

Quantifying the isolation performance of CO₂ reservoirs: Requirements, results, and challenges

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Transitioning the technical focus of CO₂ flood operations from the efficient extraction of hydrocarbons (CO₂ EOR) to the secure emplacement of CO₂ (+/- EOR) involves significant paradigm shifts for the oilfield services industry. Most important among these are new requirements to predict and monitor the fate of isolated (un-recycled) CO₂, which in turn requires baseline site (versus solely reservoir) characterization. Meeting these requirements demands the development of new modeling, monitoring, and characterization techniques. The isolation performance of engineered (and natural) CO₂ reservoirs is largely controlled by multiphase CO₂ migration, dynamic CO₂ mass partitioning among physical/chemical sinks, and reservoir/seal permeability evolution, all of which are strongly dependent upon specific integrated processes and system properties. These correlations can be quantified through reactive transport modeling, within which the operative processes of multiphase flow, geochemical mass transfer, and geomechanical deformation are explicitly integrated. In particular, important structural, compositional, and integrated-process constraints on CO₂ migration, mass partitioning dynamics, and permeability evolution can be identified, and the dependence of isolation performance (CO₂ capacity, footprint, and containment) on such migration, dynamics, and evolution can be assessed. In this paper, I will review the conceptual framework, present results obtained from applying this modeling approach to field projects, and discuss current challenges.

Manganese-oxidizing photosynthesis before the rise of cyanobacteria

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The evolution of oxygenic photosynthesis was a singularity that fundamentally transformed our planet's core biogeochemical cycles and redox state. Here we probe the geological record for clues of the evolutionary pathway to light-driven water oxidation. One attractive hypothesis from the perspective of modern photo-assembly of the water-oxidizing complex posits a Mn(II)-oxidizing photosystem as a precursor to oxygenic photosynthesis [1,2]. We tested this hypothesis by exploring early Paleoproterozoic manganese deposits (up to 17 wt. % Mn) to test this hypothesis, captured in the 2415 ± 6 Ma Kogias Subgroup from scientific drill cores retrieved by the Agouron Drilling Project in South Africa. We utilized a novel X-ray absorption spectroscopy microprobe to make redox maps of these deposits at a 2µm scale to understand their petrogenesis and textural context. Coupled to light and electron microscopy and C isotopic measurements, we determined that all of the Mn is hosted in Mn(II) carbonate minerals produced from early diagenetic reduction of Mn-oxides with organic matter. To determine whether the Mn oxidant was molecular oxygen or a Mn-oxidizing photosystem, we examined two independent redox proxies sensitive to low levels of environmental oxygen—multiple sulfur isotopes analyzed using whole-rock IRMS and texture-specific SIMS techniques, and the presence of redox-sensitive detrital grains. Both proxies indicate O₂ was < 10^{-5.7} atm [3]. Kinetic calculations reveal that these maximal levels are several orders of magnitude too low to explain the observed Mn enrichments. The 2.415 Ga Mn deposits therefore provide strong geological evidence for an early, transitional Mn-oxidizing photosystem before the evolution of oxygenic photosynthesis.

[1] Zubay (1996) Academic Press: San Diego. [2] Allen & Martin (2007) *Nature* **445**, 610-612. [3] Pavlov & Kasting (2002) *Astrobiology* **2**, 27-41.