



## Review Article

 $\delta^{13}\text{C}$  of aromatic compounds in sediments, oils and atmospheric emissions: A reviewAlex I. Holman<sup>a</sup>, Kliti Grice<sup>a,\*</sup><sup>a</sup> Western Australia Organic and Isotope Geochemistry Centre, The Institute for Geoscience Research, School of Earth and Planetary Sciences, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

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## ABSTRACT

This review discusses major applications of stable carbon isotopic measurements of aromatic compounds, along with some specific technical aspects including purification of aromatic fractions for baseline separation.  $\delta^{13}\text{C}$  measurements of organic matter (OM) in sediments and oils are routine in all fields of organic geochemistry, but they are predominantly done on saturated compounds. Aromatic compounds are important contributors to sedimentary organic matter, and provide indication of diagenetic processes, OM source, and thermal maturity. Studies have found evidence for a small  $^{13}\text{C}$ -enrichment during diagenetic aromatisation of approximately 1–2‰, but the formation of polycyclic aromatic hydrocarbons (PAHs) from combustion and hydrothermal processes seems to produce no effect. Likewise, maturation and biodegradation also produce only small isotopic effects. An early application of  $\delta^{13}\text{C}$  of aromatic compounds was in the classification of oil families by source. Bulk measurements have had some success in differentiating marine and terrigenous oils, but were not accurate in all settings.

Compound-specific analyses measure certain aromatics with strong links to source, therefore allowing more accurate source identification.  $\delta^{13}\text{C}$  measurements of individual aromatic compounds also allow identification of higher plant input in ancient sediments, even after severe diagenetic alteration or combustion to PAHs. Perylene, a PAH with a historically contentious origin, was assigned a source from wood-degrading fungi on the basis of its isotopic composition. Stable carbon isotopic measurements are also important in the analysis of organic matter from Chlorobiaceae, which is an important indicator of photic zone euxinic conditions in ancient sediments. A large range of aromatic products are formed from the carotenoid pigments of Chlorobiaceae, with an enriched carbon isotopic composition characteristic of the reverse tricarboxylic acid photosynthetic pathway employed by this family of organisms. In future, site-specific isotope analysis using techniques such as nuclear magnetic resonance spectrometry and high-resolution isotope ratio mass spectrometry may reveal more information about isotopic effects associated with aromatisation processes and maturation.

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## 1. Introduction and technical aspects

Stable carbon isotopic measurements have historically been of great importance in the analysis of organic matter (OM) in oils and sediments. Early measurements of bulk isotopic composition were applied to petroleum exploration (Sofer, 1984) and palaeoenvironmental studies (Schidlowski, 1988). The development of compound-specific isotope analysis (CSIA) revealed that sedimentary OM contains a wide range of source inputs and isotopic compositions (Freeman et al., 1990; Grice and Brocks, 2011). Compound-specific  $\delta^{13}\text{C}$  measurements are now routinely

employed in all aspects of organic geochemistry such as paleo- and modern environmental studies (e.g. Grice et al., 1996b; Diefendorf and Freimuth, 2017), and petroleum exploration (Edwards and Zumberge, 2005; Pedentchouk and Turich, 2018). The majority of studies focus only on saturated compounds, likely due to their generally greater abundance in sediments and oils and their relative ease of sample preparation. Aromatic compounds however are also important constituents of sedimentary OM. They are not biosynthesised in significant quantities by organisms, but are formed from natural precursors by processes including diagenetic alteration, natural combustion processes and anthropogenic emissions (e.g. Wakeham et al., 1980a, b; Venkatesan and Dahl, 1989; Grice et al., 2007). Therefore, the carbon isotopic composition of aromatic compounds has the potential to reveal valuable

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information about these processes. Despite some analytical challenges, such as generally low abundance in sediments and difficulties achieving baseline separation of peaks,  $\delta^{13}\text{C}$  measurements of aromatic compounds have been employed in oil family classifications and oil-source correlations, source assignment of modern and ancient OM, and palaeoenvironmental studies (see Table 1).

In this review, we summarise the range of applications for compound-specific carbon isotope measurements of aromatic compounds in sediments and oils. A review of the carbon isotope geochemistry of polycyclic aromatic hydrocarbons (PAHs) in aquatic environments is included in Abrajano et al. (2014). For detailed discussion of the technical elements of  $\delta^{13}\text{C}$  measurement, readers are directed to a number of comprehensive reviews, e.g. Sessions (2006), De Groot (2009) and Hoefs (2015), and references therein. Buczyńska et al. (2013) presents a review of analytical methodologies for CSIA of PAHs. Certain aspects related to aromatic compounds in general are discussed below.

### 1.1. Separation of aromatic compounds

Baseline separation of analyte peaks is a strict requirement of CSIA in order to achieve reliable isotope measurements (Ricci et al., 1994; Sessions, 2006). Separation of oils and source rock extracts into saturated and aromatic fractions by silica gel column chromatography (e.g. Bastow et al., 2007) is standard procedure before gas chromatography – mass spectrometry (GC–MS) and

gas chromatography – isotope ratio mass spectrometry (GC–irMS) analysis, but significant co-elution often remains in aromatic fractions (e.g. Budzinski et al., 1995; van Aarssen et al., 1999; Cesar and Grice, 2017). In such cases additional separation steps are required to achieve baseline separation. Techniques to isolate specific sections of the chromatogram include thin-layer chromatography (van Kaam-Peters et al., 1995; Grice et al., 1998a, 2005a), preparative high-performance liquid chromatography (Killops and Readman, 1985) and preparative GC (Summons and Powell, 1987). In addition, alumina column chromatography has been employed to separate aromatic fractions by number of aromatic rings (Summons and Powell, 1987; Jiang et al., 2013).

