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Oil-anhydrite TSR (thermochemical sulfate reduction) processes in the Permian Khuff Fm, Saudi Arabia

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Thermochemical sulfate reduction (TSR) occurs when anhydrite reacts with petroleum resulting in calcite, H_2S and other reduced sulfur compounds. Analysis of 10 wells from the sour Permian Khuff Fm from Ghawar and neighboring fields in Saudi Arabia using geochemistry, stable isotopes, fluid inclusions and petrography has confirmed that H₂S is due to TSR. Anhydrite has been replaced by calcite and sulfur. However, of all the various types of anhydrite, only nodules composed of microcrystalline anhydrite have undergone TSR. Replacive calcite is poorly developed in many cases with much anhydrite remaining even in reacted nodules. Some wells have no finely crystalline anhydrite, and thus have no H_2S . Fluid inclusion analysis revealed that: (1) the initial charge was oil, later displaced or diluted by gas, (2) TSR occurred between 113°C and 135°C in the presence of oil. TSR thus occurs at a lower temperature with oil than with dry petroleum gas ($>140^{\circ}$ C). Based on petrography and fluid inclusion analysis, TSR is only at an early stage at Ghawar. This may be due to one of: lower temperatures than in other sour gas provinces, recent cooling, the recent emplacement of less reactive petroleum (i.e. gas) or the isolating effect of TSR calcite that grows on the finely crystalline anhydrite nodules. The petroleum seems to have been altered by TSR since there is a correlation between the overall H_2S percentage and both the sulfur content and the sulfur isotope ratio of the liquid petroleum. As H₂S from reaction between anhydrite and petroleum accumulated there was back-reaction of H2S with remaining liquid phase petroleum and the generation of a suit of dibenzothiophenes. With advancing TSR and H₂S accumulation, the oil progressively changed from typical petroleum $?^{34}$ S values ($\geq 0\%$,) to the sulfur isotope ratio of Permian anhydrite (+9%). TSR in liquid petroleum accumulations thus not only results in the

replacement of anhydrite by calcite and petroleum fluids by H_2S , it also results in the generation of new sulphur bearing organic compounds.