

Yang, S., et al., 2020, Geological alteration of organic macromolecules by irradiation: Implication for organic matter occurrence on Mars: *Geology*, v. 48, <https://doi.org/10.1130/G47171.1>

Supplemental Material

METHODS

Uranium measurement

Uranium content for all shales except Mulga Rock was measured by ICP-MS. About 250 mg of rock powder, which had been dried at 105°C, was weighed into 15 mL teflon vials (Savillex®) and decomposed using HF, Aqua Regia (3:1 mixture of 37% HCl and 63% HNO₃) and perchloric acid (HClO₄). In a first step, 4 mL HF and 4 mL Aqua Regia were added to the samples. The tightly closed vials were placed into a heating block (160°C) for 14 hours. After cooling, 1 mL HClO₄ (70%) was added to destroy the organic material and fluorides. This solution was evaporated at 180°C to incipient dryness. The samples were re-dissolved in 1 mL 7N HNO₃ and dried. Then, the HClO₄ step was repeated twice. The samples were re-dissolved in 7N HNO₃ and kept at 100°C for 14 hours. This solution was brought to a volume of 50 mL for analysis. Data were acquired in peak jumping mode using a Galileo 4870 in pulse counting mode.

Uranium concentrations for Mulga Rock were detected in the field using a handheld Niton Xlt3 X-ray Fluorescence (XRF).

Thermal analysis

Rock–Eval pyrolysis and TOC measurements were performed using Rock–Eval 6 and Leco SC-632 analysers, respectively, following established procedures.

Pyrolysis gas chromatography was performed using the Quantum MSSV-2 Thermal Analysis System®. Thermally extracted (300°C for 10 minutes) whole rock samples were heated in a flow of helium, and products released over the temperature range 300–600°C (40K/min) were focussed using a cryogenic trap, and then analysed using a 50m x 0.32mm BP-1 capillary column equipped with a flame ionisation detector. The GC oven temperature was programmed from 40°C to 320°C at 8°C/minute. Boiling ranges (C₁, C₂–C₅, C₆–C₁₄, C₁₅+) and individual compounds (n-alkenes, n-alkanes, alkylaromatic hydrocarbons and alkylthiophenes) were quantified by external standardisation using n-butane. Response factors for all compounds were assumed the same, except for methane whose response factor was 1.1.

ESI FT-ICR-MS

Powdered samples were Soxhlet-extracted using a mixture of dichloromethane and methanol (v/v = 99:1). Ultra-high-resolution MS analyses on the resulting bitumen were performed using a Bruker Solarix FT-ICR-MS equipped with a 12 T refrigerated superconducting magnet. The negative-ion ESI operating conditions were as follows: capillary entrance 3 kV, collision voltage 1.5 V, ion accumulation time 0.05 s, dry gas flow 4 L/min, and dry gas

temperature 220 °C. Spectra were recorded in broadband mode using four megaword data sets. A total of 100 spectra were accumulated in a mass range from m/z 150 to 2000.

An external calibration was done using an in-house calibration mixture for ESI negative mode containing fatty acids and modified polyethylene glycols. Subsequently, each mass spectrum was internally recalibrated using known homologous series. A quadratic calibration mode was chosen for all samples. The RMS errors of the calibrations were between 0.001 and 0.031 ppm. Elemental formulae were assigned to the recalibrated m/z values with a maximal error of 0.5 ppm.

