AAPG HEDBERG CONFERENCE
"APPLICATIONS OF RESERVOIR FLUID GEOCHEMISTRY"
JUNE 8-11, 2010 – VAIL, COLORADO

Some Future Directions in Reservoir Fluid Geochemistry

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Introduction

Reservoir fluid geochemistry, or reservoir geochemistry, is the measurement and application of compositional variations in subsurface reservoir fluids (oil, water, gas) to the solution of practical problems in the energy and environment sector. Reservoir geochemical applications in the energy sector are now many and diverse with petroleum geochemical applications dominating, but with water geochemistry being increasingly applied to problems related to well scale, well and reservoir breaching during production and reservoir souring. Reservoir geochemistry, while now a successful mainstream industrial application area, with a defined commercial presence outside of major oil company research groups (e.g., OilTracers, 2009), continues to be an area of active research and development in industry and academia. The next decade promises great developments as more refractory unconventional resources become development targets, more high tech analytica come online and reactive enhanced oil recovery becomes more common via microbiological, chemical, thermal and/or electrical means. While the industry continues to search for ever deeper or more complex plays, there is still a push to more accurately predrill predict petroleum location and quality, to scavenge stranded resources, and to monitor recovery operations *in situ* real time as carbon management issues become a priority in all aspects of fossil fuel recovery. To date, reservoir geochemical activity has been traditionally petroleum production related and that will continue, but in the future, there will be greater focus on applications related to subsurface carbon sequestration and radioactive and other waste disposal in the deep subsurface. In particular, measurement, monitoring and verification (MMV) of subsurface carbon sequestration as part of globally regulated climate change mitigation activities will become a huge area of research and application for reservoir geochemists of all subdisciplines.

Reservoir geochemistry grew out of our ability to correlate distributions of key chemical species with system state variables for fundamental processes in petroleum systems or production. While most early work was qualitative, we have seen a persistent trend towards the use of absolute quantification of petroleum components for reservoir geochemical applications. Such studies are reliant on excellent calibration data sets, which require unaltered, carefully handled, representative samples prepared for high resolution compositional imaging and quantification with state of the art analytica. Typically, these days, sophisticated data processing using both traditional chemometric tools and supervised learning methods is used to build robust models of reservoir behavior from fluid analyses. While there have been failures, there has been considerable success in developing such models and deciphering the mechanics of petroleum systems using petroleum geochemistry, aided considerably by a consistent increase in the use of absolute rather than relative component abundance data, i.e. component concentrations rather than just component ratios.

This evolution of methodology has followed exploration for ever deeper and unconventional resources which have called for expansion of petroleum geochemical protocols beyond GC resolvable hydrocarbon analysis to examine larger fractions of petroleum using LC and MS methods as well as more routine water and produced mineral solids analysis. Analysis has moved from the lab to the wellsite and down into the reservoir itself. Although exploration continues worldwide, average recoveries are below 50% and thus the challenge today is mostly enhanced recovery engineering. Gradually, the extensive understanding of geochemists is being integrated with engineering applications to solve practical problems but siloed disciplines and organizational structures still work against this union. Nevertheless, reservoir geochemistry has started to infiltrate reservoir engineering and allowed the development of production allocation constrained reservoir simulations and reactive reservoir simulations for designing and monitoring in-reservoir enhanced recovery and upgrading processes. This paper discusses areas of ongoing and likely expansion of reservoir geochemistry, with illustrative examples from some of our ongoing work, in several of these study areas as summarized in Figure 1.

