New routes to solutions of the WCSB oil charge conundrum: γ- ray Photons and Fourier Transform Mass Spectrometry

Steve Larter, Thomas Oldenburg, Norka Marcano, Lloyd Snowdon, Jennifer Adams[*], Ken Chanthramonti, Andrew Stopford, Haiping Huang, Fuqin Song[#], Claude Laflamme and Mike Ranger.

PRG, Dept of Geoscience, University of Calgary, Calgary, Alberta. *slarter@ucalgary.ca*

[*]Currently at ConocoPhillips, Houston, Texas, USA. Currently at Gushor Inc.[#]

Summary

Riediger and others (Riediger et al., 2000), have documented the major possible source rocks charging the Alberta oil sands but quantitative estimates of the actual oil charge contributions, the migration routes and even the timing of oil charging remain elusive, despite the huge scientific and economic importance of resolving these issues. Similarly, while advances have been dramatic in understanding the quantitative aspects of the biodegradation process, further development is still needed because most conventional petroleum geochemical approaches are not reliable at the heavy and severe levels of biodegradation seen in the oil sands. In this paper we describe recent approaches which might shed light on these questions and quantitatively resolve the qualitative debates that have been raging for decades. We review the state of the art in oil charge analysis of heavy and severely degraded oils using new techniques such as FTMS and ICPMSMS, culminating in a roadmap for the development of the necessary new petroleum system technologies needed, including an approach to a practical oil reservoir-residence time dating tool.

Introduction

While more accurate mapping is undoubtedly needed, better molecular parameters diagnostic of specific charge oils, along with improved compositional basin models (simulating fluid flow of oils defined by both bulk and molecular oil composition at field and even reservoir scales) and improved biodegradation models (Head et al., 2003; Larter et al., 2003; 2006; Adams et al., 2006; Jones et al., 2008) are essential to resolving fluid property variations in the oil sands ((Adams et al., 2012). These variations in fluid properties often define production strategies and have a huge impact on process efficiency ((Larter et al., 2008). Fluid properties are controlled by source-rock charge oil contribution, oil charge maturity and post-charge alteration as well as reservoir conditions ((temperature and pressure). We need to identify source specific markers that have relatively similar concentrations in oils charged from all source-rocks and that are largely independent of maturity as well as being biodegradation resistant. Adams et al (2012), suggested diamondoid hydrocarbons may be a partial solution, as oil-sands bitumen contains diamondoid hydrocarbons up to several hundred ppm and isotopic proxies may also have utility in such settings (Marcano et al., 2012). Another, more likely possibility is using NSO-bearing high molecular weight multi-heteroatom (HMWMH) compounds (e.g., NS, NS_2 heteroatom contents - Oldenburg et al., 2010), which appear diagnostic of source facies in oils biodegraded even to PM level 8 in the Alberta oil sands and in Chinese heavy-oil fields; however, they are not necessarily invariant with maturity. These better markers can be identified with the advent of new high-resolution molecular analytical techniques (e.g., FTICRMS-HMWMH compounds; ICPMSMS-for metal speciation in oils). For instance, double collector ICP-MSMS instruments now allow isotopic characterization of most elements in the periodic table (which have multiple isotopes), including trace metallic elements that are in organic compounds resistant to biodegradation and which may likely have fingerprinting

capabilities for oil-charge and source facies variations. Such metal bearing species can also be tracked using FTMS.

Fig. 1 (after Oldenburg et al., 2010), shows the NS_n heteroatom group distribution of biodegradation resistant, high molecular weight multi -heteroatom ((HMWMH) compounds in oils from three reservoirs. The Athabasca and Peace River marine sourced oils are from W. Canada and the Liaohe lacustrine sourced oils are from N.E. China. Each oil suite has a wide range of biodegradation levels but shows no variation with biodegradation while the distributions convincingly distinguish the sulfur rich, partly Gordondale charged Peace River bitumen, from two separate accumulations in Athabasca ((Adams et al., 2012). The Chinese (Liaohe Basin) oils are sourced from lacustrine source rocks (Huang et al., 2004) and also show a different signature. Quantitative analysis of these species is underway as is analysis of a suite of type oils. Such approaches may allow a more quantitative demixing of oil charge from putative source rocks to the oil sands.

