**Pore Scale Control of Gas and Fluid Transport at Shale Matrix-Fracture Interfaces**

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**METHODS**

- **Geochemical controls over barite formation:**
  - Barium is ubiquitous in hydraulic fracturing systems:
    - > 1 g/kg oil/gas shales
    - > 10 g/kg drilling mud
    - > 5 g/L produced water
  - Depending on the shale play, barite precipitation is highly problematic.
  - Barite has low solubility for sulfates (Ksp = 10^-9.34)
  - Numerous sources of Ba:
    - Barite
    - BaCO₃
    - Ba-sorbed to clays
    - Ba-infused drilling mud
  - Unknown if organic additives in fracture fluid inhibit or enhance barite precipitation.

- **Fluid-Shale Permeability Controls**
  - Alteration in porosity, diffusivity, and permeability of shale matrix can affect the efficiency of hydrocarbon production.
  - A few studies on chemical reactions with shale samples were conducted using fractured cores and shale sands, focusing on fracture surface alteration.
  - We aim to examine chemical reactions in shale matrices, and seed answers to several questions:
    - How deep do the reactions penetrate into the matrix? Is it in nm or μm scale?
    - Does porosity alter in nanoscale or microscale?
    - What are the effects on diffusivity and permeability of the matrix?
    - How would mineralogy of the shale affect the results?
    - How does barite scale formation affect alteration of the shale matrix?

- **METHODS**
  - Whole cores of Marcellus and Eagle Ford were reacted at 80 °C and 77 bar for three weeks at both dissolution- and precipitation-favorable conditions.
  - Micro-CT images will be collected for pre- and post-reaction cores.
  - Cross sections of the pre- and post-reaction cores were cut for analyses.

- **RESULTS**
  - **Marcellus (Pennsylvania):**
    - Dissolution-favorable (Frac. Fluid)
    - Precipitation-favorable (Frac. Fluid + 30 (barite) = 1.3)
  - **Eagle Ford:**
    - Dissolution-favorable (Frac. Fluid)
    - Precipitation-favorable (Frac. Fluid + 30 (barite) = 1.3)

- **CONCLUSIONS**
  - pH and Ionic Strength have a strong influence on barite precipitation:
    - ≤ pH 2 and High I.S. (≥0.99M) lower halts precipitation.
  - Ethylene glycol (anti-scaling agent) has no effect on barite scale production.
  - Citrate, guar gum, glutaraldehyde, and polyethylene glycol slow precipitation.
  - Marcellus-derived bitumen, acetate, benzene, and methanol enhance precipitation.
  - Ammonium persulfate significantly enhance precipitation with ~2/3 of total Ba precipitated in 6 minutes.
  - Core scale experiment show that barite scale formation precipitation was most obvious in shales with high pH buffering capacity.
  - Scale formation on the shale surface inhibits Fe leaching from shale matrices.
  - Permeability measurements for shale matrices before and after reaction are in progress.

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