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The organic geochemistry of “Kolm”, a unique analogue for the understanding of molecular changes after significant uranium irradiation

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Abstract

The highly uraniferous and organic-rich material which occurs as small lenticular nodules in the Upper Cambrian Alum Shale Formation of middle Sweden is known as “Kolm”. The uranium contents in Kolm samples range from 2,000 ppm to 6,000 ppm (more than 100 times higher than typical shale), making the organic matter one of the most irradiated in the geological world with an exposure time of more than 500 Myr. Here, we show that uranium is mostly enriched on the surface of various minerals, instead of being bound to the organic matter. Although Kolm formation predates the evolution of advanced plants and the organic matter is marginally mature, thermovaporisation and pyrolysis products are exclusively composed of gaseous and low-molecular aromatic compounds. The kerogen structure is extremely heterogeneous, and rare bitumen can be extracted although the TOC content of the Kolm sample is 62 wt.%. These features are attributed to the irradiation effects of uranium which resulted in

radiolytic bond breaking, aromatisation, and polymerisation of the organic matter. The organic-uranium interactions in the investigated Kolm sample shed new light on unexpected phenomena while petroleum exploration.

Introduction

The Alum Shale is an informal name for black shale of Middle Cambrian to Lower Ordovician age in and around the Baltic Basin in Northern Europe. It occurs widely from Northern Denmark to Western Russia and can be as thick as 180 m in offshore Denmark. With the total organic carbon (TOC) content of up to 22 wt.%, the Alum Shale is considered as one of the most important source rocks for conventional and unconventional petroleum resources in the Baltic Basin ([Schulz et al., 2015](#)). At the same time, it holds the largest low-grade uranium resources in Europe ([Andersson et al., 1983](#)).

Kolm lenses are peculiar phenomena in the Furongian Alum Shale Formation and are featured by high organic matter content (37 wt.%-62 wt.%) and very high uranium content (up to 6,000 ppm). The origin of Kolm is argued to be related to current winnowing ([Schovsbo, 2002](#)), i.e., Kolm was deposited in shallow and anoxic water where sluggish and swirling currents concentrated organic matter in small sediment depressions ([Cobb and Kulp, 1961](#)). Today, these lenses are arranged with the long dimension parallel to the bedding, and can be as thick as 20 cm in the centre ([Parnell, 1984](#)).

Kolm drew interest from geologists back to the 1930s when uranium-lead ratios were investigated for dating purposes ([Baxter and Bliss, 1930](#); [Wells and Stevens, 1931](#)). In the late 1980s, intensive efforts have been made in elucidating the

influence of uranium decay and the resulting irradiation by α -particles on organic matter in the Alum Shale using Rock-Eval pyrolysis, stable carbon isotope investigations, and GC-MS techniques ([Buchardt et al., 1986](#); [Lewan and Buchardt, 1989](#)); As a result, Kolm was occasionally mentioned as special intraformational facies in those Alum Shale researches ([Dahl et al., 1988](#); [Leventhal et al., 1986](#)). Recently, new conceptual approaches and data sets confirmed how kerogen in the Alum Shale ($10 \text{ ppm} < \text{U} < 500 \text{ ppm}$) can be readily altered by irradiation ([Schulz et al., 2019](#); [Yang et al., 2018](#)). However, yet unknowns are the mechanisms and consequences of uranium-organic matter interactions in the uranium-super-enriched Kolm ($\text{U} > 2,000 \text{ ppm}$), including further unknowns such as the uranium distribution, as well as the heterogeneity and the structure of the kerogen.

Sample and methods

The investigated Kolm sample was taken from the once active open pit mine in Ranstad near Billingen (Västergötland, Sweden; Schovsbo, 2002) where Kolm is best developed ([Cobb and Kulp, 1961](#)). The sample was fresh and was devoid of any surface weathering when it was sampled. We isolated material for investigation from the internal part of the bulk Kolm ($15\text{cm} \times 15\text{cm} \times 7\text{cm}$), so that any influences from weathering can be avoided.

The uranium content was measured by ICP-MS as described by [Romer and Hahne \(2010\)](#). Rock powder, which had been dried at 105°C , was weighed into Teflon vials and decomposed using HF, Aqua Regia, and perchloric acid. Then, the vials were placed into a heating block (160°C) for 14 h. After cooling, HClO_4 (70%) was added to destroy the organic material and fluorides. The samples were

re-dissolved in HNO_3 and dried. Then, the HClO_4 step was repeated twice. The samples were re-dissolved in HNO_3 and kept at 100 °C for 14 h. 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.

Organic petrography and reflectance measurements as well as investigations by scanning electron microscopy (SEM) were conducted as described in [Schulz et al. \(2019\)](#). Analyses of electron transparent foils prepared by the focused-ion-beam (FIB) technique were carried out using transmission electron microscopy (TEM) according [Wirth \(2009\)](#).

