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The composition and radiolysis impact on aromatic hydrocarbons in sedimentary organic matter from the Mulga Rock (Australia) uranium deposit

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ABSTRACT

Our interest in the effect of ionizing radiation on sedimentary organic matter (OM) has extended to the molecular distributions and stable isotopic values of aromatic hydrocarbons. Thermally immature sediments (%Ro = 0.26; Tmax < 421 °C) spanning a 173–5280 ppm radiolytic gradient from the Mulga Rock Uranium Deposit (Western Australia) contained high abundances of vascular plant sourced aromatic (and aliphatic) terpenoids. Terpenoids with 2–5 rings and various levels of aromatisation were detected in the aromatic fractions of these sediments. The extent of aromatisation increased with sedimentary U/radiolytic levels, attributed to free-radical promoted reactions including dehydrogenation and oxidation of aliphatic precursors. The sediment with the highest U content (5280 ppm) showed only diterpenoids and low MW PAHs, reflecting complete radiolytic removal of higher MW terpenoids. A larger number and variety of terpenoid products were detected from the other sediments (U ≤ 1700 ppm) from which several radiolytically promoted reaction pathways were identified. Cadinene, for instance, was subject to competing hydrogenation and dehydrogenation reactions which gave cadinane and progressively aromatised diterpenoid analogues, respectively. Pentacyclic terpane precursors were also progressively aromatised and partially converted to des-A-triterpenoid or C-ring cleaved triterpenoid (tetracyclic) products. These reactions are typical of the natural diagenetic transformation of plant terpenoids, with the main effect of the high radiolytic levels an apparent hastening of diagenetic processes. The $\delta^{13}\text{C}$ values of several aromatised products indicated a slight ^{13}C enrichment with increasing

aromatisation, likely due to preferential abstraction of H from ^{12}C .

Keywords: Ambassador prospect; plant terpenoids; radiation; diagenesis; organic geochemistry; stable carbon isotopes

1. Introduction

Many uranium deposits contain high amounts of sedimentary organic matter (OM). The OM may be an important reductant of U species or play some other useful role in the formation of U deposits (Nakashima et al., 1984; 1999). Radioactive elements, however, can also significantly alter organic matter composition with some commonly reported changes including an increase in polymerisation and aromatization with less alkyl groups leading to lower H/C, higher O/C and less extractable OM (Bovey, 1958; Zumberge et al., 1978; Landais et al., 1987; 1988; 1990; Landais, 1996; Leventhal et al., 1987; Dahl et al., 1988; Forbes et al., 1988; Lewan et al., 1991; Mossman et al., 1993; Kr̥bek et al., 1999; Tuo et al., 2007). Specific reaction and structural rearrangement of hydrocarbons attributed to radiolysis include: (1) an impedance of the hydrogenated production of aliphatic C–H bonds and C–OH groups (Landais, 1996); (2) increased cleavage of aliphatic substituents (Forbes et al., 1988) or cracking of aliphatic chains (Dahl et al., 1988; Jaraula et al., 2015); (3) greater oxidative degradation of OM leading to an increase in oxygenated functional groups and higher O/C ratios (Kr̥bek et al., 1999); and (4) a general

increase in complexation and redox reactions (Spirakis, 1996; Court et al., 2006; Douglas et al., 2011; Jaraula et al., 2015). A ^{13}C enrichment of OM exposed to radiation has also been measured and attributed to the higher stability of the heavier isotope to polymerisation (Leventhal and Threlkeld, 1978; Court et al., 2006).

Jaraula et al (2015) recently reported several changes in the aliphatic hydrocarbon and ketone composition of Mulga Rock sediments from the Ambassador U deposit (Kalgoorlie, Western Australia) attributed to radiation from high U levels of up to ~5000 ppm. The most notable changes were a reduction in aliphatic chain lengths and the loss of the biochemically inherited carbon preference indices, both due to radiolytic cracking. Alky ketones were also produced in high abundance by the reaction of aliphatics with $\text{OH}^\cdot$ radicals (from radiolysis of water) with alkan-2-ones particularly prominent due to the impedance of isomerisation at high uranium (and concomitant sulfur) concentrations. These molecular trends were evident where traditional geological indicators of radiation were not – e.g., pleochroic haloes such as the formation of metamict from the alpha particle destruction of crystal lattice structures (Leventhal et al., 1987) – identifying the organic geochemistry of the sediments as very sensitive to low levels or short durations of radiation (Jaraula et al., 2015). Uranium emplacement at the Ambassador deposit may have been as recent as several thousand years ago (Douglas et al., 2011).