Uncertainties over the volumes of oil degraded in forming the oil-sands bitumen feed directly into uncertainties into the volumes of source-rocks needed in the oil-charge kitchens and hence the secondary migration ranges and plumbing systems required. Adams et al. ((2012) suggest that improving our understanding of the biodegradation mass loss from oil sands requires more detailed studies of charge related oils at various levels of biodegradation which, as discussed above, requires study of a more comprehensive sample suite of type oils proximal to their expulsion sites (i.e., the associated source-rock facies). These may become available as part of the renewed importance of source-rocks as exploration targets for shale gas and tight oil plays. This new activity in shale oil and gas exploration ignites a new era of source-rock studies with much better sampling of the shale sections from core analyses rather than cuttings in the basin.
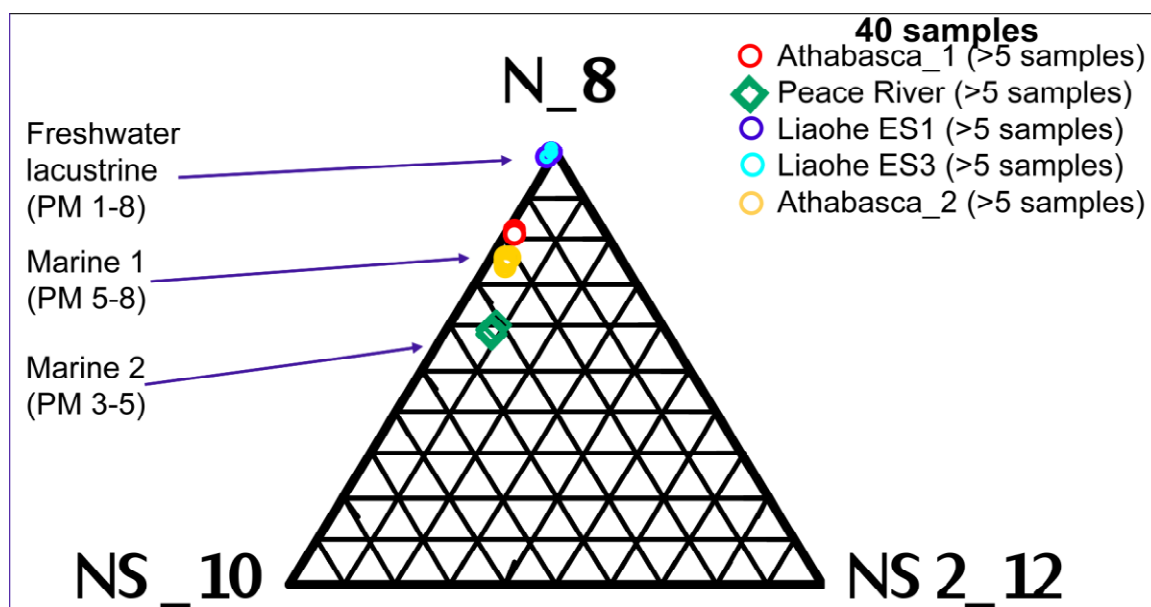

Fig 1. The NS_n heteroatom group distribution of biodegradation resistant high molecular weight multi heteroatom (HMWMH) compounds in oils from three reservoirs at a range of biodegradation levels(PM scale range shown). The Athabasca and Peace River marine sourced oils are from W. Canada and the Liaohe lacustrine sourced oils are from N.E China.

The paper mainly focuses on dating oil and gas arrival and residence time in reservoirs. Dating of geological events is one of the main tools of geological investigation, yet a practical method for dating oil field charging time from analysis of crude-oil does not exist. While forward basin models can provide estimates of oil charging times, they are unconstrained by any time dependent measurements that can

be made on the crude- oil. Biodegradation modeling has helped in that regard (Adams et al., 2006), but solutions remain equivocal. While oilfield locations and oil maturity are often used together with basin models to constrain such models (e.g., Higley et al., 2009), the reality is that solutions are totally non-unique and in the absence of true validation data of source rock contributions and oil charge times, could have errors as large as order of magnitude level. The Re-Os method (Selby and Creaser, 2005) looks interesting, but location of metals and exchange between fluids and solids in the system is not well defined and mechanisms for how an internal radiometric clock can track oil charge or residence time remain quite uncertain. Nevertheless, age dating oil-charge is now an area of active research (Larter and Adams, 2010) and we review our approaches in developing *in situ-* petroleum- gamma ray radiolysis proxies (RVWs) as a means of assessing oil residence time profiles in petroleum reservoirs. Such approaches could provide the first reliable charge dates available but many research hurdles remain, related to source irradiation issues, searching for biodegradation resistant RVW proxies and appropriately scaling field and lab radiation dosing of petroleum molecules.

