Organic Geochemistry 73 (2014) 29–34

Contents lists available at ScienceDirect

Organic Geochemistry

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

# $^{14}C$ analysis of aliphatic hydrocarbon fractions from the hypersaline Lake Tyrrell, southeast Australia

P. Sargent Bray [a,*], Jochen J. Brocks [b], Simon C. George [a]

[a] Department of Earth and Planetary Sciences, Macquarie University, Sydney, NSW 2109, Australia
[b] Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia

ARTICLE INFO

*Article history:*
Received 18 December 2013
Received in revised form 17 April 2014
Accepted 6 May 2014
Available online 17 May 2014

*Keywords:*
Geochronology
Terrestrial sedimentary organic carbon
Radiocarbon
Aliphatic hydrocarbons
Lake Tyrrell

ABSTRACT

Conventional biomarker studies typically interpret the distribution, structure and stable isotopic (e.g. $^{13}C$, D) composition of sedimentary hydrocarbons and polar compounds. However, compound and compound class specific $^{14}C$ analysis (CSRA) is becoming increasingly relevant for characterising millennial scale residence and mobilisation of sedimentary organic carbon (OC). Here, the $^{14}C$ content of the aliphatic and bulk fractions from shallow cores from the hypersaline playa, Lake Tyrrell, southeast Australia were compared. The aliphatic hydrocarbon fractions (predominantly *n*-alkanes) were substantially older than the corresponding bulk fractions, indicating the presence of active reservoirs of ancient carbon, likely derived from aeolian reworking of sediments. The $^{14}C$ ages of the aliphatic hydrocarbons in the core revealed two noticeable shifts in age and source of ancient OC that were not apparent using biomarker composition and sedimentology alone. The study shows that aliphatic hydrocarbons are relatively simple to isolate, even from organically lean (ca. 0.05% TOC) terrestrial sediments, and their $^{14}C$ ages yield information about carbon mobilisation and preservation not amenable to conventional analysis.



## 1. Introduction

Molecular characterisation and compound specific radiocarbon analysis (CSRA) of source-specific organic matter (OM) provide compelling re-evaluation of important sedimentary and biological processes (Pearson and Eglinton, 2000; Pearson et al., 2001; Raymond and Bauer, 2001; Ohkouchi et al., 2002; Mollenhauer et al., 2003; Smittenberg et al., 2006; Trumbore and Czimczik, 2008; Shah et al., 2008; Trumbore, 2009; Douglas et al., 2010; Birkholz et al., 2011). These studies concentrated largely on marine deposits and the use of CSRA for terrestrial applications should be further explored. The use of radiocarbon to characterise the processes occurring at the millennial scale in soils is becoming increasingly relevant for understanding long term residence and mobilisation of terrestrial sedimentary organic carbon (TSOC; Raymond and Bauer, 2001; Smittenberg et al., 2006; Trumbore, 2009; Battin et al., 2009; Douglas et al., 2010; Birkholz et al., 2011). TSOC flux, particularly in lakes and rivers, is increasingly being recognised as a neglected yet substantial component of the global C cycle (Battin et al., 2009) and recent reports have shown that ancient C can be a significant component (Sanderman et al., 2011; McCallister and Giorgio, 2012). Determining the mobility and availability of ancient TSOC is therefore crucial for evaluating the C reservoir potential of any terrestrial environment. However, TSOC is a complex mixture of young and old C derived from numerous sources. Sophisticated compound specific- and compound class specific-radiocarbon ($^{14}C$) analysis (CSRA) has greatly improved the ability to unravel the provenance of differing fractions of TSOC (Eglinton et al., 1997; Ingalls and Pearson, 2005; Shah et al., 2008) by critically reducing potential sources of OM. TSOC in hypersaline environments is notoriously difficult to characterise, as C is derived from numerous sources and arrives via many pathways. Furthermore, sedimentation is sporadic and may cease altogether, leading to disconformities.

However, hypersaline lakes and playas often represent the sole depocentre for large regions and, as such, are the only depositional record in some arid environments; this makes establishing accurate dates for hypersaline lakes very important in palaeoreconstruction. A $^{14}C$ study of bulk organic extracts from the hypersaline Lake Tyrrell has been reported (Bray et al., 2012); the results are presented in Fig. 2 and Table 1. Briefly, the surficial extracts yielded a modern $^{14}C$ age and progressively increased in age downcore. To test the reliability of these results based on bulk OM, and to determine the possible impact of the presence of ancient remobilized C, we here present and compare the results

* Corresponding author. Present address: Department of Environment and Geography, Macquarie University, Sydney, NSW 2109, Australia. Tel.: +61 02 9850 7981; fax: +61 02 9850 6904.

*E-mail address:* sarge.bray@mq.edu.au (P.S. Bray).

http://dx.doi.org/10.1016/j.orggeochem.2014.05.005
0146-6380/

**Table 1**
Comparison of reported bulk radiocarbon data with aliphatic radiocarbon data. Some sections were combined for TOC analysis.