Here we have investigated the impacts of radiolysis on the distribution and stable isotopic values of aromatic hydrocarbons in the Mulga Rock sediments. Whilst the impacts of radiolysis on aliphatic hydrocarbons has attracted some attention,

including our previous analyses of the saturate hydrocarbon and ketone fractions of the current Mulga Rock sample suite (Jaraula et al., 2015), few studies have investigated the radiolytic induced reactions and fate of aromatic hydrocarbons. Studies of the U-rich (≤ 250 ppm) Alum Shales of Sweden (Dahl et al., 1988; Lewan and Buchardt, 1989) did report a decrease in the alkyl substituents of triaromatic steroids suggested to be due to either lower alkylation (Dahl et al., 1988) or polymerization of larger alkyl-moieties (Lewan and Buchardt, 1989).

The Mulga Rock sediments contain high concentrations of plant-derived aromatic (and aliphatic) terpenoids well preserved at the low thermal maturity levels of the sedimentary deposit ($\%Ro = 0.26$; $T_{max} < 421$ °C). Functionalised plant terpenoids represent a very large and important group of natural products, and the sedimentary detection of related products provides valuable source diagnostic information. Plants and their exudates comprise a multitude of different terpenoid biochemicals, resolved into many different structural classes (e.g., see Anderson et al., 1992 for classification of resin terpenoids), which following deposition can be diagenetically or catagenetically transformed into an even larger range of structural variants. Numerous polycyclic terpenes have been reported from organic geochemical studies of organic sediments, woods and fossil fuels (e.g., Irie et al., 1964; Gallegos, 1981; Simoneit, 1985; Simoneit et al., 1986; 2003; Noble et al., 1986; Alexander et al., 1994; Singh et al., 1994; Murray et al., 1997; Dutta et al., 2011; Mallick et al., 2014). Radiolysis represents another secondary influence which might also contribute to the alteration of plant terpenoids following their deposition, and a greater understanding of the

reaction pathways and controls of this process will improve organic geochemical appraisals of OM exposed to high radiative levels and the veracity of their biomarker value when detected under such circumstances. Furthermore, a deeper understanding of the consistent impacts natural radiation has on the sedimentary composition of terpenoids (and other cyclic hydrocarbons) might prove practically useful for helping locate U-rich deposits of commercial value.

2. Experimental

2.1. Mulga Rock samples

Sediment samples were collected from mineralized layers of the Ambassador prospect (Mulga Rock deposit, WA), containing uranium (< 5300 ppm) finely interspersed in the attrinite matrix and enriched within liptinitic phytoclasts (mainly sporinite and liptodetrinite). A detailed description of the geological setting of the Mulga Rock uranium district in the Narnoo Basin as well as lithological details and maceral petrographical analysis are given in Jaraula et al (2015). In brief, the Mulga Rock was deposited in a spatially extensive terrestrial-bound marsh, situated on a stable basement with a low incline, far removed from marine influences (Douglas et al., 2011). Uranium species were precipitated syngenetically with OM as it was deposited during a humid phase in the Late Eocene. The uranium occurs as diffuse and non-uniform impregnations in ion-exchangeable forms within the organic matrix. The syngenetic mineralisation in Mulga Rock was believed to involve the adsorption of urano-organic complexes concentrated by epigenetic supergene processes.

Ultrafine grained minerals identified by SEM analysis included coffinite

[U(SiO₄)_{1-x}(OH)_{4x}] and uraninite [UO₂] plus unidentified sulfides that were associated with high uranium concentrations (Douglas et al., 2011).

Organic geochemical analyses were conducted on five samples (MR-49 to MR-53) from a 53–58.5 m section of Ambassador Uranium prospect drill core 5766 (Jaraula et al., 2015). The selected samples span a uranium concentration gradient of 642 to 5280 ppm. General geochemical data of the samples is given in Table 1, whilst detailed lithological and stratigraphic information on the core can be found in Jaraula et al. (2015). They were generally rich in OM, with TOC's ranging from 13% to 22%. A mean random reflectance (%Ro) value of 0.26 from pseudo vitrinite macerals indicated low thermal maturity OM.

2.2. Sample preparation and GC–MS analysis

The solvent-extractable bitumen fraction of the Mulga Rock sediments was obtained by ultrasonication in DCM and subsequently separated into polarity-based fractions by column chromatography as described in Jaraula et al. (2015). The aromatic (and saturate) hydrocarbon fractions were used for GC–MS analysis. An aliquot of the aromatic fraction of MR-50 was further separated into monoaromatic, diaromatic and triaromatic sub-fractions on an alumina column (5.5 cm × 0.5 cm i.d.) using 4 mL solvent mixtures of 99:1 (v/v) *n*-hexane:dichloromethane (DCM), 9:1 (v/v) *n*-hexane:DCM, and DCM, respectively which were used for compound specific stable isotope analysis.

