time frames. For example, periods of drought can be reconstructed from changes in lake level and salinity using microfossil assemblages (e.g., diatoms) and geochemical or physical parameters of the sediment (e.g., Wolff et al., 2011; Barr et al., 2014). These paleolimnological methods have most commonly been applied to closed-basin lakes in arid or semiarid landscapes, in which changes in lake level and salinity are closely related to shifts in hydrologic balance (e.g., Stager et al., 2013). However, deep or permanent lakes are often lacking in many arid environments, resulting in limited applicability of many proxies due to preservation issues, notably for reconstructing inputs of organic matter to lakes that can reflect hydroclimate conditions. Organic geochemical studies of depositional environments have provided molecular evidence (biomarkers) of changing hydrology under various climates, including from the studies of lakes (Leng and Henderson, 2013; Sun et al., 2013; Atahan et al., 2015), marine settings

Abbreviations: CE, Common Era; CPI, carbon preference index; CSIA, compound-specific stable isotope analysis; GC–MS, gas chromatography–mass spectrometry; IRMS, isotope ratio mass spectrometry; MW, molecular weight; OM, organic matter; TC, total carbon; TIC, total ion chromatogram.

* Corresponding author at: Centre for GeoGenetics, The Natural History Museum of Denmark, Øster Voldgade 5-7, 1350 Copenhagen K, Denmark.
E-mail addresses: alexandra.rouillard@snm.ku.dk, alexandrarouillard@yahoo.ca (A. Rouillard).

http://dx.doi.org/10.1016/j.palaeo.2016.07.023

(e.g., Castañeda et al., 2009b; Dubois et al., 2014; Pagès et al., 2014), and coastal salt-marshes and lagoons (e.g., Volkman et al., 2007; McKirdy et al., 2010; Tulipani et al., 2014). The sedimentary distribution of biomarkers and their stable carbon and hydrogen isotope compositions (i.e., $\delta^{13}C$ and $\delta^{2}H$ at compound specific level) have been widely used to investigate physiological or ecological community responses to shifts in lake salinity and water source (Romero-Viana et al., 2012; Sachse et al., 2012; van Soelen et al., 2013). Variation in the $\delta^{13}C$ values of specific compounds, e.g., long chain *n*-alkanes representative of terrestrial vegetation, have also indirectly helped resolve past hydrological changes via their sensitivity to moisture availability in the catchment, drought stress or vegetation shifts (Castañeda et al., 2007, 2009a; Kristen et al., 2010; Tipple and Pagani, 2010; Sun et al., 2013). Consequently, using biomarkers and their stable isotopes ratios to establish paleoenvironmental records for still underrepresented regions is of great interest.

Tropical arid ecosystems have proved especially challenging to paleolimnology and organic geochemical characterisation of sediments. These regions experience high seasonal and inter-annual hydroclimatic variability, typified by periods of prolonged droughts interspersed with occasional intense flooding (e.g., van Etten, 2009; Rouillard et al., 2015). First, a general lack of water, which is often coupled with low nutrient availability, severely limits biological production and in turn the deposition of organic matter (OM) to sediments (e.g., Huxman et al., 2004; Snyder and Tartowski, 2006; Collins et al., 2008; McIntyre et al., 2009a, 2009b). In Australian soils of tropical (i.e., hot) arid environments in particular, the preservation of OM is further compromised by major biological reworking by termites and other fauna (e.g., Holt, 1987; Chen et al., 2003; Austin et al., 2004) and the high frequency of fires which can accelerate the loss of organic volatiles that might otherwise form terrestrial detritus (Ford et al., 2007). Intense episodic flooding can lead to increased mobilisation and dislocation of OM from the catchment to lakes followed by pulses of high organic production in the catchment and aquatic network, resulting in non-linear OM availability and deposition patterns (Battin et al., 2008; Reid et al., 2011; Puttock et al., 2012). Shallow lakes mean that prolonged drought further exposes dried sediment to changing redox conditions and deflation, which can also cause hiatus of organic sedimentary records in many regions of the world (Verschuren,1999; Bessems et al., 2008; Argus et al., 2014, 2015). Given these challenges, there have been few attempts to characterise such sediments in northwest Australia, a region where very limited knowledge of the Holocene environmental history is available to understand long-term ecosystem processes and resilience to ongoing climate change (Gergis et al., 2014).

Plant molecular $\delta^{2}H$ signals are normally considered indicative of the isotope ratio of source water and associated hydrology (Tipple and Pagani, 2010; Romero-Viana et al., 2012; Sachse et al., 2012; van Soelen et al., 2013). However, the large evaporative shifts in lake volumes in arid and semi-arid regions generally result in salinity fluctuations that in turn affect the $\delta^{2}H$ fractionation between organisms and their source water (Sachse and Sachs, 2008). In addition, plants make physiological adjustments to both changing water availability and salinity, which can also result in further fractionation (Zhou et al., 2011; Sachse et al., 2012), making plant molecular $\delta^{2}H$ less reliable than in more temperate or non-saline ecosystems (e.g., Duan et al., 2014). Consequently, plant molecular $\delta^{13}C$ compositions of sediments, particularly of *n*-alkanes, may be a more suitable indicator for hot arid environments.