### 1.2. Aromatic VOCs

Volatile organic compounds (VOCs) are ubiquitous in the atmosphere, and are produced by both natural and anthropogenic processes (Kansal, 2009). Due to the structural simplicity of these compounds, source attribution requires the use of stable isotope measurements. Vitzthum von Eckstaedt developed a method for  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  analysis of atmospheric VOCs based on adsorption on TenaxTA resin in sampling tubes, followed by thermal desorption of analyte gasses into the inlet of a GC–irMS system via a cold trap (Vitzthum von Eckstaedt et al., 2011a). Aromatic compounds that were analysed include benzene, toluene, xylenes, ethylbenzene, styrene and naphthalene. Cross plots of  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$

**Table 1**  
Summary of  $\delta^{13}\text{C}$  values of aromatic compounds from studies discussed in the text.

Compounds	Setting	$\delta^{13}\text{C}$ (‰ VPDB)	Reference
<i>Petroleum</i>			
Bulk aromatics	Waxy oils	–31.2 to –21.8	Sofer (1984)
Bulk aromatics	Non-waxy oils	–31.0 to –16.8	Sofer (1984)
Bulk aromatics	Phanerozoic oils	–28.59 to –26.30	Andrusevich et al. (1998)
Alkylated PAHs	West Australian crude oils	–30.3 to –23.5	Maslen et al. (2011)
Alkylated PAHs	West Australian crude oils	–33.3 to –21.3	Le Métayer et al. (2014)
PAHs	Carnarvon Basin source rocks	–31.2 to –23.1	Cesar and Grice (2017)
<i>Higher plant sources</i>			
Aromatised gymnosperm and angiosperm markers	Torbanites	–25.5 to –23.0	Grice et al. (2001)
Aromatised gymnosperm and angiosperm markers	Central Arctic Ocean PETM sediments	–33 to –25	Schouten et al. (2007)
Aromatised gymnosperm and angiosperm markers	Eocene Messel Shale	–33.2 to –23.3	Freeman et al. (1994)
Aromatised gymnosperm and angiosperm markers	Tertiary brown coal	–29	Schoell et al. (1994)
Combustion PAHs	C <sub>3</sub> plants	–28.8 to –28.0	O'Malley et al. (1997)
Combustion PAHs	C <sub>4</sub> plants	–17.1 to –15.8	O'Malley et al. (1997)
Combustion PAHs	Perth Basin Permian sediments	–24.7 to –29.9	Grice et al. (2007)
Retene	Fluvial / deltaic Triassic-Jurassic sediments	–26.9 to –24.9	Grice et al. (2005a)
<i>Cyanobacterial/algal sources</i>			
Benzohopanes	Torbanites	–30.6 to –27.9	Grice et al. (2001)
Diagenetic PAHs	Perth Basin Jurassic sediments	–30.0 to –33.3	Grice et al. (2007)
Benzohopanes	Permian Kupferschiefer	–30 to –29.6	Grice et al. (1996b)
Tricyclic aromatics	Tasmanite oil shale, Tasmania	–9 to –6	Revill et al. (1994)
<i>Fungal sources</i>			
Perylene	Saanich Inlet, British Columbia	–27.7 to –23.6	Silliman et al. (2000)
Perylene	Quinpu trench, China	–26.5 to –27.5	Grice et al. (2009)
Perylene	Late Cretaceous to Paleogene terrigenous sediments	–24.5 to –21.1	Suzuki et al. (2010)
<i>Chlorobiaceae</i>			
Isorenieratane	Upper Devonian Duvernay Formation	–13.2 to –5.7	Hartgers et al. (1994b)
Isorenieratane	Permian Kupferschiefer	–16.4 to –13.4	Grice et al. (1996b, 1997)
Isorenieratane	Jiangnan Basin, China	–17.3 to –16.1	Grice et al. (1998b)
Isorenieratane	Holocene Black Sea	–17.4 to –14.8	Sinninghe Damsté et al. (1993)
Isorenieratane	West African Lower Cretaceous source rocks	–14.5	Pedentchouk et al. (2004)
Aryl isoprenoids	Silurian and Devonian Canadian oils	–24.74 to –21.61	Summons and Powell (1986)
Aryl isoprenoids	Upper Devonian Duvernay Formation	–17.7 to –5.9	Hartgers et al. (1994b)
Aryl isoprenoids	Late Devonian Canning Basin	–21 to –17	Tulipani et al. (2015)
Aryl isoprenoids	Permian Kupferschiefer	–20.4 to –15.6	Grice et al. (1996b, 1997)
Isorenieratane derivatives	Ordovician to Miocene sediments	–19.0 to –16.3	Sinninghe Damsté et al. (1995a)
Tetramethylbenzenes	Upper Devonian Duvernay Formation	–19.4 to –17.5	Hartgers et al. (1994b)
Alkylbenzenes	West African Lower Cretaceous source rocks	–22.8 to –19.3	Pedentchouk et al. (2004)
C <sub>19</sub> alkyl biphenyl	Permian / Triassic Spitsbergen sediments	–17 to –9	Nabbefeld et al. (2010b)
methyl <i>n</i> -propyl and methyl isobutyl maleimides	Permian Kupferschiefer	–18.1 to –16.7	Grice et al. (1996a)

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