| Bulk core | | Aliphatic core | | | | | |
|---|---|---|---|---|---|---|---|
| | | ANU | | | | OEP ($C_{27}$–$C_{31}$) | |
| Depth (cm) | $^{14}C$ age (yr) | Sample # | mg C | $^{14}C$ age (yr) | ± | *n*-Alkanes | TOC (%) |
| −1 (mat) | | 17,918 | 0.029 | 2740 | 160 | 3.45 | 0.16 |
| 0 | 0 | 19,817 | 0.06 | 1950 | 100 | 3.42 | |
| 1 | 0 | – | – | No $CO_2$ | – | 1.82 | 0.1 |
| 2 | 0 | 17,920 | 0.086 | 5300 | 70 | 2.15 | |
| 3 | 400 | 17,927 | 0.064 | 18,280 | 370 | 1.19 | |
| 4 | 570 | – | – | No $CO_2$ | – | 3.84 | 0.07 |
| 5 | No $CO_2$ | 19,811 | 0.039 | 13,310 | 320 | 1.38 | |
| 6 | 550 | 19,813 | 0.058 | 16,670 | 340 | 1.21 | 0.04 |
| 7 | 1800 | 19,810 | 0.07 | 14,430 | 220 | 1.41 | |
| 8 | 4550 | 19,807 | 0.054 | 18,790 | 520 | 1.25 | 0.01 |
| 9 | 4120 | 17,917 | 0.031 | 12,500 | 370 | 1.36 | |
| 10 | 6840 | 19,805 | 0.029 | 14,280 | 520 | 1.53 | 0.05 |
| 11 | 6030 | – | – | No $CO_2$ | – | 1.15 | |
| 12 | – | 19,806 | 0.044 | 25,610 | 1420 | 1.2 | 0.06 |
| 13 | – | 19,812 | 0.055 | 33,340 | 3030 | 1.05 | |
| 14 | – | 17,919 | 0.064 | 26,180 | 1030 | 1.19 | |
| 15 | – | 19,814 | 0.072 | 27,810 | 1140 | 1.14 | |
| 16 | – | 17,924 | 0.072 | 27,100 | 1020 | 1.3 | |

of $^{14}C$ analysis of aliphatic hydrocarbons with the reported bulk $^{14}C$ ages from the same locality.

### 1.1. Geological setting

Lake Tyrrell is in the semi-arid Mallee region of northern Victoria, Australia (Fig. 1). Late Miocene to Early Pliocene marine regressions in southern Australia deposited the Parilla Sand Formation, the primary aquifer in the modern lake basin (Macumber, 1992). Plio-Pleistocene uplift dammed the palaeo-Murray River, forming a freshwater mega lake, Lake Bungunnia, over hundreds of thousands of years (Stephenson, 1986). The Parilla Sand is overlain by Lake Bungunnia deposits consisting of the Blanchetown Clay (a regional aquitard) and intermittent deposits of the Bungunnia Limestone in the west of the basin (Mclaren et al., 2009). Lake Bungunnia acted as the catchment for the palaeo-Murray/Darling river system in South Australia during the Pleistocene for ca. 1.8 Ma, before lake water breached the tectonic dam and draining commenced (Stephenson, 1986). Coincident with the draining of Lake Bungunnia was the onset of aridity in southern Australia; the modern semi-arid environment in the region formed over the last 700–400 ka (Stephenson, 1986; Zhisheng et al., 1986). Modern lake sediments are unconformably deposited over the Blanchetown Clay and the expansive dune fields in the Mallee district are reworked aeolian deposits of the Parilla Sand and Blanchetown Clay (Macumber, 1992). Lake Tyrrell sediments consist primarily of sequences of massive and interbedded clays, with precipitated and displacive laminae of gypsum, halite and carbonate, relatively low abundance of other evaporites and some thin lenses of quartz sands. The most recent substantial lake-full condition is estimated to be ca. 30 ka, with a water depth of 13 m, which was followed by episodic drying and partial re-filling (Macumber, 1992). The lake is

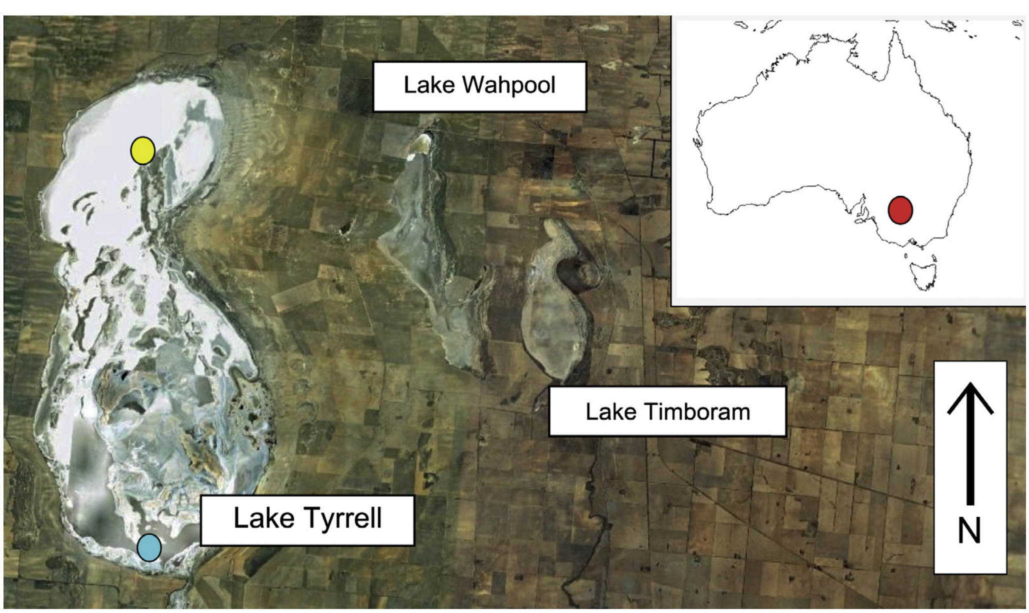


**Fig. 1.** Location of Lake Tyrrell in southeast Australia. Note the two smaller lakes, Wahpool and Timboram, to the east. Lake Tyrrell is ca. 21 km in length north to south. The red dot refers to its location in Australia, the blue dot to the study area. Image courtesy of Google Earth (for interpretation of the references to colour the reader is referred to the web version of the article).