GC–MS analyses of the aromatic fractions were carried out using an Agilent 6890 gas chromatograph interfaced to a 5973 Mass Selective Detector. A J&W Scientific

DB-5MS column (60 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m film thickness) was used with helium carrier gas (1 mL/min) and the GC oven temperature was ramped from 40 $^{\circ}$ C at 3 $^{\circ}$ C/min to 310 $^{\circ}$ C, which was held for final 30 min. Electron impact (70 eV) mass spectra were acquired over a scan range of m/z 50–550. The assignment of aromatic terpenoid products was largely based on published GC and MS data (Wakeham et al., 1980; Chaffee and Johns 1983; Wolff et al., 1989; Trendel et al., 1989; Wang, 1990; Hauke et al., 1992; ten Haven et al., 1992; Freeman et al., 1994; Tuo and Philp, 2005; Mallick et al., 2014), although some product assignments were inferred on the basis of their mass spectral similarity to known isomers or other structurally related compounds.

2.3. CSIA analysis

Stable carbon isotope ratios ($\delta^{13}\text{C}$) for several of the more abundant aromatic terpenoids were measured by gas chromatography–isotope ratio mass spectrometric (GC–irMS) analysis of the aromatic sub-fractions of MR-50. These measurements were conducted with a Thermo Scientific Trace GC Ultra interfaced to a Thermo Scientific Delta V Advantage mass spectrometer via a GC isolink and a Conflow IV using relatively standard operating conditions (Mirasol-Robert et al., 2017). The GC oven was held at 40 $^{\circ}$ C for 1 min, increased to 325 $^{\circ}$ C at 3 $^{\circ}$ C/min, then held isothermally for 30 min. A DB-5MS GC column (60 m $\times$ 0.25 mm i.d. $\times$ 0.25 μ m film thickness) was used with helium as the carrier gas at a constant flow rate of 1.5 mL/min. Average $\delta^{13}\text{C}$ values (‰ relative to the V-PDB reference standard) of at least

two analyses and with a standard deviation of less than 0.4‰ are reported for all samples.

3. Results and discussion

3.1. Aromatic terpenoid composition of Mulga Rock sediments

The aromatic terpenoid distributions of MR49 (5280 ppm) and MR51 (1161ppm) from GC–MS analysis of their aromatic fractions are shown in Fig. 1. The major products were polycyclic terpenoids with 2–5 rings, some of which were aromatic. A list of the major aromatic terpenoid products detected in one or more of the MR sediments is given in Table 2. They were assigned by mass spectral correlation (4 point mass spectra included in Table 2). Several distinctive structural groups (**I–IX**; see Appendix) were evident, including known biochemical indicators of angiosperm or other higher plant sources (e.g., cadinene (**Ia**), β -amyrin; note that both were detected in the saturate fraction of MR sediments) and their partially and fully aromatised diagenetic products (e.g., 2,9-dimethyl-picene, **VIII**). Not all of the GC–MS detected analytes could be unequivocally identified, but likely include many additional terpenoids.

MR51 contained a particularly large number and diversity of terpenoid products. The TIC of MR51 (Fig. 1B) showed a bimodal distribution of sesquiterpenoids (e.g., cadilanes) and pentacyclic triterpenoids (e.g., oleanane, ursane). Other lower concentration tri- and tetra-cyclic terpenoid products were highlighted by the selected ion chromatograms shown in Fig. 1C–F. Similarly expansive distributions of di-, tri-,

tetra- and penta-cyclic terpenoids were detected from all sediments with $U \leq 1161$ ppm (i.e., MR50-53)

The only terpenoid products of U-rich MR49 (5280 ppm) were the lower MW dicyclic diterpenoids, reflecting complete radiolytic removal or alteration of higher MW terpenoids. MR49 also had a high abundance of alkylnaphthalenes and alkylphenanthrenes. These PAHs can derive from plant terpenoids at a late stage of sediment diagenesis and abundant alkylnaphthalenes are also common in mature OM where they are often attributed to the thermal alteration of plant or other biological derived terpenoids (Ishiwatari and Fukushima, 1979; Püttmann and Villar, 1987; Strachan et al., 1988). The specific origin of alkylated phenanthrenes in sedimentary OM or fossil fuels is less clear with several potential structural precursors including triterpenoids, hopanoids and steroids (Greiner et al., 1976; Budzinski et al., 1995; Mackenzie et al., 1982). The alkyl phenanthrenes detected in the MR sediments likely derive from plant terpenoids which were detected in high concentrations.

