

## THERMODYNAMICS OF THE GEOCHEMICAL CYCLE OF SULFUR IN SEDIMENTARY BASINS

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Sulfur is involved in many reactions governing the evolution of petroleum systems, from the sulfurization of functionalized lipids by bacterially produced H<sub>2</sub>S during early diagenesis (Sinninghe Damsté et al., 1989) to the reactions occurring during thermochemical sulfate reduction (Goldstein and Aizenshtat, 1994; Machel, 2001). Recent efforts in calculating thermodynamic properties of organic compounds (Helgeson et al., 1998; Richard and Helgeson, 1998; Richard, 2001) which are consistent with those for mineral, gas, and aqueous species make it possible to characterize organic/inorganic reactions as a function of temperature, pressure, and oxygen fugacity. The purpose of the present communication is to present a comprehensive thermodynamic analysis of the reactions which are responsible for the distribution of sulfur among minerals, aqueous solutions, petroleum, and natural gas in sedimentary basins.

The calculations are based on the computation of equilibrium constants for reactions involving minerals, kerogens, liquid hydrocarbons and organic sulfur compounds, aqueous sulfur-bearing species, and H<sub>2</sub>S gas. These equilibrium constants are used together with expressions of the law of mass action to generate activity and fugacity diagrams, which can be compared with experimental studies or compositional data reported in the literature. Such comparisons demonstrate for example that in detrital source rocks, kerogen, pyrite, and organic sulfur compounds may coexist at equilibrium under low fugacities of H<sub>2</sub>S which are in the range of those generally encountered in detrital environments. In carbonate reservoirs, the absence of significant amounts of iron-rich minerals results in higher fugacities of H<sub>2</sub>S which appear to be controlled by metastable equilibrium states between hydrocarbons, organic sulfur compounds, and elemental sulfur (Richard et al., 2005). It is also found that increasing the fugacity of H<sub>2</sub>S in a reservoir results in a higher content of organic sulfur compounds in the coexisting hydrocarbon phase, which is in agreement with observations made in reservoirs affected by thermochemical sulfate reduction (Manzano et al., 1996).

Such calculations may have important implications both for the petroleum industry (e.g. in studies of enhanced oil recovery or the sequestration of CO<sub>2</sub>-H<sub>2</sub>S acid gas mixtures in

depleted hydrocarbon reservoirs) and geochemists investigating the global biogeochemical cycle of sulfur.

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