The composition and distribution of plant communities in arid ecosystems is largely driven by the availability of water as well as other flooding or waterlogging-related conditions, such as soil redox, salinity, substrate and nutrient availability and the accumulation of toxic ions (Schwinning et al., 2004; Reid et al., 2011; Argus et al., 2014). Different hydrological regimes will favour plants of specific functional types (e.g., C_3 versus C_4 photosynthetic pathways, which are readily distinguished by their $\delta^{13}C$ signatures) and tolerance to drought, waterlogging or salinity (Huxman et al., 2004; Snyder and Tartowski, 2006). Prolonged aridity can thus progressively impact vegetation assemblages at the generation level over long timescales, generally favouring C_4 grasses across catchments and chenopods (often a mix of CAM, C_4 and C_3 species) in saline wetland areas (Sage et al., 2011). The ^{13}C enrichment of C_3 plant tissue can also be driven by water stress within a matter of minutes (Cernusak et al., 2013). The dynamics of plant water stress over periods of decades to centuries may also be recorded in the wood chemistry of trees (e.g., Cullen et al., 2008; Qin et al., 2015) or at the ecosystem level in soils and lake sediment (Krull et al., 2005, 2006; Diefendorf et al., 2011; Codron et al., 2013). Plants in arid environments also produce relatively high amounts of cuticular waxes as a protection against high ultraviolet light and water loss; cuticular waxes may thus represent more promising molecular targets of organic lean dryland sediments (Hoffmann et al., 2013).

Cuticular-derived *n*-alkanes (Eglinton and Hamilton, 1967) are typically some of the more abundant products from the organic sediments of lakes (Schmidt et al., 2011), so are attractive analytes for compound specific isotopic analysis (CSIA). Characterisation of the molecular and stable isotopic abundances of *n*-alkanes has become an important paleoecological strategy to assess changes in hydrological status at catchment and continent scales (Castañeda and Schouten, 2011; Sachse et al., 2012; Leng and Henderson, 2013; Dubois et al., 2014). In recent years, the $\delta^{13}C$ values of *n*-alkanes in sediments have unlocked a wealth of paleoenvironmental information from regions and sites that had previously been difficult, including assessment of historical change in catchment land-use, eutrophication studies and shifts in vegetation composition in response to climate (e.g., Castañeda and Schouten, 2011; Fang et al., 2014). However, as with other relatively new molecular tools in paleolimnology, our capacity to make inferences of paleoflora from biomarkers is limited by uncertainties in source, transportation and preservation of OM from senescing plants (Birks and Birks, 2016). A first step is to improve the baseline of available biomarker datasets and their stable isotopic compositions from arid zone sediments with independently described paleoenvironmental histories.

Broadly, our study investigated the potential of organic molecular fossils and $\delta^{13}C$ values of plant waxes of lake sediments for reconstructing catchment vegetation history and hydroclimatic change in the arid subtropical Pilbara region of inland northwest Australia. Previously, we established centennial and millennial flood records for the Pilbara based on historical records as well as physical and geochemical analyses of sediments at the Fortescue Marsh (Rouillard et al., 2015, 2016). Here, we used a replicate core of this sediment sequence to determine if: i) organic geochemical information can be extracted to identify the major sources of sedimentary OM; ii) $\delta^{13}C$ values of individual organic molecules can be measured and related to the major vegetation types in the catchment (C_3 and C_4); and iii) the molecular and $\delta^{13}C$ distribution from the sedimentary sequence can be related to regional changes in hydrology through the late Holocene. Our analysis is considered within an interpretive framework that accounts for the specificities and challenges of extracting paleoclimate information from organic geochemical indicators in sediments developed in tropical arid ecosystems.

2. Methods

2.1. Study site

The study region and sampling is described in detail in Rouillard et al. (2016). Briefly, replicated ~60-cm sediment cores (FOR106C2 and FOR106C3) were obtained from the deepest section of the 14 Mile Pool (22.6°S, 119.9°E) of the Fortescue Marsh in the arid Pilbara region of northwest Australia (Fig. 1). The pool is the most perennial water feature of the Fortescue Marsh, which acts as a terminal lake for the Upper Fortescue River catchment (31,000 km^2) (Skrzypek et al., 2013). The Pilbara experiences highly episodic large hydrological events with high inter-annual variability, i.e., creeks and rivers are generally dry with seasonal floods commonly occurring during the austral summer