3.1.1. Dicyclic sesquiterpenoids

Four diterpenoids with a basic cadinene structure and one or two aromatic rings (**I**d–g) were prominent in the TIC of MR51 (Fig. 1B). Cadilene (**I**b) and cadilane (**I**a) were both detected in the saturate fraction of the MR sediments (data not reported in Jaraula et al., 2015). The monoaromatic dihydrocurcumene (**I**c) is structurally related to cadinene and has previously been identified in Indian resins rich in cadinene-based sesquiterpenoids (Mallick et al., 2014). Cadinenes are very abundant in resins and

essential oils of plants (Singh et al., 1994; Mallick et al., 2014) and have been classified as Type II resins associated with angiosperm sources (Anderson et al., 1992; Murray et al., 1994). These sesquiterpenoid compounds have also been detected in oils and sediments, often as more geologically mature cadinanes, where they generally imply land plant input (Radke et al., 1990; Alexander et al., 1994).

The cadinene structures detected in the MR sediments reflected various degrees of aromatisation, indicating the co-occurrence of many products of cadinol, the biochemical precursor of these compounds. Based on the sedimentary detection of a range of cadinane products, Simoneit et al. (1986) proposed a reaction scheme for the diagenetic aromatisation of cadinols and cadinenes to alkyl-naphthalenes which were detected in high abundance in MR49 (Fig. 1A). Based on the large representation of cadalene products in the MR sediments (Fig. 1; Table 2) this scheme can be extended further (Fig. 2) to reflect the participation of cadinene (**Ib**) in coincident reaction pathways including: (1) dehydrogenation to produce the alkyl-naphthalenes via a range of intermediate products of varying aromaticity; and (2) hydrogenation to produce saturated cadinane (**Ia**). Cadinane was not detected in the fossilized samples analysed by Simoneit et al (1986) but they did speculate it might be encountered in more thermally mature sediments.

The aromatisation scheme of the sesquiterpenoids shown in Fig. 2 is supported by the $\delta^{13}\text{C}$ values measured for several cadinane products which suggested a slight decline in ^{13}C value with increasing aromatisation. The $\delta^{13}\text{C}$ values of non-aromatic cadinene (-23.8‰) and fully aromatised cadilene (-25.3‰) showed a small

difference of -1.5% . This likely reflects the preferential abstraction of H's from ^{12}C ; i.e., the $^{12}\text{C}-\text{H}$ bond is easier to break than higher energy $^{13}\text{C}-\text{H}$ leading to more $^{12}\text{C}-^{12}\text{C}$ double bonds and aromatic products with depleted carbon isotope values. The $\delta^{13}\text{C}$ values of aromatic triterpenoids from microbially mediated diagenesis of an organic rich shale were reported to similarly decrease by about 1.2% compared to their saturated precursor hydrocarbons (Freeman et al., 1994). The PAH 1,6-dimethyl-naphthalene which was abundant in MR49 and a likely end-product of cadinane diagenesis, had a $\delta^{13}\text{C}$ value of -24.7% which was close to that of cadilene (-25.3%) suggesting negligible $\delta^{13}\text{C}$ fractionation with demethylation.

3.1.2. Tri-, tetra and pentacyclic terpenoids

The aromatic content of the MR sediments also included relatively large distributions of tri-, tetra- and pentacyclic terpenoids, with products of all these groups showing different degrees of aromatisation and structural alteration (e.g., rupture of rings). The different sized cyclic groups are separately highlighted by the selected ion chromatograms of MR51 shown in Fig. 1C–F.

Five tricyclic diterpenoid products were assigned: dehydroabietane (**IIa**), simonellite (**IIb**), diaromatic tricyclic totarane (**IIc**), diaromatic tricyclic sempervirane (**IId**) and retene (**IIe**). Retene and simonellite are aromatic products which derive from compounds found in conifers and have been detected in a number of mature sediments, source rocks and oils (Simoneit, 1985; van Aarssen et al., 2000; Otto and Simoneit, 2001; Otto and Wilde, 2001). With increasing maturity these compounds,

like the sesquiterpenoids, can evolve into simpler and more common aromatic hydrocarbons such as alkyl-naphthalenes and alkylphenanthrenes (Simoneit, 1985; Dzou et al, 1999).

Several tetracyclic products arise from ring alterations of pentacyclic precursors. These include des-A triterpenoids (**III**) produced by the loss of the A-ring; and C-ring cleaved triterpenoids (**IV**, also known as seco-triterpenoids) where the C-ring opens at the 8(14) bond of the pentacyclic structure of angiosperm triterpenoids with C-3 oxygenated functionality (e.g., amyrin, friedelin, lupenone, taraxerone; Chaffee and Johns, 1983; Simoneit et al., 1986; Murray et al., 1997). This reaction can be photochemically initiated or acid-catalysed (Chaffee et al., 1984) and their occurrence in MR sediments with U > 600 ppm suggests they might also be promoted by radiative elements. Both of the des-A (**III**) and C-ring cleaved (Fig. 1D) triterpenoid products of MR included a range of different aromatic levels (i.e., 1–3 aromatic rings). Polycyclic plant biomarkers may undergo aromatization processes during diagenesis or with increasing thermal maturity, and co-incident ring cleavage should produce smaller ringed products with the same range of aromatic moieties. C-ring cleaved triterpenoids are a major intermediate in the production of alkyl-naphthalenes from biogenic triterpenoids such as β -amyrin (Püttmann and Villar, 1987). This close structural relationship was also reflected by the similar $\delta^{13}\text{C}$ values of des-A- (–26.9‰ to –24.3‰; Table 2), C-ring cleaved- (–26.0‰ to –25.5‰) and pentacyclic-triterpenoids (–27.5‰ to –24.3‰).

