INSIGHTS INTO AROMATIC ORGANOSULPHUR COMPOUNDS IN SOLID BITUMEN AND HEAVY OILS FROM SOUTHEAST TURKEY

S. H. Hosseini1,2*, S. Poetz1, B. Horsfield1, H. Wilkes3, O. Kavak4, M. N. Yalçın5

1GFZ German Research Centre for Geosciences, Germany, 2Petroleum Reservoir Group, University of Calgary, Canada, 3Carl von Ossietzky University of Oldenburg, Germany, 4Dicle University, Turkey, 5Istanbul University, Turkey.

The main oil-producing region of Turkey lies in the southeast, and there are many oilfields, oil seepages and solid bitumen veins occurring in close proximity. In previous studies we have shown that Turkish solid bitumen veins display a wide variety in chemical composition and physical properties depending on geographic location and regional tectonic history. Most importantly, compressional stress did not occur with the same intensity across the region and increases towards the collision zone (Hosseini et al., 2017). Furthermore, various source-sensitive parameters obtained from aliphatic and aromatic hydrocarbons as well as compound-specific stable carbon isotope signatures of n-alkanes indicated a strong genetic relationship between surficial solid bitumen veins and heavy oils from proximal oilfields (Hosseini et al., 2018). Moreover, petroleum in the investigated region is known to be sulphur-rich, though to the best of our knowledge no attempt has been made to address the question of sulphur origin in detail.

Since organosulphur compounds in petroleum fluids are mainly present in complex macromolecules, the ability of conventional geochemical tools such as gas chromatography-mass spectrometry (GC-MS) is limited when it comes to fully unravelling their compositional complexity, and also to elucidate the mechanism(s) of sulphur incorporation into organic matter. Positive-ion atmospheric pressure photoionization coupled with Fourier transform ion cyclotron resonance mass spectrometry (APPI (+) FT-ICR-MS), has been shown to be well suited for characterizing low polarity aromatic organosulphur compounds in complex petroleum mixtures, thus providing molecular-level clues about their origins (Purcell et al., 2006, Walters et al., 2011). Here, solid bitumens and heavy oils from SE Turkey are investigated using APPI (+) FT-ICR-MS, focusing on how organosulphur compound geochemistry evolves with thermal maturation. Moreover, the possible mechanism(s) by which sulphur has been incorporated into the petroleum fluids is addressed.

A suite of sulphur-rich samples including eight solid bitumens of different degradation levels from early mature (Tmax: 433 ºC) to overmature (Tmax > 500 ºC), as well as eight heavy oils (API gravity range: 11º to 19º) from proximal oilfields have been assembled. The variation in abundances of each S-containing compound class, normalized to the sum of all sulphur-containing compound classes, with ongoing maturation for both sample types is illustrated in Figure 1. All samples are very rich in aromatic organic sulphur compounds and their relative abundances are sensitive to even very small changes in thermal maturity. Various bulk and molecular parameters such as the relatively low reservoir temperatures, a continual decrease in total sulphur and a concomitant increase in the aromatic hydrocarbons as well as the N1 classes with ongoing maturation are suggesting that organosulphur compounds have been incorporated into the source organic matter via bacterial sulphate reduction (BSR) mechanism at very early levels of diagenesis. Moreover, the existence of sulphur-rich heavy oils without any signs of biodegradation indicate that they have been yielded from kerogens with high organic sulphur content at early stages of generation,
arguing against a thermochemical sulphate reduction (TSR) mechanism which mainly occurs at relatively high temperatures. Furthermore, the evolution of organic sulphur compounds in both petroleum types is quite sensitive to variations of thermal stress and their chemical composition is clearly influenced by at least one of the thermally-induced reactions such as thermal cracking, cyclisation as well as aromatisation depending upon the petroleum phase and/or transformation levels. Most interestingly, there is an obvious reversal trend in high-thermally degraded solid bitumens ($T_{\text{max}} > 470$ °C), most likely due to the re-incorporation of the active sulphur species released from thermally decomposing polymers by one of the many known high-temperature pathways.

Figure 1 Distribution of the major S-containing compound classes normalized to the sum of all S-containing compounds from (+) APPI FT-ICR-MS and their variations as a function of maturity.

References