Hypothesis, methods and results:

Radiometric dating of geological events was a pivotal achievement (Holmes, 1911). Dating petroleum charge times; oil residence times and charge rate in a trap would be equally pivotal and eliminate at a stroke, much arm-waving, geopoetry and speculation, concerning charging times and routes. Charge times and rates are key variables in controlling hydrocarbon prospectivity as they define volumes of trapped petroleum and the dynamics of trap integrity, including leakage phenomena. Such constraints would allow for basin scale prospectivity estimates based on assessment of fraction of total basin charge trapped and more realistic assessment of regional caprock efficiencies when only limited cored cap rock material is available. This would be an important parameter in assessment of undersampled caprocks associated with potential CO_2 storage sites for CCS. While forward basin models provide estimates of oil charging times they are unconstrained by real measurements made on the crude oil. Oilfield locations and oil maturity can constrain models but solutions are non -unique and charge times have errors as large as an order of magnitude level. The most robust dating methods must involve oil components that do not exchange with reservoir media.

Definition of oil or gas residence time dating tools would be valuable for petroleum systems studies, and have major impacts on Alberta basin geoscience, linked with the charge studies described above. It would also potentially allow assessment of caprock efficiencies in reservoirs targeted as CCS CO_2 storage repositories even when limited coring of the caprock does not provide an adequate spatial description of caprock variability and quality. Fig. 2 shows a schematic illustration of fluid fluxes (oil, gas, water OR CO_2) in and out of a reservoir. A charged flux of a fluid (q1), contributes via storage and transport in the reservoir to leakage through the caprock-flux (q2),, and spillage from the spill point of the trap-flux (q3).. By age dating the fluid residence time profile in the reservoir and using an advective-diffusive fluid age mixing model, linked to in reservoir radionuclide distributions, in principle, the charge history and fluxes may be delimited.
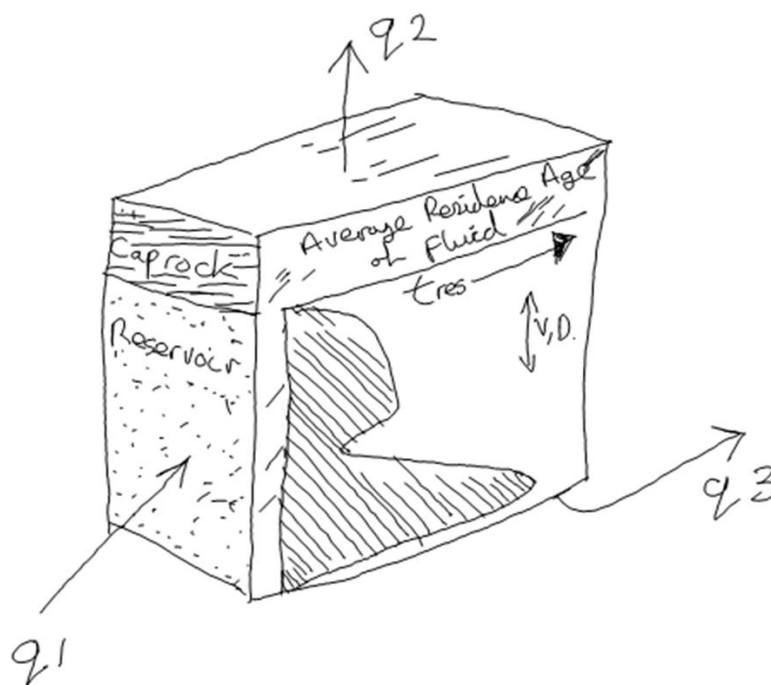
Fig 2. Schematic illustration of fluid fluxes (oil, gas, water, CO_2) in and out of a reservoir. For example a charged flux of say, oil q1, contributes via storage and transport in the reservoir to leakage through the caprock-q2 and spillage from the spill point of the trap-q3. By age dating the fluid residence time profile in the reservoir and comparing it with radio nuclide distribution using a fluid age mixing model, in principle, the charge history and fluxes may be delimited.