The pentacyclic triterpenoids detected in the MR sediments also showed a range

in structural aromaticity (1–5 aromatic rings). Many of the aromatic triterpenoids had oleanane (e.g., **VIa**), lupane (e.g., **VIb**, **VIIb**) or ursane (e.g., **VIIc**, **VIIId**) type structures which all share an angiosperm plant origin (Moldowan et al., 1994; Rullkötter et al., 1994; van Aarssen et al., 2000; Simoneit et al., 2003), specifically deriving from natural product precursors α -amyrin and β -amyrin (Simoneit et al., 2003; Peters et al., 2005; Bouvier et al., 2005) which were both present in the ketone fractions of the Mulga Rock sediments (data not shown in Jaraula et al., 2015).

Aromatisation can be initiated by the reduction of the C-3 functional groups on the A-ring of saturated terpenoids, followed by progressive aromatisation of rings A to E. Various aromatisation and ring alteration reaction pathways have been proposed for the diagenetic alteration of angiosperm triterpenoids (e.g., Chafee and Johns, 1983; Tuo and Philp, 2005; Mallick et al., 2014) and in Fig. 3 we provide a scheme relating to the transformation of α -amyrin into many of the aromatised triterpenoids detected in the Mulga Rock sediments.

$\delta^{13}\text{C}$ values were measured for several triterpenoid products reflecting different stages of ring aromatisation and these showed a general trend of lower values (i.e., greater ^{13}C depletion) with increasing aromatisation. For instance, the plant biomarker α -amyrin had a $\delta^{13}\text{C}$ of -24.3‰ (β -amyrin = -25.0‰) and a similar $\delta^{13}\text{C}$ value was measured for the A-Ring mono-aromatic product (**V**, -24.7‰) shown in the pentacyclic aromatization pathway of Fig 3a, but the $\delta^{13}\text{C}$ values of the tri- (**VIb**, -25.8‰), tetra- (**VIIc**, -27.1‰) and penta-aromatic (**VIII**, -27.6‰) products reflect progressive ^{13}C depletion with the $\delta^{13}\text{C}$ value of the fully aromatised product $\sim 3\text{‰}$

lower than non-aromatic α -amyrin. This mirrored the trend of declining $\delta^{13}\text{C}$ values observed with diterpenoid aromatisation (Fig 2) attributed to abstraction of H from ^{12}C in preference to ^{13}C .

3.2. Radiolytic alteration of aromatic terpenoid composition

Radiolytic effects can significantly alter organic matter composition and a greater understanding of the reaction pathways and controls on this type of alteration may help to: (1) more fully appreciate the robustness (or secondary influences) of traditional organic geochemical parameters based on aromatic hydrocarbon abundances (e.g., the triaromatic steroid thermal maturity index); (2) identify organic molecular parameters useful for locating U-rich sediments; and (3) establish the importance of OM to the formation of U-deposits – carbonaceous substances including sedimentary organic matter may reduce and fix soluble U(VI) under diagenetic or hydrothermal conditions to form insoluble U(IV) minerals (i.e., uraninite).

The total aromatic terpenoid signal and their ring size distribution as a proportion of the total TIC signal of each MR sediment is shown in Fig. 4. The abundance of the aromatic terpenoid products, particularly of the larger ringed structures, decreased with higher U content. Expansive distributions of 2–5 ringed terpenoids displaying varied degrees of aromatization were detected for each of MR50-53 (< 1700 ppm), whereas only diterpenoids (at just 24% of the total TIC signal) and low MW PAHs were detected in MR49 (5280 ppm U) reflecting complete removal of higher MW

terpenoids at this high U level. Given the similar burial and thermal history of the MR49-54 sediments (Jaraula et al., 2015) these changes can be reliably attributed to the impacts of U radiolysis.

The high abundances of aromatic hydrocarbons (e.g., alkylated phenanthrenes and naphthalenes) in MR49 reflects the complete aromatisation of saturated and intermediate terpenoid precursors at high uranium radiation levels. The reaction pathways contributing the aromatic terpenoids compete with other diagenetic reactions including hydrogenation reactions producing saturated products (e.g., tricyclic terpanes fichtelite, 19-*nor*isopimarane, 19-*nor*labdane; Laflamme and Hites, 1978; Otto and Simoneit, 2001). The equilibrium and rates of these reactions can be influenced by a range of impacts known to include microbial and abiotic (e.g., clay catalysis) processes (Laflamme and Hites, 1978; Otto and Simoneit, 2001) and the present results indicate radiolysis can also have an influence.

