

Evidence for cross formation hot brine flow from integrated $^{87}\text{Sr}/^{86}\text{Sr}$ and REE data in Central Tarim

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In Central Tarim, commercially oil and gas has been produced from fluorite reservoirs in the Ordovician carbonates. The fluorite occurs as replacement of carbonate wallrock and fracture fillings. Associated minerals with the fluorite include barite, anhydrite, calcite, quartz and pyrite. Calcite veins show wide ranges of fluid inclusion homogenization temperatures (HTs) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.70797 to 0.70977) and have $\delta^{13}\text{C}$ values close to the ambient limestone. Anhydrite and fluorite veins have lower HTs and show much higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.70912 to 0.71036) than barite (~ 0.7090) and bulk limestone (0.7064 to 0.7094), but closer to the present brines (0.71026 to 0.71109), suggesting mixing of relatively hot Ba-rich and ^{87}Sr -depleted fluid with relatively cool ^{87}Sr -rich fluid. The cooler ^{87}Sr -rich fluid has been proposed to have been derived from the west to the Central Tarim (Cai *et al.*, 2001a). The hotter fluid was most likely derived from pre-Cambrian clastic rocks or/and from the basement. This proposal is supported by REE data. REE data of calcite, anhydrite and fluorite veins are characterized by a similar pattern with a positive Eu anomaly and LREE enrichment relative to HREE. The positive Eu anomaly indicates a reducing, hot fluid ($>200^\circ\text{C}$) during migration. The positive correlative relationships of Eu to Ba, Sr and Zn suggest that the hotter fluid was enriched in Eu^{2+} , Ba^{2+} , Sr^{2+} and Zn^{2+} . When the hotter fluid mixed with the cooler fluid, barite and calcite precipitated at $\sim 145^\circ\text{C}$. With increasing mixing proportions of the cooler ^{87}Sr -rich fluid and decreasing temperatures (~ 100 to 120°C), Eu^{2+} was reoxidized to Eu^{3+} , subsequently Eu^{3+} , Ba^{2+} , Sr^{2+} and Zn^{2+} replaced Ca^{2+} and entered into Ca-minerals including calcite, anhydrite and fluorite, resulting in the Ca-minerals having more radiogenic Sr than earlier precipitated barite. The hotter fluid was likely up-migrated from the pre-Cambrian clastic rocks and/or the basement through faults because all $^{87}\text{Sr}/^{86}\text{Sr}$ measurements on brines and veins are higher than the underlying Ordovician and Cambrian carbonates. The hotter fluid collected H_2S with $\delta^{34}\text{S}$ values of +15 to +18‰ generated by thermochemical reduction of brine sulfates in the Cambrian and Ordovician (Cai *et al.* 2001b), resulting in very positive $\delta^{34}\text{S}$ values of barite ($\sim +45\%$).

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References

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Significance of the variation characteristics of interlayer water in smectite of source rocks

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The characteristics of interlayer water bonded to organic matter in interlayer of smectite were determined by thermo-XRD, DTA, TG and PY-GC for organo-clay complexes extracted from source rocks, and it plays an important role in explaining formation and migration of hydrocarbon in source rocks. As revealed by XRD curves, the d_{001} reflected peak decreases under temperature of 250°C - 500°C and not reaches 1.00nm until 550°C , which is obviously different from smectite that keeps on 1.00nm from 250°C to 500°C . Similarly, DTA curves show some exothermic peaks in the same temperature range. These observations clearly indicate that there is organic matter in smectite interlayers. PY-GC results show that the number of expelled organic matter is large under temperature of 250°C - 500°C and in turn the temperature range is the just expulsive temperature span for interlayer organic matter. These pyrolysis products have a bimodal distribution dominated by short-chained C5 and long-chained C25 hydrocarbon, suggesting the interlayer organic matter correlate to oil components.

There are two vales, interlayer water and textural water endotherm vales, near 100°C and 600°C respectively, in DTA curves, which are similar to smectite completely, while a new endotherm vale appears at 500°C , which is characteristic of organo-clay complexes. PY-GC results also provide evidences supporting the existence of endotherm vale at 500°C . Moreover, there was still diffraction peak corresponded to smectite at 500°C XRD curve, implying smectite structure kept intact and the expelled water is interlayer water rather than structure water of clay.

Taken together, we find interlayer organic matter expelled at 500°C , followed by expulsion of interlayer water, suggesting the water may be water bridge between organic matter and smectite, which has a great influence on the hydrogenation on hydrocarbon generation. Curve fitting of the DTA and TG show that the expelled water at 500°C accounts for 4-6%, which may provide dynamic force and be a good medium for petroleum migration.

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