IDENTIFICATION OF NSO COMPOUNDS TRAPPED IN FLUID INCLUSIONS USING FT-ICR-MS -A CASE STUDY FROM THE PANNONIAN BASIN (HUNGARY)

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Introduction

Minerals such as quartz, calcite and fluorite often contain oil- and gas-bearing fluid inclusions, and aqueous inclusions with dissolved organic matter. Geochemical information from small organic molecules such as methane, ethane or propane can be gained from individual intact inclusions using spectroscopic methods. However, higher molecular weight compounds including biomarkers are generally characterized using bulk samples. Common approaches for gas chromatography – mass spectrometric (GC-MS) analysis involve sample crushing in an online system followed by thermal extraction (suitable for gases and light hydrocarbons) or GC-MS analysis of offline solvent extracts (suitable for C_{12+} compounds including biomarkers). While hydrocarbons and GC-amenable low molecular weight polar NSO compounds have been widely evaluated, very little is known about the nature of more complex medium to high molecular weight NSO compounds or high molecular weight aromatic hydrocarbons in inclusion oils. Fourier transform-ion cyclotron resonance-mass spectrometer (FT-ICR-MS) in combination with Atmospheric Pressure Photoionisation (APPI) or Electrospray Ionisation (ESI) is well suited for characterising these compounds in complex organic mixtures such as these.

In this study we aim to address this deficiency, by comparing FT-ICR-MS derived NSO compound compositions in a fluid inclusion oil (FIO), a produced oil (PO) from the same well, two source rock extracts (Marl S1 and Marl S2) and two reservoir rock extracts (U65A 1 and 2) from the Üllés Field in the southern part of the Pannonian Basin in Hungary with those obtained from conventional analyses using GC-MS (Szabó et al., 2016). A comparison of the organic matter inventory of these fluids offers an opportunity to gain insights into fluid properties of the oil field in the past and into its filling history. Our study extends work presented in Noah et al. (2018) with APPI data, and to the best of our knowledge is the first study of NSO compounds in fluid inclusion oils using FT-ICR-MS.

Results

A comparison of the NSO compositions gained using ESI in negative ion mode (ESI(-)) shows that the source and reservoir rock extracts are dominated by oxygen and nitrogen-oxygen-containing compounds, whereas both oils are strongly dominated by nitrogen-containing compounds (Figure 1). The PO contains a much lower proportion of O_2 and N_1O_{1-2} compounds compared to the FIO, possibly indicative of production fractionation, since these compounds show quite high abundances in all other samples. NSO compounds in the FIO are more diverse than in the PO, which is dominated by N_1 compounds and shows the lowest NSO compound diversity of all samples. An elevated abundance of NSO compounds in fluid inclusion oils compared to crude oils has been noted previously (e.g. Pang et al. 1998) and

may reflect the greater affinity of NSO compounds to polar mineral surfaces, where oils can be trapped as fluid inclusions on crystal imperfections.
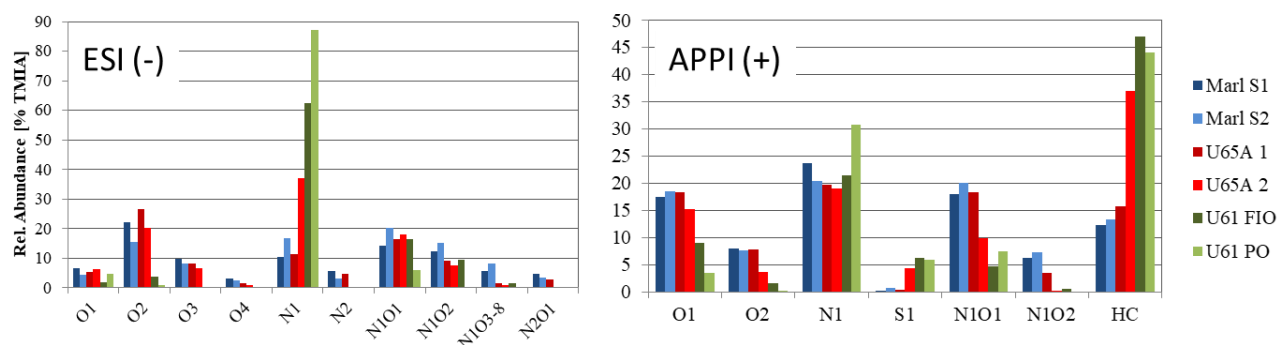
Figure 1 *Relative abundances of compound classes (source rocks in blue, reservoir rocks in red, oils in green) in ESI(-) and APPI(+).*

Specific N_1 compounds (carbazoles, benzocarbazoles and dibenzocarbazoles) were used for the maturity assessment of the FIO and PO. When applying relationships published in Oldenburg et al. (2014), both oils are of similar maturity level of ca. 1% vitrinite reflectance equivalent (VRE). This is broadly in line with results from conventional GC-MS analyses (0.7 to 1.0% VRE according to Szabó et al., 2012).

APPI in positive ion mode (APPI(+)) was used to extend the polarity spectrum and to gain access to high molecular weight aromatic hydrocarbons with masses up to 997 Da in this sample set. These results show the highest abundance of aromatic hydrocarbons (HC) and S_1-containing compounds in the FIO and PO. In line with ESI(-) results APPI(+) data show that O_2 compounds are depleted in the oils (Figure 1). Both oils are more closely related to Marl S2 than to Marl S1 judging by the overall NSO compositions. This corroborates a correlation of oils to Marl S2 based on biomarkers (Szabó et al., 2012). However, the FIO seem to be less altered and fractionated than the PO, since it shows a higher similarity to the source and reservoir rock extracts (Noah et al., 2018).

Conclusion

In this study we demonstrate for the first time that FT-ICR-MS can be used as a tool to extract detailed information on NSO compounds in fluid inclusion oils. First high resolution MS results show systematic variations in NSO compound composition between sample types. This proof of concept opens an exciting domain of research into mineral-fluid interaction and the evolution of petroleum reservoirs.

References

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