The relative abundance of the dicyclic aromatic terpenoids (i.e., sesquiterpenoids) steadily increased with U at concentrations < 1700 ppm (MR50-53; Fig. 5), and these were the only terpenoids detected in the U-rich MR49 (Fig. 4). The corresponding abundance profiles of cadinene (**Ia**) and cadinane (**Ib**) across the 643–1700 ppm U gradient are also separately depicted in Fig. 5. These two products show contrasting trends with the abundances of cadinene (**Ia**) declining and cadinane (**Ib**) increasing with higher U consistent with competing hydrogenation (producing cadinane) and dehydrogenation (cadinene and other aromatics contributing to total dicyclic aromatic terpenoids) reaction pathways as shown in the cadilene diagenetic reaction scheme

(Fig. 2).

The aromatisation pathway to the right of the diagenetic scheme in Fig. 2 is similar to a sesquiterpenoid aromatization scheme previously proposed by Simoneit et al. (2006) and Freeman et al. (1994). Freeman et al. (1994) also reported a small ^{13}C depletion ($\delta^{13}\text{C}$ change of approx. -1‰) in aromatic terpenoids from low thermal maturity Messel shales reflecting a similar aromatic progression to that observed in the MR sediments. The MR aromatic terpenoids also reflected a $\delta^{13}\text{C}$ change of approx. -1‰ (Fig. 2). This $\delta^{13}\text{C}$ change is similar to aromatisation in the Messel shales with no history of ionizing radiation and thus provides no evidence that U species (like highly oxidizing UO_2^{2+}) have any significant carbon isotope fractionation effect.

The exclusivity of dicyclic sesquiterpenoids in MR49 is probably due to the radiolytically catalyzed diagenetic degradation of larger ringed systems, and possibly also the aromatization of aliphatic precursors. A previous study of modern and fossil resins reported sesquiterpenoids to be more vulnerable to diagenetic transformation than the larger, structurally more stable triterpenoids (Mallick et al., 2014). The opposite effect here is likely the result of ionizing radiation disrupting the equilibria of competing diagenetic processes.

The abundances of all pentacyclic products and separately the des A-ring and C-ring cleaved groups across the 642–1700 ppm (MR50-53) U gradient are shown in Fig. 6. The abundance and distributions of the triterpenoids are clearly influenced by ionizing radiation at these U levels with total pentacyclic signal decreasing with U

and the triaromatic C ring-cleaved and des-A ring terpenoid groups both increasing in their relative abundances. Photochemical process and acid catalysis had previously been reported to initiate C-ring cleavage (Chaffee et al., 1984) and radiolysis may have a similar effect. Mechanistically this could involve polarity effects from electrophilic U-oxides (e.g., UO_2^{2+}) reducing the activation energy required to rupture the C–C bonds of cyclic or substituted hydrocarbon structural moieties.

4. Conclusions

The U in Mulga Rock sediments contributed to an increase in the aromatic content of a reduced extractable/bitumen fraction. At the molecular level this was reflected by transformation of plant terpenoids into smaller and increasingly more aromatic structural analogues. These products included cadilane-based diterpenoids from angiosperm plants and tricyclic terpenoids (e.g., retene, simonellite) diagnostic of conifer inputs. Many were intermediates in the diagenetic transformation of plant terpenoids via dehydrogenation/aromatisation reactions and C-ring or functional group cleavage. The main mechanistic effect of U on the terpenoid composition of the MR sediments was to hasten these diagenetic pathways, possibly due to free-radical interference induced by strongly oxidizing U species (e.g., UO_2^{2+}). The lack of any additional structural alteration of the biologically derived terpenoids confirms their biomarker value in sediments with contact to radiative elements. However, towards end diagenesis the terpenoids had been converted into simple PAHs (e.g., alkylated naphthalenes and phenanthrenes) which were particularly abundant in MR-49 with the

highest U content. Such basic aromatic structures can derive from a multitude of sources and so carry minimal biomarker information.

The diagenetic transformation of unsaturated terpenoid precursors to PAHs via varyingly aromatised intermediates showed small $\delta^{13}\text{C}$ fractionations; i.e., $\sim -1\text{‰}$ for dicyclic structures and $\sim -3\text{‰}$ for pentacyclic compounds. This trend is attributed to preferential H-abstraction from the lighter ^{12}C isotope and was probably not directly impacted by the radiative U since a ^{13}C depletion of similar magnitude (i.e., $\delta^{13}\text{C}$ decline of $\sim 1\text{‰}$ in dicyclic compounds) was previously reported for diagenetic aromatisation reactions in immature sediments not exposed to radiation.