Frolov et al. (1998) described production of olefins in crude oils from natural radiation damage (radiolysis). If calibrated for reservoir radioactive isotope load (U, Th, K, Rn), measurement of radiolysis markers (RVWs in our parlance)), could in principle provide radiometric routes to dating reservoir residence time, but olefins are reactive, biodegradable, non-ideal proxies. Further, in-source rock irradiation loads generally exceed in-reservoir levels so an innovative approach is needed to decoupling source and reservoir irradiation effects! Our own experiments using gamma ray irradiated and non-irradiated oil samples with radiation doses equivalent to natural in-reservoir irradiation loads over geological timescales, suggest radiolysis of whole crude oils or model compound fractions, produces alternate stable hydrocarbon radiolysis markers (RVWs), including ring opened biomarkers such as secosteranes, and novel bimolecular addition compounds, as well as olefins. Polar fractions of irradiated oils also undergo change. Some RVW compounds such as secosteranes and any high molecular weight polar compounds produced likely have high biodegradation resistance.

Fig 3. illustrates two new classes of radiolysis proxies(RVWs) that have characteristics more advantageous than olefinic components. The figure shows the TIC, GCMS traces of the alkane fraction of a γ-irradiated mixture of cyclohexane and androstane. The three groups of peaks in the product represent ; 1-a series of hexane derived dimers,; 2- unreacted androstane plus ring opened steranes (secosteranes) and 3-a series of steroid-hexane reaction products. These are a few of our current RVW candidate targets and we describe some of our progress to date.

We describe a roadmap of technological needs to achieve a new generation of quantitative, highly biodegradation resistant oil charge proxies and we also analyze and describe our progress aimed at the more demanding challenge of developing and deploying a practical fluid residence time profiling tool for sedimentary basins and identify the key technical barriers to be resolved.
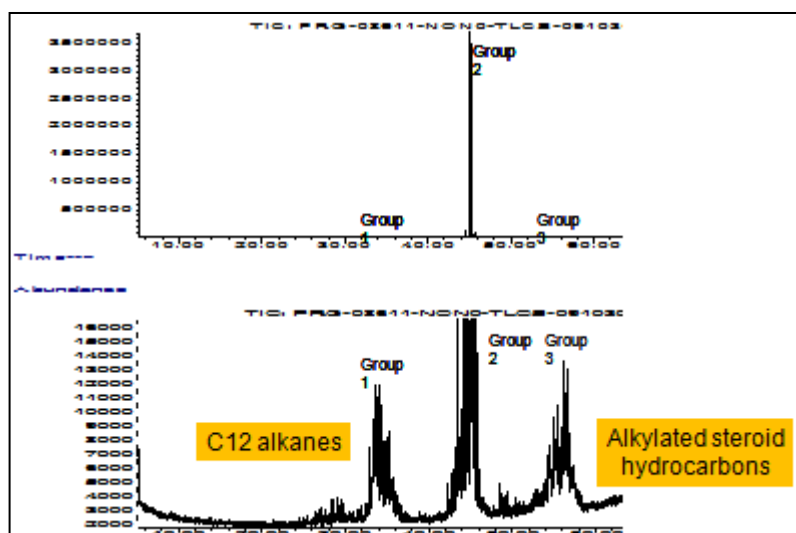
Figure 3. The figure shows the TIC, GCMS traces of the alkane fraction of a γ-irradiated mixture of cyclohexane and androstane. The three groups of peaks in the product represent; 1-a series of hexane dimers; 2- unreacted androstane plus ring opened steranes (secosteranes) and 3-a series of steroid-hexane reaction products.

Conclusions

We have reviewed the state of the art in oil charge analysis of heavy and severely degraded oils using new techniques such as FTMS and showed a roadmap for the development of the necessary new petroleum system technologies needed, including an approach to a practical fluid reservoir-residence time dating tool. Together, with larger and more comprehensive source rock and type oil samples sets, these may finally enable a quantitative solution to the which, by what route and when, of oil charging in the WCSB and elsewhere.

Acknowledgements

References

Adams, J.J., Larter, S.R., Bennett, B., Huang, H., Westrich, J. and van Cruisdijk, C. (2012) The dynamic interplay of oil mixing, charge timing and biodegradation in forming the Alberta oil sands: insights from geological modeling and biogeochemistry. AAPG Memoir- Oil sands and heavy oils of the world, Ed. Hein et al., AAPG in review.

