



In-situ infrared spectroscopy as a non-invasive technique to study carbon sequestration at high pressure and high temperature



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ABSTRACT

Storage of carbon dioxide in geological formations involves changes in wettability to the host formation during injection and ultimately the formation of inorganic carbonates through mineral trapping. Sequestration locations will be at high pressure and high temperature, thus providing a challenging environment for *in-situ* study. However, infrared spectroscopy (FTIR) with the use of photons is not limited in temperature or pressure and therefore is applicable to study chemical changes to minerals occurring during carbon sequestration. Through the commission of a high pressure/high temperature *in-situ* FTIR cell and the subsequent spectroscopic following of carbonation reactions in synthesised silicate mineral analogues, we document fundamental chemical changes occurring at the nanoscale during carbon storage. Speciation, coordination of carbonate ions to the surface of silicate mineral analogues and changes in surface hydroxyl coverage are observed and discussed, in the context of CO₂ injection and dissolution/mineralisation reactions of reservoir silicate minerals.

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1. Introduction

Capture and geological storage of carbon dioxide (CCS) is typically envisaged for depleted oil and gas reservoirs or saline aquifers (Bachu, 2008; IPCC, 2013). These subsurface formations are ideally suited as they are below depths of 800 m ensuring the presence of scCO₂, which is advantageous due to efficient pore filling of the high density fluid. Furthermore these locations are widely distributed and have a highly connected large pore volume (Benson and Cole, 2008; Haszeldine, 2006). A large volume of potential storage, successful trapping of hydrocarbons, experience with CO₂ injection for enhanced oil recovery (EOR) and successful monitoring and verification in numerous injection projects gives increased confidence in storage security and safety in these locations (Jenkins et al., 2015). However, careful consideration must be given to the tectonics of the reservoir, hydrodynamics of the formation brine and mineralogical aspects when evaluating a potential geological formation (Bachu, 2000).

There are four carbon dioxide trapping mechanisms in geological burial sites, different in the physics, times scales, storage capacity and security: stratigraphic trapping from low permeability caprock; solubility trapping at the CO₂/brine interface; residual trapping by capillary forces during plume migration and finally mineral trapping involving the precipitation of solid carbonates (Boot-Handford et al., 2014). *In-situ* mineral carbonation to form solid carbonates offers the ultimately secure storage mechanism. It is of fundamental importance to understand the chemical reactions occurring during mineralisation to discover the ultimate state and the effect it may have on the mobility of the subsequently injected supercritical fluid (Cardoso and Andres, 2014). During injection of CO₂ there will be four chemically distinct regions containing decreasing amounts of CO₂ and increasing amounts of water/formation brine, as distance to the injection well increases. The mutual solubility of CO₂ and water is well known (Spycher et al., 2003). Dry scCO₂ will exist near the injection site (Pruess and Müller, 2009) before the scCO₂ plume containing water (wet scCO₂) is present. At the edge of the plume significant amounts of CO₂ will be dissolved in the formation brine with CO₂ concentration decreasing until brine with minimal amounts of dissolved CO₂ is found (Zhang and Bachu, 2011). It is of importance to study wet scCO₂ as it is known to react extensively with both steel

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pipelines and silicate minerals, with the theoretical potential to aid in “self-sealing” of fractured caprocks through mineralisation with the water carried by the migrating scCO_2 itself (McGrail et al., 2009). Furthermore given the increased buoyancy and diffusivity relative to brine, wet scCO_2 might dominate the caprock-reservoir interface during injection (Loring et al., 2011).

Typically the approach to understand carbonation involves *ex-situ* measurements to quantify carbonate conversion over longer time periods, relevant to the slow reaction kinetics of the overall process (Sanna et al., 2014), particularly mineral dissolution. However, carbonate formation on reactive cations located on the surface should occur on much shorter timescales and it is known that changes in surface area due to chemical reaction are critical to understand permeability in storage formations (Bolourinejad et al., 2014; Bourg et al., 2015). *In-situ* spectroscopic techniques provide a tool to follow chemical reactions at the molecular scale, assuming suitable integration with high pressure and high temperature reaction cells.

In-situ infrared spectroscopy has been applied previously to study the interaction of CO_2 with alkaline cations at high pressure in clays (Krukowski et al., 2015; Loring et al., 2014, 2012a; Schaefer et al., 2015), mineral carbonation reactions with silicate minerals (Loring et al., 2012b, 2011; Miller et al., 2013; Murphy et al., 2011, 2010; Thompson et al., 2013) and carbon storage related fluid mixtures (Danten et al., 2005; Foltran et al., 2015; Oparin et al., 2005, 2004; Wang et al., 2013). An example of the design and construction of an automated high-pressure titration system with *in-situ* infrared access and subsequent application to CO_2 sorption in clay, carbonation of silicate mineral and determination of water solubility all at 50°C and 90 bar serves as an excellent introduction to this approach (Thompson et al., 2014).

