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

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

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41 **Abstract**

42 Storage of carbon dioxide in geological formations involves changes in wettability to the host
43 formation during injection and ultimately the formation of inorganic carbonates through
44 mineral trapping. Sequestration locations will be at high pressure and high temperature,
45 thus providing a challenging environment for *in-situ* study. However, infrared spectroscopy
46 (FTIR) with the use of photons is not limited in temperature or pressure and therefore is
47 applicable to study chemical changes to minerals occurring during carbon sequestration.
48 Through the commission of a high pressure/high temperature *in-situ* FTIR cell and the
49 subsequent spectroscopic following of carbonation reactions in synthesised silicate mineral
50 analogues, we document fundamental chemical changes occurring at the nanoscale during
51 carbon storage. Speciation, coordination of carbonate ions to the surface of silicate mineral
52 analogues and changes in surface hydroxyl coverage are observed and discussed, in the
53 context of CO_2 injection and dissolution/mineralisation reactions of reservoir silicate
54 minerals.

55 **Keywords**

56 Carbon capture and storage

57 *In-situ* infrared spectroscopy

58 Supercritical carbon dioxide

59 Geological carbon sequestration

60 Sandstone reservoir

61 Silicate surface chemistry

62

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 $scCO_2$, 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 CO_2 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 CO_2/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 CO_2 there will be four chemically distinct regions containing decreasing amounts of CO_2 and increasing amounts of water/formation brine, as distance to the injection well increases. The mutual solubility of CO_2 and water is well known (Spycher et al., 2003). Dry $scCO_2$ will exist near the injection site (Pruess and Müller, 2009) before the $scCO_2$ plume containing water (wet $scCO_2$) is present. At the edge of the plume significant amounts of CO_2 will be dissolved in the formation brine with CO_2 concentration decreasing until brine with minimal amounts of dissolved CO_2 is found (Zhang and Bachu, 2011). It is of importance to study wet $scCO_2$ as it is known to react extensively with both steel 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; Schaef 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 *p*H 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. The 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

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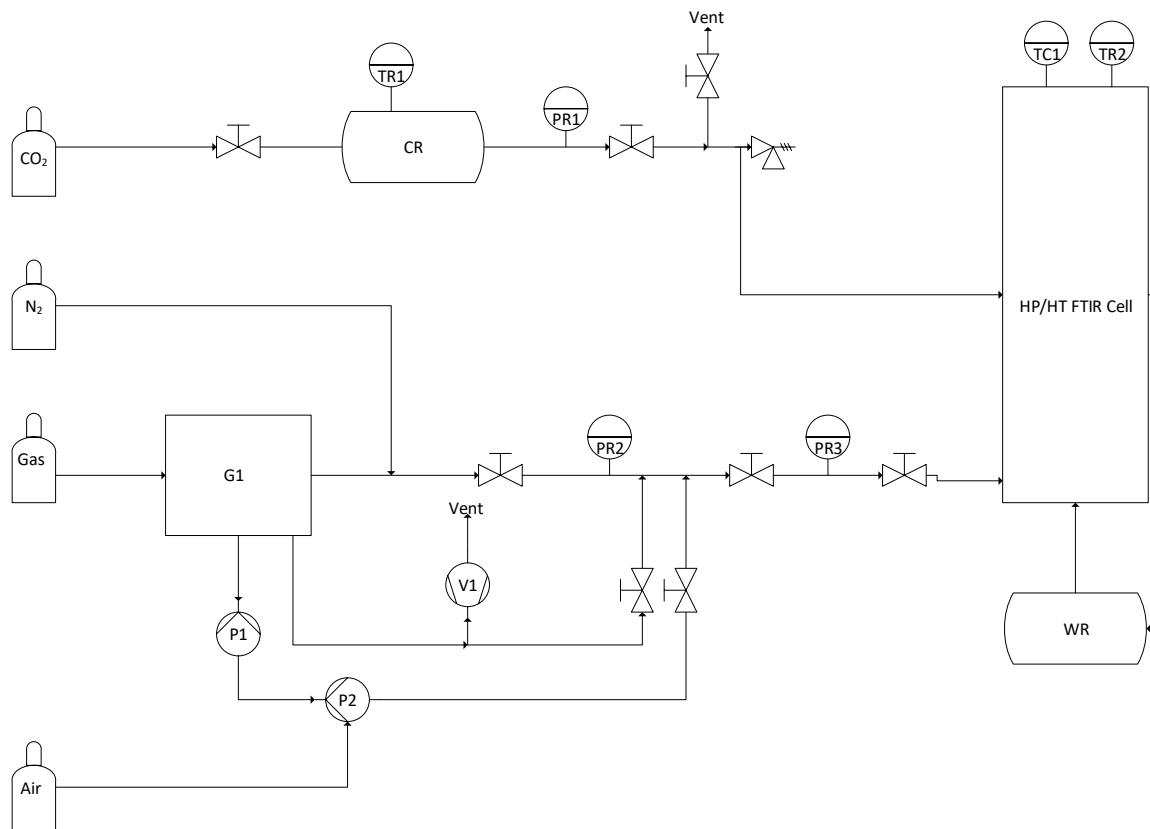
2.2 High pressure/high temperature *in-situ* FTIR spectroscopy

A high pressure/high temperature FTIR apparatus (Figure 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.