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Figure Captions

Fig. 1. GC–MS analysis of aromatic fraction of Mulga Rock sediments showing total ion chromatograms (TICs) of: (A) MR49 representative of high U content sediment (5280 ppm); (B) MR51 representative of moderate U content sediment (1161ppm); and (C–F) selected ion recordings (SIRs) extracted from MR51 to specifically highlight different terpenoid groups.

Fig. 2. Sesquiterpenoid diagenesis: Reaction scheme for the aromatisation of cadinenes and cadinols (extension of schemes by Simoneit et al., 1986). $\delta^{13}\text{C}$ values for several products from CSIA of MR51 are shown in parentheses.

Fig. 3. Triterpenoid diagenesis: Reaction scheme for the aromatisation of ursane-type triterpenoids (extension of schemes by Chaffee and Johns, 1983; Tuo and Philp, 2005). $\delta^{13}\text{C}$ values for several products from CSIA of MR51 are shown in parenthesis.

Fig. 4. TIC proportion of total terpenoid products (and their ring size distribution, inset) vs sediment U concentration (642–5280 ppm).

Fig. 5. Concentrations of total sesquiterpenoids; and cadinene and cadinane vs

sediment U concentration (642–1700 ppm).

Fig. 6. Concentrations of total pentacyclic-, des-A ring- and C-ring cleaved-triterpenoids vs sediment U concentration (642–1700 ppm).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table 1. Basic geochemical data of Mulga Rock samples

Sample ID ^a	Depth (m)	U (ppm) ^b	TOC (%) ^c	"A" (wt% of rock)	Polarity Fractions		
					Saturates	Aromatics	Polars
MR49	53–53.5	5280	15.1	0.05	35.9	30.5	33.6
MR53	54–54.5	1700	21.8	0.67	23.7	10.4	65.9
MR50	55.5–56	642	15.9	0.55	4.4	7.9	87.7
MR51	56.5–57	1161	20.7	0.51	8.1	6.5	85.4
MR52	58–58.5	686	12.6	0.23	11.7	6.0	82.2

^a All samples were collected from the Ambassador Uranium prospect drill core 5766

^b Data measured from a handheld Niton Xlt3 X-ray Fluorescence (XRF) and reported previously in Jaraula et al. (2015).

"A" = Chloroform A extraction

Table 2. Terpenoid products detected in Mulga Rock sediments, along with their 4-point MS data and $\delta^{13}\text{C}$ values where measured. Most product assignments were correlated with literature data (Wakeham et al., 1980; Chaffee and Johns, 1983; Murray et al., 1997; Tuo and Philp 2005; Mallick et al., 2014).

Peak Nos	Product	MF	MW	Major MS peaks – m/z (%)	$\delta^{13}\text{C}$ (‰)
<i>Ia</i>	Cadinene	$\text{C}_{15}\text{H}_{24}$	204	105(100), 161(24), 204(17), 106(11)	–23.8
<i>Ib</i>	Cadinane	$\text{C}_{15}\text{H}_{28}$	208	109(100), 165(82), 95(62), 81(34)	
<i>Ic</i>	Dihydrocurcumene	$\text{C}_{15}\text{H}_{24}$	204	119(100), 120(12), 204(11), 105(11)	
<i>Id</i>	Calamenene	$\text{C}_{15}\text{H}_{22}$	202	159(100), 160 (15), 202(12), 129(11)	–24.9
<i>Ie</i>	5,6,7,8-Tetrahydrocadalene	$\text{C}_{15}\text{H}_{22}$	202	187(100), 159(49), 202(33), 188(19)	–22.7
<i>If</i>	Cadalene	$\text{C}_{15}\text{H}_{18}$	198	183(100), 198(45), 168(31), 153(18)	–25.3
<i>Ig</i>	Isocadalene	$\text{C}_{15}\text{H}_{18}$	198	183(100), 198(67), 168(32), 153(19)	–25.3
<i>IIa</i>	Dehydroabietane	$\text{C}_{20}\text{H}_{30}$	270	255(100), 173(74), 159(66), 270(44)	–28.2
<i>IIb</i>	Simonellite	$\text{C}_{19}\text{H}_{24}$	252	237(100), 252(38), 195(26), 238(21)	
<i>IIc</i>	Diaromatic tricyclic totarane	$\text{C}_{19}\text{H}_{24}$	252	237(100), 252(48), 195(27), 165(20)	–24.6
<i>IId</i>	Diaromatic tricyclic sempervirane	$\text{C}_{19}\text{H}_{24}$	252	237(100), 252(34), 195(21), 238(21)	
<i>IIe</i>	Retene	$\text{C}_{18}\text{H}_{18}$	234	219(100), 234(74), 204(36), 202(24)	
<i>IIIa</i>	Diaromatic 8,14-secotetracyclo-oleanane	$\text{C}_{23}\text{H}_{30}$	306	187(100), 306(25), 119(20), 131(16)	–25.1
<i>IIIb</i>	C_{22} Diaromatic-de-A-lupane	$\text{C}_{22}\text{H}_{28}$	295	295(100), 296(57), 157(55), 213(33)	–25.6
<i>IIIc</i>	C_{22} Diaromatic-de-A-oleanane	$\text{C}_{22}\text{H}_{28}$	292	292(100), 293(22), 181(17), 178(13)	–26.8
<i>IIId</i>	C_{22} Diaromatic-de-A-ursane	$\text{C}_{22}\text{H}_{28}$	292	292(100), 207(98), 208(38), 209(34)	–27.6
<i>IIIe</i>	C_{21} Triaromatic-de-A-lupane	$\text{C}_{21}\text{H}_{22}$	274	231(100), 215(30), 216(23), 274(18)	–24.3
<i>IIIf</i>	C_{21} Triaromatic-de-A-ursane	$\text{C}_{21}\text{H}_{22}$	274	274(100), 218(88), 242(76), 307(60)	–25.8
<i>IIIg</i>	C_{21} Triaromatic-de-A-oleanane	$\text{C}_{21}\text{H}_{22}$	274	218(100), 274(92), 219(25), 202(20)	–29.1
<i>IVa</i>	C_{27} Triaromatic	$\text{C}_{27}\text{H}_{32}$	356	169(100), 356(40), 313(27), 157(29)	–25.5

