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Source ages of hydrocarbons: ^{129}I investigations of oil field brines, gas hydrates and coal-bed methane

U. FEHN¹, G.T. SNYDER² AND J.E. MORAN³

¹ University of Rochester, USA (fehn@earth.rochester.edu)

² Rice University, USA (gsnyder@rice.edu)

³ Lawrence Livermore National Laboratory, USA
(moran10@llnl.gov)

Iodine is a strongly biophilic element and has one long-lived radioisotope, ^{129}I , with a half-life of 15.7 Myr, which is formed by the interaction of cosmic rays with xenon isotopes in the atmosphere and by spontaneous fission of ^{238}U in the crust. Because iodine has a long residence time in the oceans, the marine isotopic signal is uniform and can be used as the starting signal for iodine dating. The input ratio of $^{129}\text{I}/\text{I}$ into marine sediments is 1500×10^{-15} [1], which, together with the detection limit (10×10^{-15}) of AMS, results in a dating range of about 80 Myr for this system. Currently, about 0.5 mg of iodine is needed to make a reliable AMS determination.

While iodine is prevalent in many organic compounds, it is typically released into the accompanying aqueous fluids during decomposition and maturation of hydrocarbons. As a consequence, iodine is often strongly enriched in fluids associated with hydrocarbons. Whereas seawater contains only 0.4 μM of iodine, oil field brines and coal-bed methane fluids typically contain around 50 μM , pore waters associated with gas hydrates 1000 μM or more of I. These high concentrations allow determinations of source ages in fluids associated with hydrocarbons. We applied this system for the determination of dates in oil field brines [2], gas hydrates [3] and coal bed methane deposits [4], and are currently working on gas hydrate occurrences from ODP 201 (Peru Margin) and 204 (Hydrate Ridge). The results for oil field brines and gas hydrates demonstrate the derivation of iodine (and, by association, of hydrocarbons) from sources other than their current host formations and are used to identify potential source formations for the hydrocarbons. An important result is the prevalence of dates around 50 Ma in many of the gas hydrate deposits currently under investigation. In the case of coal bed methane deposits of the Fruitland Formation, CO, the results are in good agreement with the depositional age of the source coals, indicating that fluids there have been stagnant for periods of 60 Myr or longer.

References

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- [2] Moran et al., (1995), *GCA* **59**, 5055.
- [3] Fehn et al., (2003), *Geology* **31**, 521.
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A novel approach to hydrocarbon systems: Application of the ^{187}Re - ^{187}Os geochronometer

D. SELBY AND R.A. CREASER

University of Alberta, Edmonton, AB, Canada, T6G 2E3
(dselby@ualberta.ca; robert.creaser@ualberta.ca)

Rhenium (Re) and osmium (Os) are enriched in organic-rich sedimentary rocks that are sources for natural hydrocarbons, and the ^{187}Re - ^{187}Os chronometer can yield absolute depositional ages for these rocks. Hydrocarbon maturation does not impact the ability of the chronometer to determine ages from the hydrocarbon source rocks, however detailed information about the Re and Os abundances and isotope systematics in the produced natural hydrocarbons is lacking. The potential of the Re-Os isotopic system for geochronology and as an isotopic tracer for hydrocarbon systems is evaluated here based upon Re-Os isotopic analyses of natural hydrocarbons including bitumen, crude oils and tar sands. We find that bitumen formed from migrated oil in both Alberta tar sand deposits and a Paleozoic Mississippi Valley type Pb-Zn deposit contains significant Re (tens of ppb) and Os contents (ppt to ppb) readily measured by Negative Ion Mass Spectrometry methods. We also find that heavy and light crude oils derived from the same source rock contain grossly different Re and Os abundances. The heavy oil shows similar Re and Os contents to bitumens, whereas the light oil is essentially devoid of these elements, suggesting that Re and Os are dominantly contained in the asphaltene fraction of oil. Bitumen from the Polaris MVT deposit shows significant variation in $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ values between samples on a deposit and drillhole scale. The majority of these analyses define a linear array on a Re-Os isochron diagram and yield a Re-Os regression age of 369.5 ± 5.4 Ma (Model 3, MSWD = 3.1) in excellent agreement with the age of this deposit independently determined by Rb-Sr dating of sphalerite, and paleomagnetic methods. Bitumen from one Alberta tar sand deposit sampled from a drillhole over 18m depth, yields Re-Os analyses with a large range in $^{187}\text{Re}/^{188}\text{Os}$ (1050-1400) and $^{187}\text{Os}/^{188}\text{Os}$ (3.6 - 4.2) defining an apparent Late Cretaceous age; the host sandstone unit is of Middle Cretaceous age. These data may represent the period of *in situ* radiogenic growth of ^{187}Os following hydrocarbon migration and reservoir filling, thus directly dating these processes. The very high initial $^{187}\text{Os}/^{188}\text{Os}$ for this regression implicates rocks significantly older than Cretaceous for the hydrocarbon source. In contrast, Re-Os data from a second deposit show higher $^{187}\text{Re}/^{187}\text{Os}$ (1350-1550) and $^{187}\text{Os}/^{187}\text{Os}$ (4.1-5.1) values, which may represent either modification of the Re-Os isotope system by biodegradation, or suggest that more than one source contributed to these deposits. The Re-Os data demonstrate the promising utility bitumen has to yield valuable age information on the timing of hydrocarbon migration.