Here we report the synthesis and characterisation of silicate mineral analogues, by locating a reactive cation on the surface of amorphous silica, to facilitate the study of surface chemistry changes occurring during CO_2 storage and carbonate mineralisation. Although the synthesised material surface is unrealistically reactive as compared to natural subsurface silicate minerals, it provides the opportunity to study carbonate speciation at realistic storage conditions and on a timescale amenable to *in-situ* spectroscopic investigation. Amorphous silica consists of silicon-oxygen tetrahedra (Zhuravlev, 2000) which are a constituent motif in many subsurface solids. For example muscovite, commonly known as mica, consists of two tetrahedral silicate layers and an intermediate octahedral aluminium layer, with surface charge balance achieved by K^+ (Wan et al., 2014). Clay minerals in general are composed of silica and/or alumina tetrahedra/octahedra, as are chain, sheet and framework silicate minerals. These are of interest for mineralisation when considering the release of reactive cations due to the pH drop associated with CO_2 injection (Yang et al., 2014). Sandstone formations, consisting primarily of quartz, feldspars, dolomite, calcite, siderite and kaolinite contain sources of divalent and monovalent cations available for mineral trapping (De Silva et al., 2015) forming insoluble and soluble carbonates respectively. The release of cations is also associated with enhancing solubility trapping; dissolution of feldspar is known to aid solubility trapping through increasing the concentration of soluble carbonates and bicarbonates in solution (Xu et al., 2004). The increased concentration of potassium in reservoir brine has been used as an indicator of the dissolution of K-feldspar due to the interaction with CO_2 (Horner et al., 2015; Pauwels et al., 2007). Furthermore the solubility of silicate minerals generally are known to be sensitive to the presence of carbonate ligands and oxalate ligands (Berg and Banwart, 2000; Wigley et al., 2013), highlighting the importance of understanding the formation of both soluble and insoluble carbonates at sequestration conditions.

In this work traditional surface chemistry techniques were applied to study cation distribution and the formation of surface carbonates *in-vacuo*. Custom-made high pressure/high temperature *in-situ* FTIR apparatus was subsequently used to spectroscopically follow the carbonation reaction at conditions relevant to geological storage of CO_2 , particularly those of wet scCO_2 as above. Carbonate formation was confirmed with coordination to the surface elucidated, a fundamental level of detail often included in surface chemistry/catalysis works but less common in the CCS literature. Changes in surface hydroxyl coverage and the influence of these on the interpretation of the carbonation results are discussed.

2. Experimental

2.1. Methodology

Identification of chemisorbed carbonate species formed during carbon storage is fundamental for understanding mechanistic details of mineral carbonation. To gain such a level of detail it is necessary to study carbonate formation at the individual ion level at realistic process conditions. Therefore a silicate mineral analogue (K-SiO_2) was prepared that located a reactive cation on the surface of amorphous silica (SiO_2) through an ion-exchange procedure with surface hydroxyl groups. A detailed description of the synthesis procedure can be found in the Supplementary information. The synthesised material was first characterised with N_2 adsorption/desorption, thermo-gravimetric analysis (TGA), powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) to understand physico-chemical changes occurring during the ion-exchange synthesis and to determine the extent of metal loading. Detail on the apparatus and experimental procedures can be found in the Supplementary information. A comparison was made between amorphous SiO_2 and potassium doped SiO_2 to ensure successful cation exchange on the blank silica material. Pellets of the potassium doped SiO_2 were first studied under high-vacuum conditions with transmission *in-situ* FTIR capabilities, where control of the surface chemistry and surface cleaning through high temperature pre-treatment was relatively simple. The sample was exposed to minute quantities of CO_2 allowing spectroscopic identification of the initial stages of carbonate formation. Carbonate coordination to the reactive cation was also established. To ensure similarity between K-SiO_2 as prepared and that studied following the high temperature pre-treatment *in-vacuo*, physico-chemical characterisation was conducted on a portion of potassium doped silica calcined at a temperature above that of the pre-treatment condition (K-SiO_2 -450). In subsequent experiments potassium doped SiO_2 was exposed to wet scCO_2 at conditions relevant for geological sequestration, with high pressure/high temperature transmission *in-situ* FTIR investigation. As the reaction proceeds rapidly in these conditions due to the highly reactive synthesised surface, automated spectral acquisition was employed. Similarities in carbonate speciation in the two different pressure regimes were investigated. Finally the effect of temperature on the carbonate and water content was explored.

2.2. High pressure/high temperature *in-situ* FTIR spectroscopy

A high pressure/high temperature FTIR apparatus (Fig. 1) was commissioned in-house from a custom Inconel 600 transmission FTIR cell with an internal volume of 23 mL, water-cooled optical grade CaF_2 windows, high performance O-rings (Kalrez®) and gaskets (AgCu), adapted from a previous design (Anderson et al., 1991; Gallei and Schadow, 1974). The internal optical path length of the cell was reduced to <1 mm by inclusion of a CaF_2 spacer.

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