

Geochemistry of shale-fluid reactions at pore and fracture scales

J.R. BARGAR¹, A. JEW², A. HARRISON³, A. KISS⁴, A. KOHLI⁵, Q. LI⁶, K. MAHER⁷, AND G.E. BROWN, JR.⁸

¹ SLAC National Accelerator Laboratory, Menlo Park, CA, USA. bargar@slac.stanford.edu

² Geological Sciences, Stanford University, Stanford, CA. adamjew@stanford.edu

³ Géosciences Environnement Toulouse, CNRS, Toulouse, France. anna.harrison@get.omp.eu

⁴ SLAC National Accelerator Laboratory, Menlo Park, CA, USA. andykiss@slac.stanford.edu

⁵ SLAC National Accelerator Laboratory, Menlo Park, CA, USA. ahkoli@stanford.edu

⁶ SLAC National Accelerator Laboratory, Menlo Park, CA, USA. qyli@stanford.edu

⁷ Geological Sciences, Stanford University, Stanford, CA. kmaher@stanford.edu

⁸ Geological Sciences, Stanford University, Stanford, CA. gordon.brown@stanford.edu

Fluid-rock geochemistry profoundly impacts the behavior and response of shales to hydraulic fracturing. Stimulation fluids are at disequilibrium with shale reservoirs and drive porosity alteration and mineral precipitation, with important implications for transport of fluids, gases, and contaminants. The complexity of these processes, shale texture and pores structure, and variability in fracture fluid compositions hinder modeling and quantitative understanding of shale-fluid interactions. Better knowledge of fundamental shale-fluid interactions is needed to increase hydrocarbon production efficiencies and reduce environmental impacts.

We have systematically investigated geochemical reactions between fracture fluids and shales, with emphasis on carbonate, pyrite and kerogen reactivity. Reaction products in shale pores have been studied with multi-scale synchrotron computed tomography and spectroscopy, and geochemical modeling has been performed to quantify mineral dissolution, precipitation, iron redox, and contaminant release. Reaction progress was strongly dependent on shale mineralogy. For example, low pH inhibited precipitation of Fe(III) oxyhydroxides and aluminosilicates. At near-neutral pH, Fe(II) oxidized more rapidly and precipitated as Fe(III)(oxy)-hydroxides. Natural organics and additives dramatically accelerated oxidation Fe(II), even under acidic conditions. Uranium initially released was subsequently attenuated by uptake on Fe(III)(oxy)-hydroxides. Our new process models provide the foundation for predictively model modifications to the shale matrix-fluid interfaces and their impacts on hydrocarbon migration and pore fluid composition.