

Mapping the Complex Phase Formation at the Surface of Supercritical CO₂-Reacted Fayalite for Geologic Sequestration of Greenhouse Gases

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Geologic materials have the potential to serve as a media for the long-term removal of the greenhouse gas CO₂ by the injection of supercritical (sc) CO₂ into host rock mineral in deep subsurface formations. During mineral trapping, the scCO₂ reacts with the rock mineral to form insoluble secondary mineral carbonates to effectively remove CO₂. A specific class of minerals known as Olivines appears to have the highest potential to permanently sequester CO₂ by mineral trapping [1, 2]. Olivines are a class of neosilicates with end members rich in either Fe (fayalite) or Mg (forsterite). During reactions with aqueous solutions, fayalite, (Fe, Mg)₂SiO₄, dissolution occurs releasing Fe and Si which can precipitate with nearby anions to form secondary minerals including hematite, goethite, sulfates, carbonates, and amorphous silica [2]. An atomic-scale understanding of the formation and composition of the secondary phases is largely unknown and precludes a full understanding of the reactions that take place.

In this work, we use a combination of atom probe tomography (APT) and transmission electron microscopy (TEM) to map the atomic-scale composition of both unreacted and scCO₂-reacted natural fayalite mineral. The reaction conditions for the water-saturated scCO₂-reacted fayalite are described in detail in Ref [2]. Upon the reaction with water-saturated scCO₂, precipitates with a plate-like morphology are found to form on the surface of the fayalite as shown in Figure 1a. Energy dispersive x-ray spectroscopy (EDX) in Figure 1 b) indicates the plate-like features have a ferrite core with a silica shell. A tom probe tomography is being applied to map the composition of both the unreacted and reacted fayalite (Figure 2). In Figure 2 a), a homogenous distribution of Si, Fe, and O is observed, along with a homogenous distribution of Mg, Mn, and Ca impurities. In contrast, APT analysis of the reacted fayalite reveals an interface between a Fe-rich/Si-rich phase (Figure 2 b), with the same Mg, Mn, and Ca impurities localized within the Si-rich phase at the interface defined by a 25% isoconcentration surface. Correlative TEM/APT is being pursued to phase structure and composition in order to understand the formation mechanism of the plate-like precipitates and bring us further to understanding the complex reactions that take place between scCO₂ and fayalite for carbon sequestration.

- [1] Felmy, A.R., et al., Reaction of water-saturated supercritical CO₂ with forsterite: Evidence for magnesite formation at low temperatures. *Geochim Cosmochim Ac*, 2012. **91**: p. 271-282.
- [2] Qafoku, O., et al., Fayalite dissolution and siderite formation in water-saturated supercritical CO₂. *Chem Geol*, 2012. **332**: p. 124-135.
- [3] The research was supported through the user program at Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory under user proposal# 39937

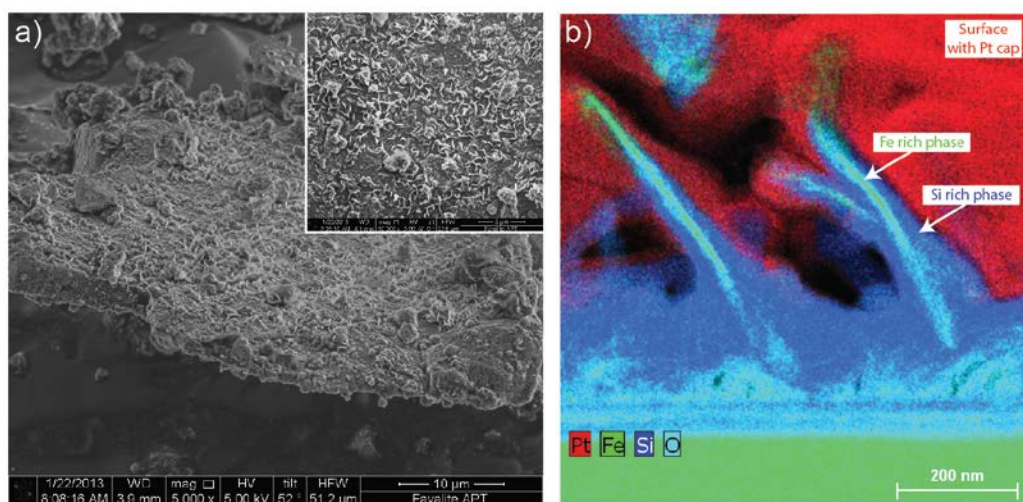


Figure 1. a) SEM image of the surface morphology of scCO_2 -reacted fayalite; inset is closer view of surface. b) cross-section EDX composition map taken in a TEM of the scCO_2 -reacted fayalite surface.

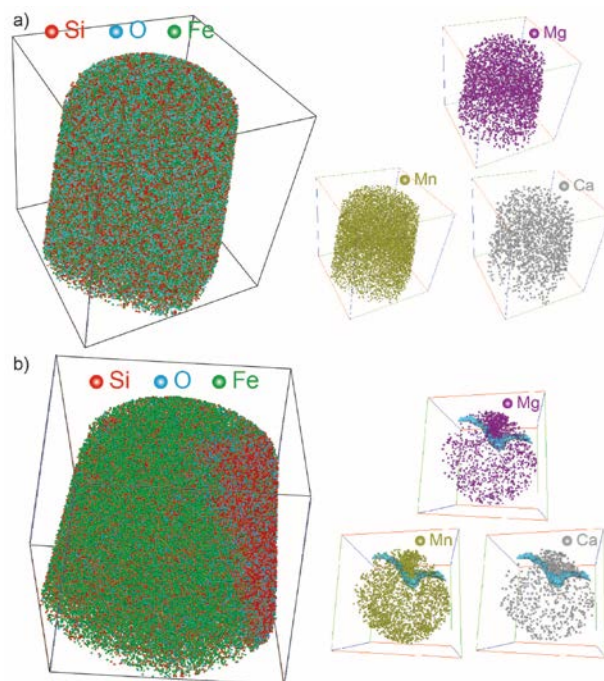


Figure 2. APT reconstruction of natural (a) and reacted (b) fayalite. Impurity distributions are shown to the right. Note in b) the interface between Si-rich/Fe-rich phase; impurities are localized at interface defined by a 25% O isoconcentration surface within the in the Si-rich phase.