For pyrolytic investigations the sample was powdered to 20–30 μm grain size and homogenized. Rock–Eval pyrolysis and TOC measurements were performed using Rock–Eval 6 and Leco SC-632 analysers, respectively, by Applied Petroleum Technology AS (Norway) following established procedures ([Behar et al., 2001](#)). Open system pyrolysis (Py) and thermovaporisation (Tvap) were performed using the Quantum MSSV-2 Thermal Analysis System interfaced with an Agilent GC-6890A gas chromatograph ([Horsfield et al., 2014](#)). (1) For Py-GC, the coarsely crushed sample was filled into a small open glass tube and heated at 300 °C for three minutes to vent the free hydrocarbons. Hydrocarbons generated between 300 and 600 °C were collected and measured. (2) For Tvap-GC, around 10 mg of sample was weighed into MSSV glass capillary tubes, which were then sealed using a hydrogen flame. After introduction into the Quantum MSSV-2 Thermal Analysis System, the external surfaces of the tube were purged for five minutes at 300 °C; thereafter the tube was cracked open using a piston device to transfer the volatiles into a liquid nitrogen cooled trap. Quantifications of

individual compounds for Py-GC and Tvap-GC were conducted by external standardisation with *n*-butane. Bulk kinetics pyrolysis was performed using a source rock analyzer (SRA) at three different heating rates (0.7, 2, and 5 K/min) following established procedures ([Yang and Horsfield, 2016](#)). The discrete activation energy (E_a) distribution optimization with a single frequency factor (A) was performed using the KINETICS 2000 program.

Results and discussions

Uranium was suggested to be associated with organic matter ([Leventhal, 1981](#)) or with the inorganic fraction, e.g., phosphate substances in shale ([Parnell, 1984](#)). However, the uranium content in Kolm is not correlated with either TOC nor phosphorus contents ([Schovsbo, 2002](#)). Although the method used here has a lower limit for uranium detection, the SEM-EDX results highlight that most uranium is concentrated on the surface of minerals, e.g., clay minerals, pyrite, and K-feldspar ([Fig. 1A, B, C, D](#)) or occurs in diagenetic agglomerates ([Fig. 1E, F](#)). These diagenetic agglomerates resemble the so-called clay-organic nanocomposites ([Kennedy et al., 2014](#)) and point to uranium entrapment due to weathering in the catchment area before sedimentation. Similar features occur throughout Kolm ([Fig. 2A-C](#)) and emphasize the importance of high surface area clay minerals for uranium fixation. It is a quadrivalent uranium species that is adsorbed in the Alum Shale; one possible option is of UO_2 ([Schulz et al., 2019](#)). With key Rock-Eval parameters highly comparable with previous findings ([Fig. 3A](#)), the investigated sample is a representative Kolm. It contains 2,289 ppm uranium and has a TOC content of 62 wt.%. The remaining hydrocarbon generation potential can be evaluated by its hydrogen index of 142 mgHC/gTOC

and the weak fluorescence under UV light (Supplementary Fig. 1). In the terms of maturity considerations, the organic matter can be viewed as “marginally mature” based on its T_{max} value of 438 °C ([Peters, 1986](#)). Since the Kolm formation predates the evolution of terrestrial plants, vitrinite-like particles, e.g., zooclasts and solid bitumen, were investigated for maturity assessments. A conversion of the reflectance measured on vitrinite-like particles to the commonly used vitrinite reflectance was proposed by [Petersen et al. \(2013\)](#) suggesting that the average vitrinite reflectance-equivalent of this samples is around 0.9% (Fig. 3B and C). It needs to be pointed out that the surrounding Alum Shale in middle Sweden are exclusively immature based on T_{max} values and organic petrological observations ([Buchardt et al., 1997](#)).

The Rock-Eval pyrogram reveals that there are “tails” for both the S1 and S2 signals, i.e., the generation amounts are not zero at 300 °C and 600 °C, respectively (Fig. 4A). Compositional examinations of these two peaks show that both the “pyrolyzable hydrocarbons (S2)” (Fig. 4B) and the “thermoevaporized hydrocarbons (S1)” (Fig. 4C) are exclusively composed of gaseous and low-molecular aromatic hydrocarbons. [Yang et al. \(2018\)](#) reported that the gas/oil ratio and the aromaticity of both pyrolysis and thermovaporisation products are proportional to the uranium contents (from 14 to 413 ppm) in immature Alum Shale, and thus this Kolm sample serves as a meaningful end member for previous correlations. In addition, the wide distribution of the activation energy in the bulk kinetic data set is similar to the reflectance of vitrinite-like particles (Fig. 3C and 4D) and highlights that the kerogen is extremely heterogeneous. An

attempt to extract any bitumen from the Kolm sample failed which is atypical considering its maturity and TOC content.

