



Residency of rhenium and osmium in a heavy crude oil

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Abstract

Rhenium-osmium (Re-Os) isotope geochemistry is an emerging tool for the study of oil formation and migration processes, and a new technology for petroleum exploration. Little is known, however, about the residency of Re and Os within asphaltene and maltene sub-fractions of crude oil. This information is crucial for understanding the ¹⁸⁷Re-¹⁸⁷Os radiometric clock held in petroleum systems and for interpreting geochronology for key processes such as oil formation, migration, and biodegradation.

In this study, a heavy crude oil was separated into soluble (maltene, MALT) and insoluble (asphaltene, ASPH) fractions using *n*-heptane as the asphaltene-precipitating agent. The asphaltenes were separated sequentially into sub-fractions using two different solvent pairs (heptane-dichloromethane and acetone-toluene), and the bulk maltenes were separated into saturate, aromatic, and resin (SAR) fractions using open column chromatography. Each asphaltene and maltene sub-fraction was analyzed for Re and Os. The asphaltene sub-fractions and the bulk ASPH, MALT, and crude oil were analyzed for a suite of trace metals by ICP-MS.

Our results show that Re and Os concentrations co-vary between the asphaltene sub-fractions, and that both elements are found mostly in the more polar and aromatic sub-fractions. Significant Re and Os are also present in the aromatic and resin fractions of the maltenes. However, each asphaltene and maltene sub-fraction has a distinct isotopic composition, and sub-fractions are not isochronous. This suggests that asphaltene sub-fractionation separates Re-Os complexes to the point where the isotopic integrity of the geochronometer is compromised. The mobility of individual Re and Os isotopes and the decoupling possibilities between radiogenic ¹⁸⁷Os produced from ¹⁸⁷Re remain elusive, but their recognition in this study is a critical first step. Re and Os correlate strongly with Mo and Cd in the asphaltene sub-fractions, suggesting that these metals occupy similar sites. Re-Os and Ni-V budgets also show some similarities, indicating that at least some Re (and possibly Os) could be present in metalloporphyrin form. We conclude that progressive asphaltene precipitation during migration and mixing of oils can change the isotopic ratios of the resultant oil. A sense of process is key to interpretation of Re-Os data for tar mats and live oils, whether isochronous or scattered datasets result. Optimally, by combining data from source rocks, oils, and asphaltenes generated along the migration pathway, we can construct temporal histories for whole petroleum systems.

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1. INTRODUCTION

The affinity of Re and Os with organic compounds permits application of the Re-Os geochronometer (based on the decay of ¹⁸⁷Re to ¹⁸⁷Os; $\lambda = 1.666 \pm 0.017 \times 10^{-11}$

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y^{-1} ; Smoliar et al., 1996) to petroleum systems to constrain the timing of bitumen and oil generation (Selby et al., 2005, 2007; Selby and Creaser, 2005; Rooney et al., 2012; Georgiev et al., 2016). In reducing environments, Re and Os are drawn down from seawater during sedimentation and then incorporated into organic-rich shales (Ravizza and Turekian, 1989; Cohen et al., 1999; Selby and Creaser, 2003), and are later transferred from kerogen to bitumen to oil. Application of this chronometer to oils and bitumen requires a closed system for the material analyzed. That is, no Re or Os are removed or added to the bitumen or oil after its formation. Therefore, interpretation of Re-Os isochrons requires understanding the residency of Re-Os in these hydrocarbons and the processes that may subsequently affect the mobility of these elements. In this contribution, we provide new understanding on the residency and mobility of Re and Os in a previously characterized oil sample from the Gela field in Sicily, Italy (Georgiev et al., 2016).

Crude oil can be separated into two solubility-defined fractions: asphaltenes (ASPH, insoluble in *n*-alkane) and maltenes (MALT, soluble in *n*-alkane). Recently, ASPH have been described by the Yen-Mullins model (Mullins et al., 2012, 2013), in which single asphaltene molecules (~7 aromatic rings) can stack and form nanoaggregates (<10 molecules) which can form clusters when highly concentrated (<10 nanoaggregates) (Mullins et al., 2012, 2013). The *n*-alkane-soluble remainder of the crude oil, the maltenes (MALT), can be divided by column chromatography into saturates, aromatics, and resins, or its “SAR” fractions. The saturates contain saturated hydrocarbons (e.g., alkanes and cycloalkanes), while the aromatics contain compounds with conjugated rings or ring systems (e.g., benzene, naphthalene, and substituted aromatics), and the resins contain heteroatomic and aromatic polar compounds (e.g., furans, thiophenes, pyridines) (e.g., Andersen and Speight, 2001; Speight, 2006). Polarity and molecular weight increases from saturates to aromatics to resins; the resins are separated from the ASPH essentially by molecular weight and solubility in the precipitating *n*-alkane (Andersen and Speight, 2001).

