



# Sedimentary reservoir oxidation during geologic CO<sub>2</sub> sequestration

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## Abstract

Injection of carbon dioxide into subsurface geologic reservoirs during geologic carbon sequestration (GCS) introduces an oxidizing supercritical CO<sub>2</sub> phase into a subsurface geologic environment that is typically reducing. The resulting redox disequilibrium provides the chemical potential for the reduction of CO<sub>2</sub> to lower free energy organic species. However, redox reactions involving carbon typically require the presence of a catalyst. Iron oxide minerals, including magnetite, are known to catalyze oxidation and reduction reactions of C-bearing species. If the redox conditions in the reservoir are modified by redox transformations involving CO<sub>2</sub>, such changes could also affect mineral stability, leading to dissolution and precipitation reactions and alteration of the long-term fate of CO<sub>2</sub> in GCS reservoirs. We present experimental evidence that reservoirs with reducing redox conditions are favorable environments for the relatively rapid abiotic reduction of CO<sub>2</sub> to organic molecules. In these experiments, an aqueous suspension of magnetite nanoparticles was reacted with supercritical CO<sub>2</sub> under pressure and temperature conditions relevant to GCS in sedimentary reservoirs (95–210 °C and ~100 bars of CO<sub>2</sub>). Hydrogen production was observed in several experiments, likely caused by Fe(II) oxidation either at the surface of magnetite or in the aqueous phase. Heating of the Fe(II)-rich system resulted in elevated  $P_{H_2}$  and conditions favorable for the reduction of CO<sub>2</sub> to acetic acid. Implications of these results for the long-term fate of CO<sub>2</sub> in field-scale systems were explored using reaction path modeling of CO<sub>2</sub> injection into reservoirs containing Fe(II)-bearing primary silicate minerals, with kinetic parameters for CO<sub>2</sub> reduction obtained experimentally. The results of these calculations suggest that the reaction of CO<sub>2</sub> with reservoir constituents will occur in two primary stages (1) equilibration of CO<sub>2</sub> with organic acids resulting in mineral–fluid disequilibrium, and (2) gradual dissolution of primary minerals promoting significant CO<sub>2</sub> reduction through the release of Fe(II). The reduction of CO<sub>2</sub> is identified as a new trapping mechanism that could significantly enhance the long-term stability of GCS reservoirs. Identification of reservoir characteristics that promote CO<sub>2</sub> redox transformations could be used as an additional factor in screening geologic reservoirs for GCS.

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## 1. INTRODUCTION

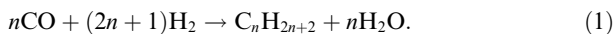
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The sequestration of industrial carbon dioxide emissions into geologic formations is considered a viable strategy to mitigate the rise in atmospheric CO<sub>2</sub> (cf. [Xu et al., 2004](#);

Benson and Cole, 2008; Bickle, 2009). The fate of injected CO<sub>2</sub> depends on physiochemical interactions with reservoir mineral and fluid phases, which control the long-term stability of geologic carbon sequestration (GCS) reservoirs (Hitchon, 1996). Geologic reservoirs in sedimentary rocks currently being considered for GCS contain complex assemblages of detrital and authigenic minerals, saline aqueous solutions, and variable amounts of liquid, gaseous, and solid hydrocarbons. Geochemical investigations into the fate of CO<sub>2</sub> in these reservoirs have focused on three primary trapping mechanisms, including (1) capillary trapping of CO<sub>2</sub> bubbles in constricted pores, (2) solubility trapping of CO<sub>2</sub> dissolved into the aqueous brine, and (3) carbonate mineralization, including magnesite, calcite, and siderite formation (Xu et al., 2004; Benson and Cole, 2008). A fourth possible fate is conversion of CO<sub>2</sub> to more reduced hydrocarbon or organic acid molecules via redox reactions. Carbon dioxide reduction to organic molecules can be catalyzed by Fe-oxide minerals such as magnetite (McCullom and Seewald, 2007; Luquot et al., 2012), which are common in sedimentary formations. Extensive CO<sub>2</sub> reduction in sedimentary reservoirs would affect the stability of detrital and authigenic Fe(II)-silicate and -sulfide minerals, which in turn could modify reservoir porosity, permeability, trace element release, and ultimately the fate of sequestered CO<sub>2</sub>.

