

## URANIUM RADIOLYTIC IMPACTS ON AROMATIC HYDROCARBON COMPOSITION OF MULGA ROCK SEDIMENTS

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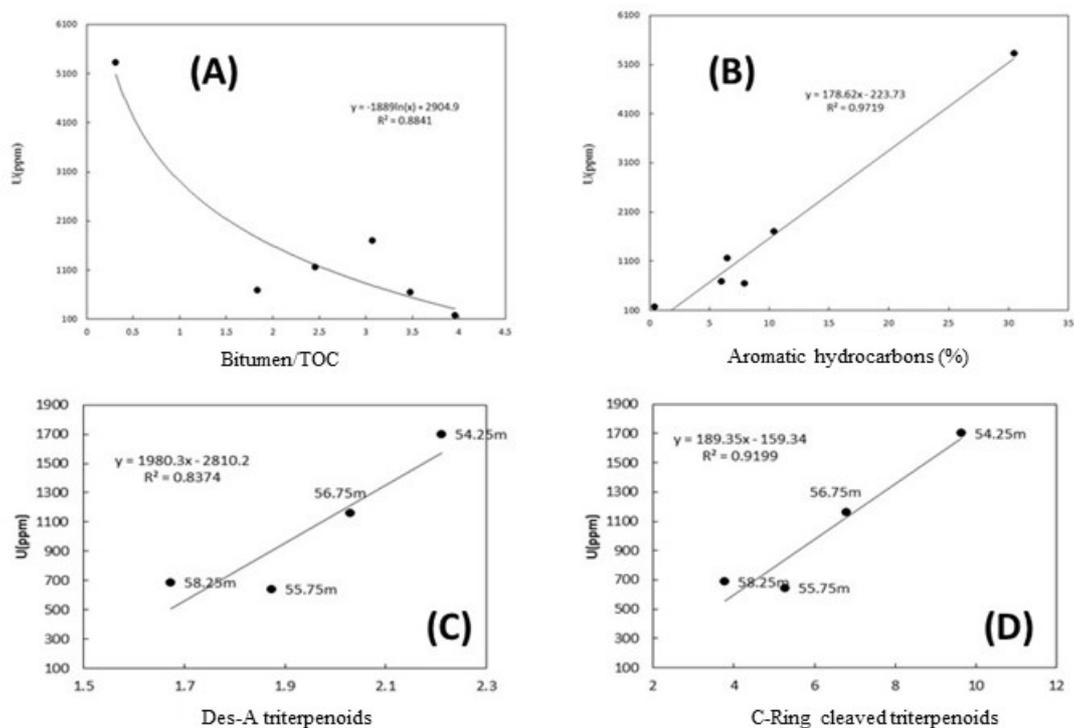
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Many uranium deposits contain high amounts of sedimentary organic matter (OM). A greater understanding of the reactions between uranium and organic compounds will help clarify i) the potential importance of OM to the formation of U-deposits; ii) the susceptibility of sedimentary organic compounds to radiolytic alteration and thus the robustness of traditional biomarker parameters – e.g., thermal maturity indicators based on the relative abundances of aromatic compounds such as triaromatic steroids when exposed to radiative elements; and iii) the discovery of new organic based parameters useful for locating U-rich sediments.

Geochemical evaluations of the radiolytic alteration of OM have often focused on elemental distributions (e.g., C, H, O, N, S %) or the relative proportions of different polarity based fractions (e.g., Bovey, 1958; Landais, 1990, 1996; Kr̆ibek et al., 1999; Tuo et al., 2007). Several studies have investigated the hydrocarbon composition of adjacent uranium mineralised and barren sediments (e.g., Landais et al., 1996; Jaraula et al., 2015). Our group recently reported several changes in the hydrocarbon distributions of the aliphatic and ketone fractions of sediments spanning a 500 - 5000 ppm radiation gradient across the Eocene uranium deposit at Mulga Rock (W. Australia; Jaraula et al., 2015). Radiolytic alterations included a reduction in aliphatic chain length (due to radiolytic cracking) and an increasing proportion of alkenones (from the reaction of aliphatics with OH- radicals from radiolysis of water), particularly alkan-2-ones (due to isomerisation impedance at higher U and concomitant S concentrations). These molecular trends were evident where traditional geological indicators (e.g., pleochroic haloes) were not, indicating a higher sensitivity to relatively low levels or short durations of radiation. With increasing radiation levels the bitumen fraction of the Mulga Rock sediments declined (Fig. 1A), but also showed a relatively larger aromatic moiety (Fig. 1B), attributed to the relatively high susceptibility of aliphatic hydrocarbons to free radical polymerisation and functional group's to condensation reactions (Bovey, 1958).

Here we will report the radiative impacts on aromatic hydrocarbon compositions of the Mulga Rock Sediments. The low thermal maturity Mulga Rock sediments ( $R_r = 0.26\%$ ;  $T_{max} < 421^\circ\text{C}$ ) contained a v. a high abundance of higher plant sourced aromatic (and aliphatic) terpenoids. Many of the aromatised terpenoids were recognised as intermediate or end products of the diagenetic aromatization of diterpane (e.g., cadilane) and triterpane (e.g., amyryl) precursors. Radiolysis alteration included aromatization, cleavage, or oxidation *via* free-radical reaction mechanisms driven by the strong oxidizing property of uranyl ( $\text{UO}_2^{2+}$ ). The abundances of aromatic hydrocarbons and average polycyclic aromatic hydrocarbon (PAH) size both increased with uranium content, partly due to dehydrogenation and oxidation of aliphatic compounds. At low U levels the radiolysis was shown to variedly impact the rates of different aromatisation schemes. For instance, higher abundances of triaromatic C ring-cleaved and aromatic des-A triterpenoid hydrocarbons were measured in higher U content sediments across the range of 640 ppm to 1700 ppm (e.g., Fig 1C and D). The sediment with the highest U content of  $> 5000$  ppm showed only diterpenoids and low MW PAHs, reflecting complete

radiolytic removal of higher MW terpenoids. A slight  $\delta^{13}\text{C}$  depletion evident in increasingly aromatised triterpenoids was likely due to preferential H-abstraction from  $^{12}\text{C}$ .



**Figure 1** Profiles of (A) Bitumen content; (B) Aromatic fraction (%); and (C-D) concentrations of aromatic triterpenoid groups versus U concentration

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