Previous research has shown that Re and Os contents in crude oil vary between the ASPH and MALT fractions (e.g. Selby et al., 2007; Georgiev et al., 2016). As with most other trace metals (e.g., Manning and Gize, 1993), both Re and Os are preferentially concentrated in the ASPH fraction, with far subordinate amounts in the complementary MALT fraction. Analyses of Re and Os concentrations in ASPH sub-fractions show that the most polar-aromatic ASPH sub-fractions are also the most enriched in Re and Os, suggesting that the complexes that house Re and Os are highly polar and/or aromatic (Mahdaoui et al., 2013). No work has been done on determining Re-Os systematics and residency within the SAR sub-fractions; the general expectation based on decreasing Re-Os content with decreasing ASPH sub-fraction polarity (Mahdaoui et al., 2013) is that resins should carry the largest amount of Re and Os within the MALT sub-fractions. Selby et al. (2007) also suggest that Re and Os may be present in the aromatics.

Trace metal contents (e.g., Ni and V), and their ratios in crude oil are useful for source rock-oil and oil-oil correlations, and provide constraints for the type and depositional environment of source rocks (e.g., Lewan, 1984; Barwise, 1990). These applications are especially valuable in biodegraded oils that lack an abundance of biomarkers. In crude oil, trace metals are mostly housed in salts (Na, K, Mg, Ca, Mn), oil-soluble compounds and organometallic complexes (V, Cu, Ni, Fe), and organometallic soaps (Zn, Ti, Ca, Mg) (e.g., Speight, 2006; Wu et al., 2014). Ni and V are known to form metalloporphyrins (Filby and Van Berkal, 1987; Filby, 1994), a class of cyclic molecules composed of a porphyrin ring and a central metal ion. In natural systems, copper porphyrins were identified in deep-sea sediments (e.g. Palmer and Baker, 1978; Baker and Louda, 1986) and iron porphyrins have been identified in crude oil (e.g. Franceskin et al., 1986). Most metals are stable when chelated to the porphyrin ring (Buchler, 1975, 1978). However, several factors, such as availability of ions, stability of metal-nitrogen bonds, and reducibility of metal oxides influence whether or not certain metalloporphyrins will be found in nature (Quirke, 1987; Furimsky, 2016).

Calculated stability indices show that Re and Os can form stable metalloporphyrins (Buchler, 1975, 1978), and it has been suggested that Re (but not Os) metalloporphyrins might be found in sedimentary environments (Miller, 2004). Like Re-Os, V, Ni, Fe, and Cu are most concentrated in the ASPH fraction (Dreyfus et al., 2005; Speight, 2006), which is also the largest sink for porphyrin rings (Speight, 2006). However, Mahdaoui et al. (2013) suggest based on Ni-V and Re-Os concentration profiles of ASPH sub-fractions that Re and Os do not exist as metalloporphyrins within crude oil, but rather are bound to more polar compounds.

Initial reports on Re-Os isotope systematics in crude oils and fractions show generally similar isotopic ratios between crude oils and respective ASPH and MALT fractions with few exceptions (Selby et al., 2007). Subsequent improvements in digestion protocols and analytical procedures revealed that the $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios systematically decrease from ASPH to crude oil to MALT, such that a single sample of crude oil and its fractions can be used together as points to form an isochron (Georgiev et al., 2016). Selby et al. (2007) hypothesize that biodegradation could account for Re and Os isotopic partitioning between the ASPH and MALT, but the unbiodegraded Noto oil studied by Georgiev et al. (2016) shows the characteristic decline in isotopic ratios from ASPH, to crude oil, to MALT. Later experiments define oil-water interaction as an additional process that can change or overprint the isotopic composition of oil (Mahdaoui et al., 2015; Hurtig et al., 2016), suggesting that preferential uptake of Re and Os in the ASPH relative to the MALT fraction during oil-water interactions may cause the spread in Re/Os ratios between ASPH and MALT (Hurtig et al., 2016).

The effect of ASPH precipitation on crude oil Re/Os isotopic ratios is poorly understood. This is critical, as Re-Os geochronology relies on precise measurements of both $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios. Mahdaoui et al.

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