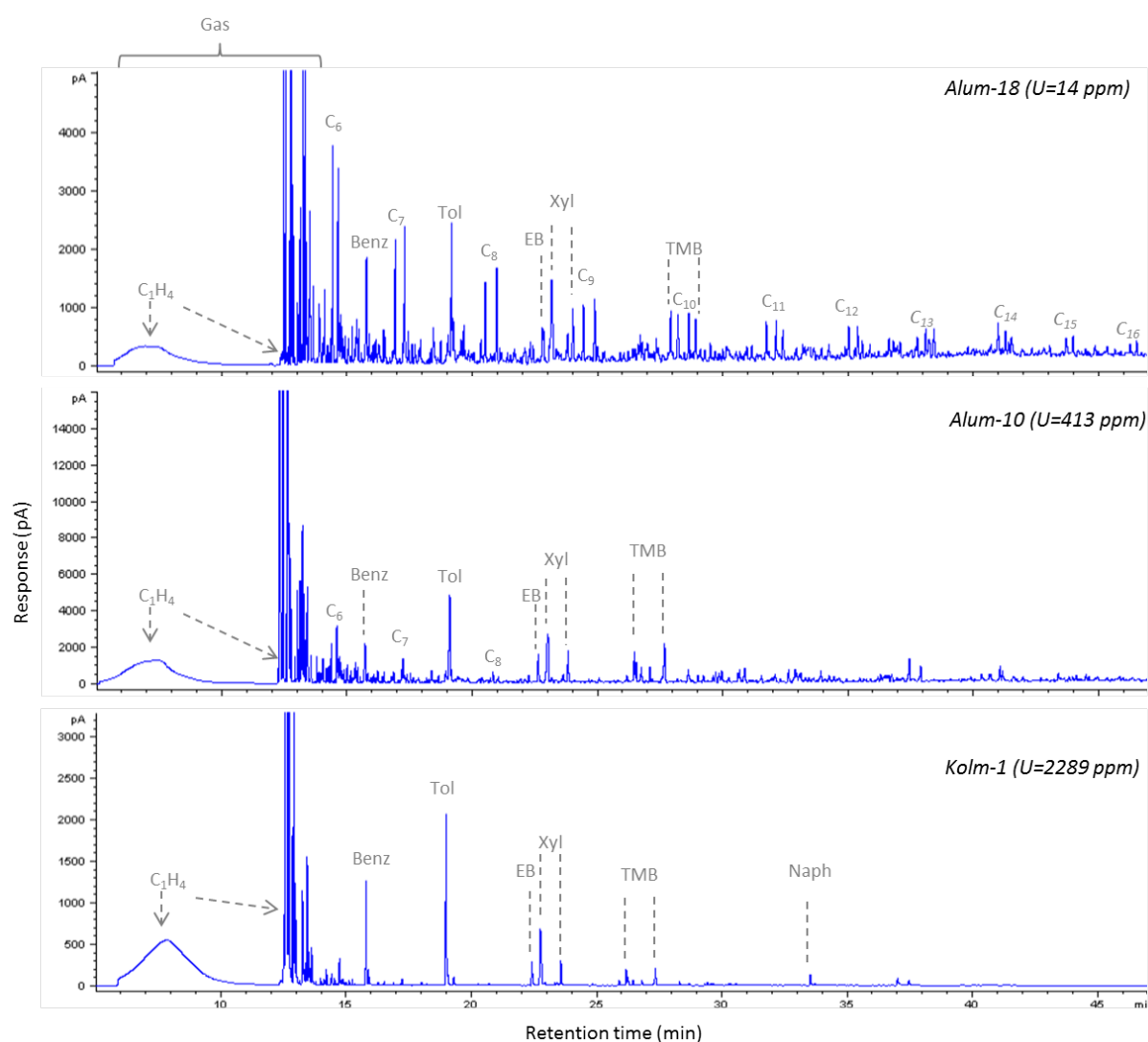


Figure S1

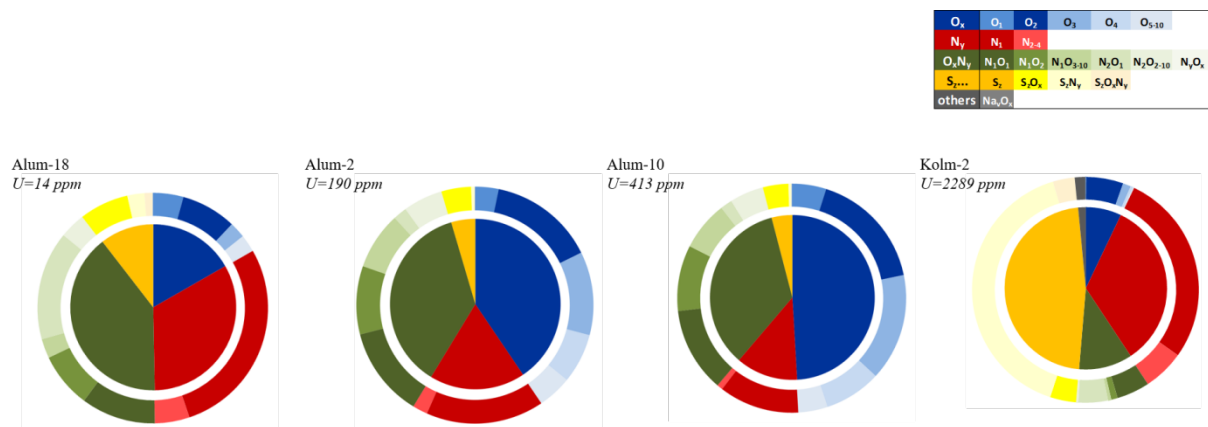


Figure S2