

## Mo and Ni isotope systematics in petroleum fluids across subsurface alteration gradients

COREY ARCHER<sup>\*1</sup>, TIM ELLIOTT<sup>1</sup>, SANDER VAN DEN BOORN<sup>2</sup>,  
PIM VAN BERGEN<sup>3</sup>

<sup>1</sup>Bristol Isotope Group, School of Earth Sciences, University of Bristol, BS8 1RJ, UK (\*c.archer@bristol.ac.uk)

<sup>2</sup>Shell Projects and Technology, Rijswijk, The Netherlands

<sup>3</sup>Shell Upstream International Europe, Aberdeen, UK

The presence of trace metals in oils has long been of interest for both their beneficial and detrimental effects during hydrocarbon exploration and processing, respectively. For example, the diagnostic potential of trace metals incorporated in fluids and source rocks has been successfully applied in various fingerprinting studies. The majority of work to date has focussed on the two most abundant metals in oils, vanadium (V) and nickel (Ni), where abundances and elemental ratios have been used as tools in correlation and fingerprinting, and provide information on redox conditions during source rock deposition [1]. Here, we focus on the molybdenum (Mo) isotope system, well known to display a bi-polar redox chemistry [2], and similarly explore the potential of Ni isotopes, with the aim of developing valuable new tools to exploit in petroleum systems' studies.

We have developed techniques for the determination of Mo and Ni isotopes in hydrocarbon (HC) fluids. The analyte is extracted from its complex organic fluid matrix, through high pressure ashing, which renders the complete decomposition of the HC fluid, allowing the Mo and Ni from the same sample fraction to be purified via conventional ion-exchange methods. Data from replicate analyses of both samples and an NIST HC standard suggest a precision of better than 0.1‰ in both  $\delta^{98/95}\text{Mo}$  and  $\delta^{60/58}\text{Ni}$ . These techniques are applied to co-genetic oil samples from a well characterised petroleum system to investigate Mo and Ni isotope systematics across subsurface alteration gradients (e.g. maturation, biodegradation and migration).

The co-genetic samples thus far analysed show remarkably invariable  $\delta^{98/95}\text{Mo}$  values along various alteration gradients, such as maturation. This is in contrast to many organic geochemistry proxies which are traditionally employed to examine these changes in HCs, and an overall  $\delta^{98/95}\text{Mo}$  range of ~1.5‰ for the entire HC dataset (incl. samples from other petroleum systems). Ni is much more variable along the studied gradients, displaying a range in  $\delta^{60/58}\text{Ni}$  from -0.5‰ to +0.8‰, suggesting a different mechanistic behaviour to Mo. These results highlight the potential of Mo isotopes to be used as a new tool in oil-oil/source rock correlations on a basin-wide scale, whereas Ni isotopes may prove to be useful in the characterization of processes operating on more restricted spatial scales.

[1] Lewan, M.D. (1984). *Geochim. Cosmochim. Acta* **48**, 2231-2238. [2] Erikson, B.E. and Helz, G.R. (2000). *Geochim. Cosmochim. Acta* **64**, 1149-1158.

## Stable isotope geochemistry and the optimization of hydraulic fracturing of petroleum wells – lessons from the Bakken Formation in Canada and the USA

SERGUEY ARKADAKSKIY<sup>1\*</sup> AND BEN ROSTRON<sup>2</sup>,

<sup>1</sup>Isobrine Solutions Inc., Edmonton, Canada, [serguev@isobrine.com](mailto:serguev@isobrine.com) (\*presenting author)

<sup>2</sup>University of Alberta, Earth and Atmospheric Sciences, Edmonton, Canada, [ben.rostron@ualberta.ca](mailto:ben.rostron@ualberta.ca)

Hydraulic fracturing (a.k.a. fracing) is an established method for petroleum well stimulation used to enhance reservoir permeability through the creation of artificial fractures by injecting aqueous fluid under high pressure in the target zone. Recent developments of that technology have allowed petroleum production from low permeability reservoirs previously considered uneconomic. Hydraulic fracturing combined with precise horizontal drilling has provided access to tens, perhaps hundreds of Bbbls of high quality light crude oil in the late Devonian/early Mississippian Bakken Formation in the Williston Basin [1]. The Bakken reservoir is a thin (13 m on average) dolomitic silt/sandstone horizon sandwiched between two organic-rich marine shales. Oil and gas generated in the shales migrated to and remained for the most part within the Middle Bakken reservoir [2], which close to the basin center (USA) is largely water unsaturated but exhibits various degrees of water saturation in the thermally immature parts near the edges of the basin (Canada). Unexpected and/or excessive water co-production following high volume multistage fracing of horizontal wells drilled throughout the basin has been of concern lately. Since both the overlying (i.e., the Mississippian Lodgepole) and the underlying (the Devonian Torquay and Nisku/Birdbear) formations are water-saturated, it has been hypothesized that fracing may have resulted in fracture propagation into these formations. Questions have also been raised about the presence and/or apportioning of fracing fluids and/or other service/maintenance fluids in the co-produced waters. While standard formation water identification techniques have been largely unable to provide unambiguous answers to those questions, stable isotope geochemistry and other geochemical techniques have met with greater success. In this presentation we will discuss the application of stable isotope geochemistry and other geochemical methods for identifying the source(s) of different fluids in waters co-produced from horizontal Bakken wells stimulated with hydraulic fracturing. We will also discuss the impact our findings have been having on petroleum producers in the basin and the changes these have made to their hydraulic fracturing practices in order to minimize unwanted water co-production.

[1] Flannery & Kraus (2006) *Am. Assoc. of Petrol. Geol. Search and Discovery Article* No.10105 [2]. Halabura, Buatois, Angulo and Piche (2007) in *Summary of Investigations 2007 vol. 1, Sask. Geol. Surv. Misc. Rep.* 2007-4.1 pp.8