	8,14-seco-lupane				
IVb	C ₂₇ Triaromatic 8,14-seco-pentacyclo- oleanane	C ₂₇ H ₃₂	356	169(100), 356(30), 187(23), 153(9)	-25.5
IVc	C ₂₇ Triaromatic 8,14-seco-pentacyclo- ursane	C ₂₇ H ₃₂	356	169(100), 356(36), 145(31), 187(26)	
IVd	C ₂₈ Diaromatic 8,14-seco-pentacyclo-t riterpane	C ₂₈ H ₃₈	374	169(100), 170(48), 374(23), 109(18)	
V	C ₂₈ Monoaromatic-pentac yclo-triterpane	C ₂₈ H ₄₂	378	145(100), 144(19), 146(16), 378(12)	-23.5
VIa	C ₂₆ Triaromatic-18 α (H)-ol eanane	C ₂₆ H ₃₀	342	342(100), 343(28), 243(12), 242(11)	-24.8
VIb	C ₂₆ Triaromatic-ursane	C ₂₆ H ₃₀	342	342(100), 257(93), 258(37), 259(36)	-25.6
VIc	C ₂₆ Triaromatic-18 β (H)-ol eanane	C ₂₆ H ₃₀	342	342(100), 257(43), 243(31), 259(20)	-24.8
VIIa	C ₂₂ Tetraaromatic-triterpa ne	C ₂₂ H ₁₈	282	282(100), 283(24), 265(23), 281(18)	
VIIb	C ₂₅ Tetraaromatic-lupane	C ₂₅ H ₂₄	324	281(100), 265(29), 324(25), 266(25)	-25.8
VIIc	C ₂₅ Tetraaromatic-ursane	C ₂₅ H ₂₄	324	324(100), 309(78), 279(33), 308(29)	-27.1
VIIId	C ₂₅ Tetraaromatic-oleanan e	C ₂₅ H ₂₄	324	324(100), 268(68), 325(27), 252(19)	-26.8
VIII	2,9-Dimethyl-picene	C ₂₄ H ₁₈	306	306(100), 307(26), 289(21), 305(11)	-27.6
	Ursa-9(11),12-dien-3 β -ol	C ₃₀ H ₄₈ O	424	424(100), 255(37), 425(33), 43(27)	
	β -amyrin	C ₃₀ H ₅₀ O	426	218(100), 203(51), 69(21), 95(20)	
	α -amyrin	C ₃₀ H ₅₀ O	426	218(100), 203(51), 69(21), 95 (20)	
	Lupan-3 β -ol	C ₃₀ H ₅₂ O	428	95(100), 207(85), 189(84), 191(69)	

Highlights:

- Molecular and isotopic distribution of U-rich Mulga Rock sediments reported.
- Ionizing radiation effects on aromatic terpenoids were identified.
- Radiolysis hastened the diagenetic transformation of plant terpenoids.
- The aromatic terpenoid distributions showed no other major radiolytic effects.
- Diagenetic products showed a slight ^{13}C enrichment with increasing aromatisation.