Fig 1. Areas of Likely Expanded Developments in Reservoir geochemistry

- Incorporation of new and advanced analytica and data processing methodologies
- Integration of reservoir geochemistry and reservoir engineering
- Real time reservoir geochemistry and well site decision making
- Downhole fluid composition and property sensing
- Studies of Unconventional gas reservoirs including shales
- Input into design of Carbon efficient energy recover processes
- Carbon sequestration reservoir design and monitoring

Incorporation of new and advanced analytica and data processing methodologies

Petroleum geochemistry is founded on the ability to resolve and measure the compositions of complex petroleum mixtures and correlate these to a fundamental process of interest (e.g. field charging) or to differentiate between samples (e.g. barrier assessment or production allocation). The field was always driven by analytical advances coupled with effective data processing systems (e.g., CGCMS in the 1970's heralding practical source rock facies and maturity molecular concepts in use today). Today, molecular oil characterization is key to deciphering complex processes in reservoirs involving non-hydrocarbons as well as hydrocarbons, such as *in situ* processing, biodegradation, identifying key functional groups in petroleum components related to corrosion or fluid viscosity control or designing downstream processing systems for complex polar compound heavy oil mixtures. These applications require ability to examine higher molecular weight heteroatomic molecules than is possible with GC methods and to image larger fractions of oils. While a variety of more advanced GCMS technologies have been developed more recently (HTGCMS, GCMSMS, 2DGCMS, GCTOFMS), as with all GC techniques, they image only a small fraction of the total oil. The earliest tools were ideally suited to analysis of light, sweet crude oils, but now acidic, sulphur rich, polar compound rich heavy oils are becoming mainstream and require additional preparation for use of traditional GCMS methods.

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Also in the 1970's, Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICRMS) was being developed at the University of British Columbia. FTMS is capable of analyzing thousands of components in a petroleum mixture at once founding the concept of ***petroleomics*** whereby direct composition to property prediction becomes possible (Marshall and Rodgers, 2004). Four decades after invention, FTMS, often linked to advances in LC systems, has evolved into a commercially available front line tool usable by petroleum geochemists as a geochemical tool. This analytical technology will, in our view, usher in a dramatic revolution in reservoir geochemical capability. Data processing is key as data sets are measured in the gigabytes and geochemists have to learn the tricks of bioinformaticians and others. Current GCMS based petroleum geochemical protocols quantitatively determine perhaps a few hundred components. FTICRMS can potentially resolve 1000 times this number of components, which when quantitated and with accompanying molecular formulae, opens the door, ***in principle,*** to computational routes to fluid property and phase behavior calculations directly from molecular analysis. Problems with alkane ionization are being tackled (e.g. Shea et al., 2007) and we and others are researching solutions to very variable response factors and poor quantitation which are the current FTICRMS barriers to real practical utility. We describe some application areas for FTMS in the reservoir geochemical arena with examples of heavy oil variability imaging with FTICRMS and advanced data processing. Developing applications will include, in addition to high resolution versions of current applications, reservoir profiling for refinery feedstock assessment, petroleum systems studies of severely degraded oils with no conventional biomarkers and direct assessment of fluid properties and phase behavior for flow assurance and engineering applications from chemical analysis.

We also discuss the analytical challenges of two new, upcoming geochemical applications. The first is the search for effective sample storage history proxies to track sample alteration and we illustrate the use of biodegradation resistant volatile molecular indicators, such as diamondoid species in this role. Secondly, we identify dating oil residence time in a reservoir from analysis of reservoir fluids as a remaining grand challenge of petroleum systems geochemistry and we discuss possible routes to solving this challenging problem!

Integration of reservoir geochemistry and reservoir engineering

Coupling petroleum geochemical data to basin modeling simulation has been routine for many decades yet the more plausible linkage of geochemistry with reservoir simulation has yet to become routine (Larter et al., 2008). Such an application is most beneficial for heavy oil recovery operations because a defining characteristic of heavy oilfields is the systematic variation in geochemical and fluid properties over short distances within the reservoirs. High resolution geochemical fingerprints of oils extracted from reservoir core and vertical or horizontal well cuttings routinely permit high resolution fluid property mapping. These geochemical data can be tagged to simulator oil end members to predict production fluid molecular compositions for history matching to actual produced fluid chemistry, thus serving as a sophisticated 4D monitoring tool. Bennett et al. (2008) showed the application of molecular markers in produced oils to track thermal recovery and even *in situ* upgrading processes. Similarly, these types of parameters could potentially be routinely incorporated in compositional reservoir simulations in the years ahead. We describe how spatially variable geochemical signals can be coupled to reactive reservoir simulators and some of the applications of such approaches. Coupling fluid property heterogeneities to compositional reservoir simulation permits more accurate history matching procedures whereby oil composition, as well as flow data, is used to refine production models. Gas, oil and water geochemistry enabled reactive reservoir simulations will be a central part of *in situ* upgrading, carbon management and sequestration process design in the years ahead.