Early speculations suggested that the aromatic characteristics of the Alum Shale kerogen might be related to some special types of precursors ([Bharati et al., 1995](#)), e.g., *Chlorella marina* ([Derenne et al., 1996](#)). However, the results gained by investigation of the described Kolm sample contradict this hypothesis as there is rare organic matter that would generate only gas and is non-extractable at this stage of maturity. Therefore, the ionizing effect from the uranium decay is considered to control most of the unique geochemical features of Kolm. The α -particles released by the decay of uranium bombarded the long aliphatic chains in kerogen, turning them into short chains and polycyclic aromatic hydrocarbons via radiolytic bond breaking, aromatisation, and polymerisation mechanisms ([Court et al., 2006](#)). This would also explain the absence of an oil generation potential and the dominance of gaseous and aromatic compounds in the products. The contact of uranium and organic matter is not a clearly defined interface in the Kolm, and thus the organic matter is altered at different levels depending on its distance to the ionizing source. This may serve as explanation for the considerable heterogeneity of the organic matter from the perspectives of microscopic reflectance ([Fig. 3B](#)) and thermal stability ([Fig. 4D](#)).

For petroleum exploration, Rock-Eval and pyrolysis-GC are frequently used to assess the hydrocarbon generation potential of source rocks. The organic-uranium interactions revealed here shows that both the quantity and quality of the pyrolysates can be influenced by the α -particle irradiation. Misleading conclusions might be drawn without considering this effect, e.g., underestimation

of the hydrocarbon generation potential, whereas the gas generation preference and the thermal maturity may be overestimated. Furthermore, investigations on the molecular level demonstrate that the gas sorption capacity positively correlates with the aromaticity of the labile kerogen ([Mahlstedt and Horsfield, 2019](#)). This, in turn, indicates that uranium irradiation can increase the gas retention ability of the source rock and can be responsible for the presence of the S1“tail”, i.e., some free hydrocarbons are carried over to S2 (**Fig. 4A**). Such a hypothesis is supported by the fact that the gas adsorption capacity of the uranium-rich Alum Shale is abnormally high, i.e., significantly higher than that of the Barnett Shale (Fort Worth Basin, USA) and the Posidonia Shale (Lower Saxony Basin, Germany) ([Gasparik et al., 2014](#)).

Conclusions

Uranium is not evenly distributed in the Kolm, instead, it is concentrated on the surface of minerals or occurs in diagenetic agglomerates (comparable to clay-organic nanocomposites). The organic matter was severely altered by the irradiation of α -particles induced by uranium-decay, i.e., standard maturity indicators were increased, the oil generation potential and solvent extractability were nearly completely destroyed, the gas retention capacity was enhanced, in summary causing a pronounced heterogeneity.

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Figures

Fig. 1 (A) High-magnification scanning transmission electron microscopy (STEM) image (high angle annular dark-field mode) showing dissolved quartz with adsorbed uranium in the surrounding clay cover instead of being enriched in the OM matrix. Dotted line shows transect for uranium detection in (B) with uranium counts by EDX. (C) BSE image of pyrite clay minerals and K-feldspar in OM matrix. (E) BSE image showing an agglomerate made up of pyrite (white) and clay minerals (grey) in an organic matter matrix (black). (D, F) Uranium maps of (C, E). Scale is based on uranium counts per pixel (brightest green stands for maximum uranium counts of 23). Image resolution: 1024 by 768, image pixel size: 0.07 μm, map resolution: 512 by 384, map pixel size: 0.13 μm.

Fig. 2 High-magnification scanning transmission electron microscopy (STEM) images (high angle annular dark-field mode) showing amorphous Fe, Mg-bearing aluminosilicates with detectable uranium contents surrounded by U-free OM matrix.

Fig. 3 The thermal maturity of the Kolm sample as shown by Rock-Eval parameters (A) and the reflectance heterogeneity of a selected vitrinite-like particles (B). Template for figure A is after [Cornford et al. \(1998\)](#). Details about the reflectance heterogeneities of 100 measured vitrinite-like particles in the Kolm sample are given in histogram in (C). Petersen et al. (2013) suggested that vitrinite equivalent (VR_{eqv}) can be calculated from the reflectance vitrinite-like particles (R_{v-l}) by $VR_{eqv} = 0.73 R_{v-l} + 0.16$.

Fig. 4 Rock-Eval pyrogram showing the S1 and S2 peaks (A). Detailed compounds generated by pyrolysis and thermovaporisation are shown in (B) and (C), respectively. Main aromatic compounds include benzene (Benz), toluene (Tol), ethylbenzene (EB), and xylene (Xyl). Bulk kinetic data in (D) reveal the stability and heterogeneity of the kerogen structure.