

Pyrite Oxidation in Shale Matrices after Exposure to Fracture Fluid

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Introduction of fracture fluids into shales initiates a myriad of fluid-rock reactions that can strongly influence migration of fluid and hydrocarbon through shale/fracture interfaces. In this study, we quantify the reaction depth in the shale matrices as a function of shale structure, mineralogy composition, and aqueous chemistry of the fracture fluid. Marcellus (high clay and low carbonate) and Eagle Ford (low clay and high carbonate) shale cores were reacted with fracture fluids for 3 weeks at elevated pressure and temperature (80 °C, and 77 bars). In the carbonate-poor Marcellus system, fluid pH increased from 2 to 4. Sulfur and iron X-ray fluorescence maps of the cross sections show partial oxidation of pyrite by oxygen in fracture fluids within the entire 1-cm-diameter core. When additional Ba²⁺ and SO₄²⁻ were present ($\log_{10}(Q/K)=1.3$), barite precipitation was observed close to the surface of the core, and pyrite oxidation in the core is reduced, indicating that the layer of barite secondary precipitates has reduced diffusivity of the shale matrix. In the carbonate-rich Eagle Ford system, fluid pH increased from 2 to 6 due to calcite dissolution. This rapid change in pH resulted in more extensive barite precipitation in the system, which is expected to reduce matrix diffusivity more significantly. The changes in transport property of the shale matrices are expected to alter the efficiency of gas production.