Transition metal and metal oxide mineral surfaces are known to catalyze the reduction of inorganic carbon to more reduced hydrocarbon molecules and even to graphite. The most widely recognized mechanism of abiotic carbon reduction and hydrocarbon generation is known as Fischer–Tropsch synthesis (FTS), for which a general reaction can be written:



Gas-phase reduction of CO<sub>2</sub> to form CO in reaction 1 is commonly catalyzed by magnetite (e.g., Grenoble and Estdt, 1981):



Numerous experimental and computational efforts have been directed toward identifying and optimizing key FTS catalysis mechanisms on the surfaces of transition metals and metal oxides (Niemantsverdriet and van der Kraan, 1980; Dictor and Bell, 1986; Van Der Laan and Beenackers, 1999; de Smit and Weckhuysen, 2008; Gracia et al., 2009; Huo et al., 2009; Zhuo et al., 2009; Marshall and Medlin, 2011; Thüne et al., 2012). Despite these efforts, the conditions under which FTS reactions can occur remain poorly constrained.

The abiotic synthesis of reduced carbon species including organic acids, hydrocarbons, and graphite has been inferred from multiple geologic settings such as meteorites (Schulte and Shock, 2004), hydrothermal systems (Shock, 1990, 1995; Shock and Schulte, 1998; Horita and Berndt, 1999; McCullom and Seewald, 2006; Fu et al., 2007; Shock et al., 2013), and Earth's mantle (McCullom and Seewald, 2001; Schulte et al., 2006). Prior determinations of the thermodynamic stability of numerous organic molecules (Shock and Helgeson, 1990; Schulte and Shock, 1993;

Shock, 1995) have enabled calculations of the chemical affinity of postulated abiotic organic synthesis reactions arising from fluid mixing in real hydrothermal systems (Shock and Canovas, 2010). Several studies have attempted to duplicate the geochemical conditions leading to abiotic carbon reduction using hydrothermal reactors, producing carboxylic acids (Chen and Bahnmann, 2000; McCollom and Seewald, 2003a), complex organic molecules (Williams et al., 2011), and amorphous carbon associated with nanoparticulate magnetite (Luquot et al., 2012). Both experiments and thermodynamic calculations have improved our understanding of the processes controlling abiotic transformations of organic matter. Such transformations are thought to be catalyzed by the surfaces of naturally occurring minerals, including clays and magnetite (Palmer and Drummond, 1986; Shock, 1995). In fact, the magnetite surface is known to participate in other geochemically significant redox reactions, such as reduction of Cr(VI) in contaminated groundwater (Peterson et al., 1996).

Studies of petroleum reservoirs suggest that redox reactions among inorganic carbon (IC) and organic carbon (OC) species likely control the redox environment of relatively low-*T* reservoirs (Helgeson et al., 1993). Organic acid anions are a major constituent of oilfield brines (Kharaka et al., 1977), and the assumption of metastable equilibrium among organic acids and IC species has been used in the past as an indicator of reservoir hydrogen fugacity (cf. Shock, 1988; Helgeson et al., 1993). Metastable equilibrium occurs when a subset of phases or species obtains chemical equilibrium but is not necessarily chemically equilibrated with other phases or species in the system. In oilfield brines, the aqueous hydrogen activity is constrained by the metastable reaction between carbon dioxide and acetic acid (CH<sub>3</sub>COOH):



where “g” and “aq” denote gas and aqueous species, respectively, and “l” denotes the liquid solvent. True equilibrium between aqueous CO<sub>2</sub> and H<sub>2</sub> would result in the formation of methane, but methane equilibration with CO<sub>2</sub> is extremely slow, requiring >10<sup>5</sup> years at temperatures <300 °C (Giggenbach, 1987; Shock, 1990). The lowest temperature of isotopic equilibration between CH<sub>4</sub> and CO<sub>2</sub> in hydrothermal settings is 320 °C (Shock, 1990), which is significantly higher than typical reservoirs considered for GCS. The activity of H<sub>2</sub>(aq), *a*<sub>H<sub>2</sub></sub>, can be determined from the equilibrium constant (*K*) for reaction 3, and the fugacity of CO<sub>2</sub> and activity of acetic acid (*f*<sub>CO<sub>2</sub></sub> and *a*<sub>Ac</sub>, respectively) assuming unit activity of water:

$$\log(a_{\text{H}_2}) = \frac{1}{4} (\log(a_{\text{Ac}}) - 2 \log(f_{\text{CO}_2}) - \log(K)). \quad (4)$$

We note that the activity and fugacity of hydrogen are among a number of thermodynamic variables (e.g., *a*<sub>H<sub>2</sub></sub>, *f*<sub>H<sub>2</sub></sub>, *a*<sub>O<sub>2</sub></sub>, *f*<sub>O<sub>2</sub></sub>, and *pe*) that can be used to describe the redox environment and that are related by established equilibria between the liquid and gas or supercritical fluid phases. Helgeson et al. (1993) calculated the *f*<sub>O<sub>2</sub></sub> of oilfield waters as a function of temperature, assuming metastable

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