APPLICATION OF TWO-DIMENSIONAL GAS CHROMATOGRAPHY IN FINGERPRINTING SOUR GAS ASSOCIATED OILS: MOLECULAR CONSTRAINTS FOR BSR AND TSR RELATED SULFUR ISOTOPE FRACTIONATION

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Understanding the origin of the H_2S has important implications for petroleum exploration, health and safety, reservoir management, and production facilities and well design in carbonate-evaporite basins. Many geochemical parameters have been developed to delineate the chemical and isotopic effects due to bacterial (BSR) and thermochemical sulfate reduction (TSR), with various degrees of success. In this study, we apply the state-of–the-arts two dimensional gas chromatography to fingerprint sour gas associated oils as a rapid tool for decoupling what was involved in sulfur isotope fractionation at the molecular level. This paper reports the results and data interpretation strategies from a well-documented case study in Western Canada Sedimentary Basin and applies the same approach to the ZLZ field in the Bohai Bay Basin where the origin of high H_2S gases remains problematic.

The Upper Devonian Nisku Formation reservoirs in west-central Alberta, Canada produce oil and sweet and sour gas condensate (Manzano et al., 1995). Generally, oil pools are located updip in the study area and sour (6-31% H_2S) gas condensate downdip. H_2S in the study area was formed by TSR, and all liquid hydrocarbons probably have one source, with the Duvernay Formation being the most likely candidate. The origins of the gases are supported by their chemical compositions, stable carbon and sulfur isotopes of various chemical species, and the occurrence of pyrobitumens in the reservoir. The distribution of the gas accumulations is controlled dominantly by reservoir temperature. The TSR origin of H_2S in the gases is clearly reflected by the occurrence of little or no common polycyclic and aromatic hydrocarbons, but rather by the abundance of sulfur-containing heterocycles with random chemical structures that show $\delta^{34}S$ values approaching those of the starting sulfate (Fig. 1A).

The ZLZ gas field in the Jinxian Sag, Bohai Bay Basin represents a contrasting case where gases containing 40-92% H_2S are co-produced with sulfur-rich heavy oils of less than 12^{o}API. Both the source and reservoir rocks of this petroleum system are within the Eocene-Oligocene lacustrine clastic-evaporitic sequence. As many of the reservoirs show temperatures below 80-90°C, the very high concentrations of H_2S were probably generated external to the reservoir. Molecular evidence for the origin of the heavy oils from a hypersaline lacustrine source rock include relatively low pristane/phytane ratios, high gammacerane/hopane ratios, and extremely high (pregnane + homopregnane)/C_{27}-C_{29} sterane ratios. The low abundance of n-alkanes relative to acyclic isoprenoid/cyclic alkanes in the oils was more likely the result of early generation from a sulfur-rich kerogen, rather than oil biodegradation in the reservoir. The availability of extensive cores and other fluids in the ZLZ Field also enabled us to obtain valuable sulfur isotope data from various geological substrates, but unfortunately no gas samples were available for determining the $\delta^{34}S$ values of H_2S. The $\delta^{34}S$ values of the anhydrite samples in the likely source rocks range from +30 to +35 ‰CDT, whereas those of the elemental sulphur in the reservoirs and sour gas associated oils are approximately 20-30‰ lighter. This large fractionation is incompatible with a simple TSR origin. The presence of abundant backbone benzothiophenes and dibenzothiophenes (**1** & **2**, Fig. 1B) together with structurally highly specific hopanoid and steroid thiophenes (**3** & **4**, Fig. 1B) indicates that the extreme sulfur enrichment in the oil could result from back-reactions between TSR-derived H_2S and evaporite-sourced petroleum.

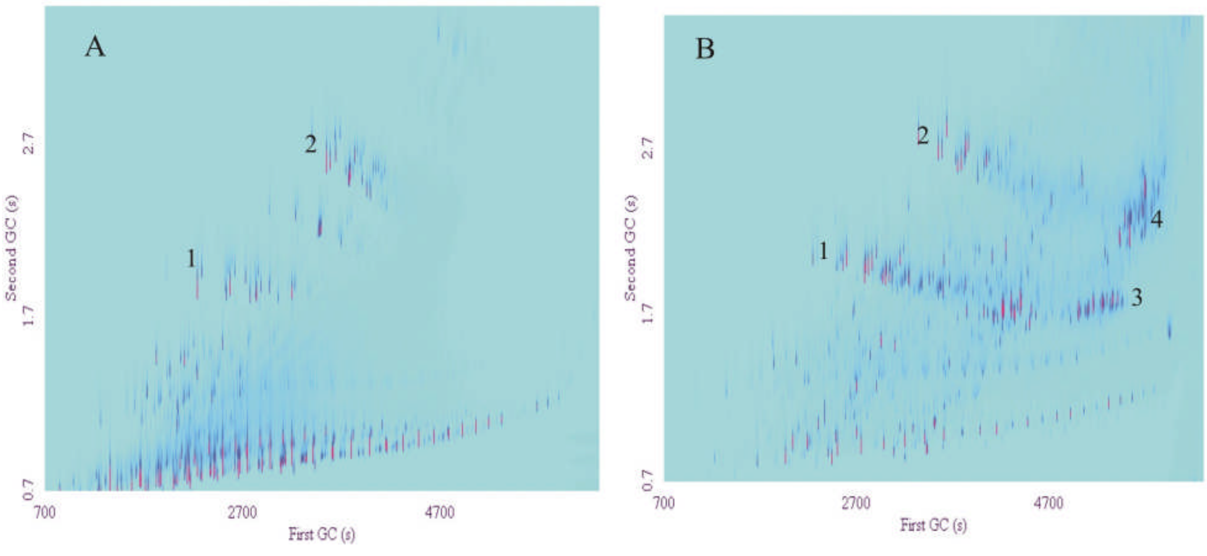

Figure 1. GCxGC-FID data showing molecular distributions in two sour gas associated oils: (A) light condensate from Pool P, Nisku reservoir, Alberta; (B) heavy oil from Zh7 well, Jinxian Sag, Bohai Bay Basin. Compounds: 1. benzothiophenes; 2. dibenzothiophenes; 3. steroid thiophenes; 4. hopanoid thiophenes.

REFERENCES

Manzano, K., Fowler M., Machel, H.G. (1997) The influence of themochemical sulphate reduction on hydrocarbon components in Nisku reservoirs, Brazeau river area, Alberta, Canada. *Organic Geochemistry* **27**, 507-521.