Real time reservoir geochemistry and well site decision making

Onsite applications of reservoir geochemistry have grown dramatically (e.g. McKinney, 2009) and this will continue. One area we have been pursuing is fluid property determination of heavy oils and bitumen at rigsite a short time after core or cuttings samples are collected. This allows several operational actions to take place while the drilling rig is still onsite, i.e.,

1. Decisions regarding the feasibility of sampling or well testing to recover production data or fluids from vertical or horizontal wells (MDT, DST or extended production test) can be made based on data generated in real time at wellsite from core or cuttings;
2. Decisions on where to place a horizontal cold production well to maximize recovery, can be made from analysis of fluid property variations from a vertical pilot well segment while the rig is still onsite minimizing drilling costs; and,
3. Recovery of ultrafresh samples for accurate fluid property or geochemical measurement, free from sample handling artifacts, which can be substantial in super heavy oils.

Measured oil viscosity is now known to be a function not only of intrinsic oil properties (source and maturity) and in reservoir alteration processes, but also sample storage conditions (Adams et al., 2008). Volatilization of light ends during sample storage, handling, extraction and cleaning most significantly affects the measured viscosity of heavy oils and bitumen. Geochemical composition of oils with relevance to reservoir geochemists can also change with storage so some geochemical measurements are best made with very fresh samples. We describe onsite reservoir geochemical studies looking at changes in heavy oil fluid properties through time and discuss impact of storage time effects on molecular oil geochemistry comparing fresh samples with conventionally stored and processed reservoir samples.

Downhole fluid composition and property sensing

Chemical and fluid property analysis of reservoir fluids extracted from the reservoir under *in situ* reservoir conditions is a holy grail of reservoir geochemistry. This is especially important in heavy oil fields where the petroleum often will not flow at native reservoir conditions. Great advances in our ability to sample and characterize reservoir fluids under *in situ* conditions have been made in the last decade with dynamic well testing systems coupled to optical spectrometers leading the way currently (Mullins et al., 2002; Vanuffelen et al., 2008). While developments have been dramatic and successful, current tools cannot provide the molecular information necessary for many geochemical applications. Given our capabilities to send advanced analytical instrumentation across the solar system it is surprising that more sophisticated instrumentation is not used a mere few kilometers below our feet! We can expect an explosion of activity in this area given the looming need to design and monitor carbon dioxide injection and storage programs associated with carbon management activities. We expect carbon management associated reservoir geochemistry and downhole sensors for CO_2 and storage reservoir water chemistry to be a large expansion area in the next decade as monitoring and verification of the quantities of large volume carbon dioxide storage becomes routine. We discuss the challenges of such sensors.

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We summarize our own attempts to develop instrumentation for direct sampling and geochemical or fluid property analysis of reservoir fluids (oils, waters, gases) *in situ* and describe key technical boundaries to be crossed if high resolution molecular geochemical applications of such data to practical problems are to be performed *in situ* on a routine basis. We provide one roadmap of *in situ* geochemical fluid analysis and application from the perspective of a petroleum geochemist.

Geophysics is the primary tool of petroleum exploration and geochemists always played an important, but often secondary, geoscience role in that arena. In the 21st century however, production and carbon management issues will dominate. Global energy demands require significant and rapid upscaling of the current energy supply systems system while synchronously reducing carbon emissions through more carbon efficient recovery processes and carbon capture and storage. This presents entirely new challenges to reservoir geochemists who will emerge from their traditional supporting roles to take centre stage in the integrated, chemically constrained, reservoir geoengineering disciplines that are emerging. Just as chemistry is now the backbone of biology and materials science, reservoir geochemistry will become the keystone of the reactive reservoir engineering discipline that will underpin 21st century reservoir management.

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