

## SULFUR ISOTOPES AS MARKERS OF OIL-SOURCE CORRELATION AND THERMOCHEMICAL SULPHATE REDUCTION IN CENTRAL TARIM

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Oils and natural gas have been found from the Carboniferous, Silurian and Ordovician in Central Tarim. However, there still exists debate on the source of the petroleum since the potential source rocks (Cambrian and Lower Ordovician and/or the Middle-Upper Ordovician) show high maturity and similar biomarker and carbon isotopic composition. Thus, we report an attempt to apply  $\delta^{34}\text{S}$  values to oil-source rock correlation here.

Two potential source rock samples were analyzed for  $\delta^{34}\text{S}$  values. One is marlstone taken from the Upper Ordovician from Well TZ12 with TOC of 0.8% and vitrinite reflectance value ( $R_o$ ) of 0.8%. The other is mudstone from Well TD2 with TOC of 1.8% and  $R_o$  of 1.7%. Kerogen separated from the Middle-Upper Ordovician marlstone has  $\delta^{34}\text{S}$  value of 0.86‰. The value is much lower than that of kerogen from the Cambrian mudstone (22.5‰).

Whole oils from the Ordovician are relatively sulphur-poor, and have  $\delta^{34}\text{S}$  values from 13.6 to 19.9‰ (n=6) and  $\delta^{13}\text{C}$  values from -31.3 to -32.7‰ (n=4). Carboniferous and Silurian oils are relatively rich in sulphur, and have  $\delta^{34}\text{S}$  values from 20.0 to 25.8‰ and  $\delta^{13}\text{C}$  values from -30.3 to -32.6‰ (n=5). The oils show similarly low  $\delta^{13}\text{C}$  value, but significantly higher  $\delta^{34}\text{S}$  values than the Upper Ordovician kerogen. If an oil is directly decomposed from kerogen,  $^{32}\text{S}$ -rich components are expected to be preferentially cracked down, producing an oil with relatively low  $\delta^{34}\text{S}$  value and residual kerogen with high  $\delta^{34}\text{S}$  value. Thus, based on the  $\delta^{34}\text{S}$  values, it can be concluded that the oils in the Central Tarim are unlikely to have been derived from the Middle-Upper Ordovician kerogen, but most likely from the Cambrian and Lower Ordovician. The proposal is supported by the fact that most of the oils have  $\delta^{34}\text{S}$  values lower than the Cambrian kerogen. However, one oil sample from the Silurian has  $\delta^{34}\text{S}$  value of 25.8‰, being significantly higher than the Cambrian kerogen. Additionally, positive correlative relationship occurs between sulphur content and  $\delta^{34}\text{S}$  value. The features can not be explained by kerogen decomposition, but have been concluded to be a result of incorporation of TSR-derived  $^{34}\text{S}$ -rich  $\text{H}_2\text{S}$  into biodegraded oils. TSR in Central Tarim is further supported by new data in this study, as explored in the following.

In the Ordovician, 0.1% to 2%  $\text{H}_2\text{S}$  by volume were detected in gas cap associated with oil pools or in separated gas pools.  $\text{H}_2\text{S}$  may be up to 3.75% after acidification and

abundant pyrite were found in the reservoirs such as in wells TZ83 and TZ12 in Central Tarim. H<sub>2</sub>S and pyrite have  $\delta^{34}\text{S}$  from 15 to 29.7‰. In the Silurian and Carboniferous, up to 3% cubic pyrite was found in sandstone reservoirs but no sulphate minerals occur. The  $\delta^{34}\text{S}$  values of pyrite have a wide range from 9.5 to 34‰ (Cai et al., 2001). Abundant sulphides (H<sub>2</sub>S and pyrite) and variable  $\delta^{34}\text{S}$  values have been concluded to have a complex origin, i.e., from both TSR in the Cambro-Ordovician and epigenic BSR (Cai et al., 2001).

Anhydrite and barite veins in Ordovician limestone show  $\delta^{34}\text{S}$  values from 24.5 to 45.9‰ (n=3), and from 45.3 to 46.6‰ (n=2), respectively. Most of the values are significantly higher than that of unaltered anhydrite in the Ordovician and Cambrian with  $\delta^{34}\text{S}$  of 26‰ and 34‰, respectively. Replacement of barite by calcite and high homogenization temperatures of barite and calcite (90 to 140°C) indicate that abnormally <sup>34</sup>S-rich sulphates may be a residue of TSR (Alonso-Azcarate et al., 2001) but not of BSR since the temperatures are generally thought to be too high for bacteria to grow. Given TSR occurs in the veins, H<sub>2</sub>S and pyrite with low  $\delta^{34}\text{S}$  values are expected to generate due to sulphur isotope fractionation, thus sulphides with  $\delta^{34}\text{S}$  values from 9.5 to 20‰ may have resulted from TSR in Upper Ordovician vein, organic and/or epigenic BSR origin. In contrast, H<sub>2</sub>S with high  $\delta^{34}\text{S}$  values may have been derived from TSR in the Cambrian and Lower Ordovician (Cai et al., 2001), resulting in cubic pyrite in the Ordovician and Silurian reservoirs with  $\delta^{34}\text{S}$  values higher than 25‰.

In summary, TSR may have occurred in Cambro-Ordovician, resulting in <sup>34</sup>S-rich residual sulphates. Oils from the Palaeozoic reservoirs were unlikely derived from Upper Ordovician kerogen but most likely from the Cambrian based on  $\delta^{34}\text{S}$  values. Subsequently, TSR-derived <sup>34</sup>S-rich sulphides may have been incorporated into the oils, resulting in part of the oils have  $\delta^{34}\text{S}$  values higher than the potential source rock and positive relationship between  $\delta^{34}\text{S}$  value and sulphur content.

#### ACKNOWLEDGEMENTS

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