Adams, J.J., Riediger, C.L., Fowler, M.G., and Larter, S.R. (2006) Thermal controls on biodegradation around the Peace River oil sands, paleo-pasteurization to the west: Journal of Geochemical Exploration, 89, 1-4.

Frolov, E.B., Smirnov, M.B., Melikhov, V.A. and Vanyukova, N.A. (1998) Olefins of radiogenic origin in crude oils. Organic Geochemistry, 29, 409-420.

Head, I.M., Jones, D.M., and Larter, S.R. (2003) Biological activity in the deep subsurface and the origin of heavy-oil: Nature, v. 426, p. 344-352.

Higley, D.K., Lewan, M.D., Roberts, L.N.R. and Henry, M. (2009) Timing and petroleum sources for the Lower Cretaceous Mannville Group oil-sands of northern Alberta based on 4-D modeling: AAPG Bulletin, 93, 203-208.

Holmes, A. (1911) The association of lead with uranium in rock-minerals and its application to the measurement of geological time, Proc. Royal Society, Ser. A, 85, 248-256.

Huang, H., Larter, S.R., Bowler, B.F.J. and Oldenburg, T.B.P. (2004) A dynamic biodegradation model suggested by petroleum compositional gradients within reservoir columns from the Liaohe basin, NE China: Organic Geochemistry, v. 35, p. 299-316.

Jones, D. M., Head, I. M., Gray, N. D., Adams, J. J., Rowan, A. K., Aitken, C. M., Bennett, B., Huang, H., Brown, A., Bowler, B. F. J., Oldenburg, T., Erdmann, M., Larter, S. R. (2008). Crude-oil biodegradation via methanogenesis in subsurface petroleum reservoirs. *Nature* **451**, 176-180.

Larter, S.R., Wilhelms, A., Head, I., Koopmans, M., Aplin, A., di Primio, R., Zwach, C., Erdmann, M. and Telnaes, N. (2003) The controls on the composition of biodegraded oils in the deep subsurface, Part 1, Biodegradation rates in petroleum reservoirs. Organic Geochemistry, 34, 601-613.

Larter, S.R., Huang, H., Adams, J.J., Bennett, B., Jokanola, O., Oldenburg, T.B.P., Jones, M., Head, I., Riediger, C. and Fowler, M. (2006) The controls on the composition of biodegraded oils in the deep subsurface, Part II - Geological controls on subsurface biodegradation fluxes and constraints on reservoir-fluid property prediction. AAPG Bulletin, 90, 921-938.

Larter, S. R., Adams, J.J., Gates, I. D., Bennett, B., and Huang, H. (2008) The origin, prediction and impact of oil viscosity heterogeneity on the production characteristics of tar sand and heavy-oil reservoirs.: Journal of Canadian Petroleum Technology, 47, 52-61.

Larter, S.R. and Adams, J.J. (2010) Constraining oil-charge rates and oil reservoir residence time-key variables in prospect analysis and heavy-oil fluid property prediction: AAPG Annual Convention 2010, Calgary, Alberta, 4 p.

Marcano, N.I., Mayer, B.M. and Larter, S.R. (2012) The impact of severe biodegradation levels on the stable isotopic and molecular compositions of oils in the Alberta Basin. To be submitted to Organic geochemistry.

Oldenburg, T.B.P., Brown, M., Huang, H., Adams, J.J., Bennett, B., Marcano,N. and Larter, S. (2010) Applications of FTICRMS towards evaluating source charge contributions in severely biodegraded oils; examples from the Alberta oil sands and the Liaohe basin, NE China, in AAPG International Conference & Exhibition - Frontiers of Unconventional Thinking: Saddle Up for the Ride: American Association of Petroleum Geologists, September 12–15, TELUS Convention Centre, Calgary, Alberta, Canada.

Riediger, C., Ness, S., Fowler, M.G. and Akpulat, T. (2000) Timing of oil migration: Paleozoic and Cretaceous bitumen and heavy-oil deposits, eastern Alberta. GeoCanada 2000, Paper 419, 4 p.

Selby, D. and Creaser, R.A. (2005) Direct radiometric dating of hydrocarbon deposits using rhenium-osmium isotopes. Science, 308, 1293-1295.