Instrument List		Equipment List	
Displayed Text	**Description**	**Displayed Text**	**Description**
PR1	RS Components 0 - 25 MPa Pressure Transducer	CR	Liquid CO_2 Reservoir
PR2	Omega 0 - 25 MPa Pressure Transducer	P1	Maximator DLE 75-50 Pneumatic Gas Booster
PR3	Bourdon Gauge Pressure Transducer	P2	ASF 8050 D Mechanical Pump
TC1	Eurotherm 818 Temperature Controller	V1	Edwards E2M2 Rotary Vane Vacuum Pump
TR1	Omega Class A Pt100 Resistance Temperature Detector	WR	Haake K20 Circulating Water Reservoir
TR2	K-Type Thermocouple	G1	Signal, Series 850 Gas Blender

Figure 1 - Schematic of high pressure/high temperature in-situ FT-IR spectroscopy apparatus.

Liquid CO_2 (BOC, 99.98%) was first collected in a gas sampling cylinder liquid CO_2 reservoir, followed by expansion through high pressure 316-type stainless steel Swagelok® tubing, fittings and valves into the FTIR cell. Pressure and temperature within the liquid CO_2 reservoir were monitored by a high accuracy pressure transducer (PR1) (Omega®, 0 – 25 MPa, ± 0.05%) and a surface-mounted Class A Pt100 resistance temperature detector RTD (TR1). Temperature and pressure within the FTIR cell were monitored and controlled by a K-type thermocouple (TR2) positioned directly above the sample, a temperature controller (TC1) (Eurotherm Controls, 818), two 500 W, 240 V cartridge heaters and pressure transducer (PR3) (RS Components, 0 – 25 MPa, ±0.25 %), respectively. The cell is operational to 20 MPa and 500 °C and also includes the possibility to control temperature *via* a circulating water bath (Haake K20), evacuate the entire apparatus (V1) (Edwards, E2M2 Rotary Vane Dual Stage) and pressurise gas mixtures through a combination of gas blender (Signal, Series 850), mechanical pump (P2) (ASF, 8050 D) and pneumatic gas booster (P1) (MAXIMATOR, DLE 75-50).
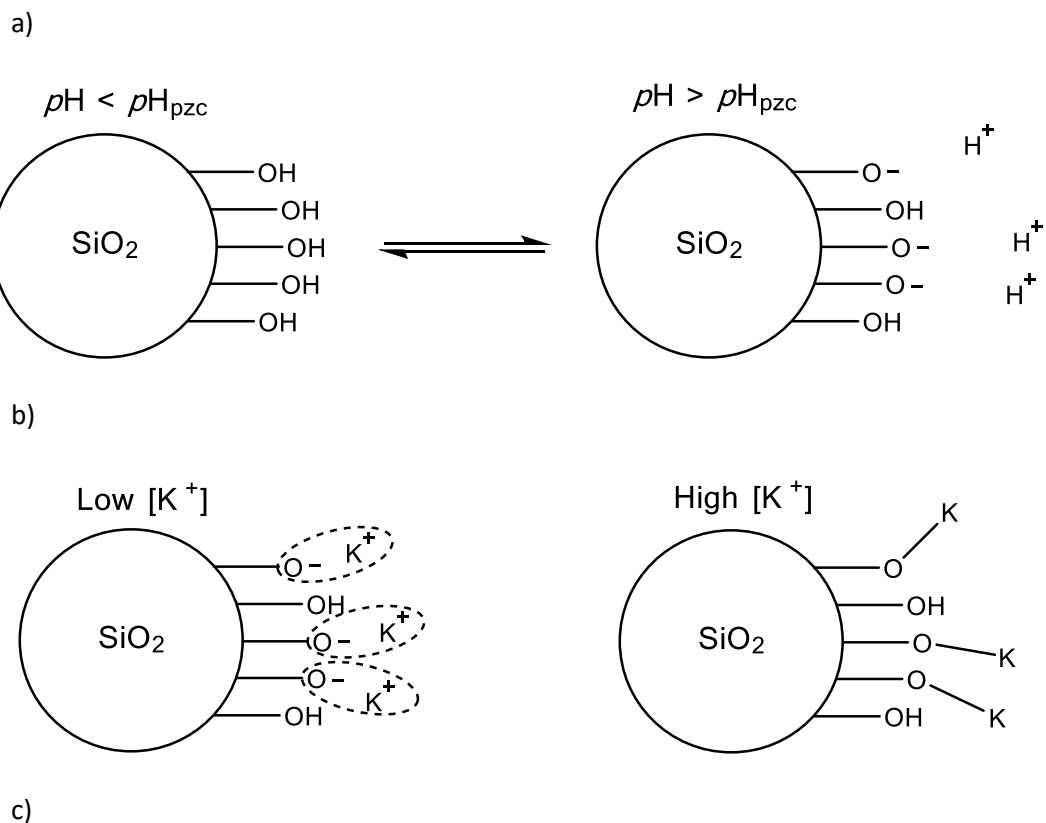
Self-supporting pellets of *ca*. 40 mg of $K-SiO_2$ were prepared in a 23 mm diameter press at 2 tons (Specac 15.011 Manual Hydraulic Press). Pellets were < 1mm thick and prior to loading in the FTIR cell were cut in half to allow additional discrete monitoring of the fluid phase.
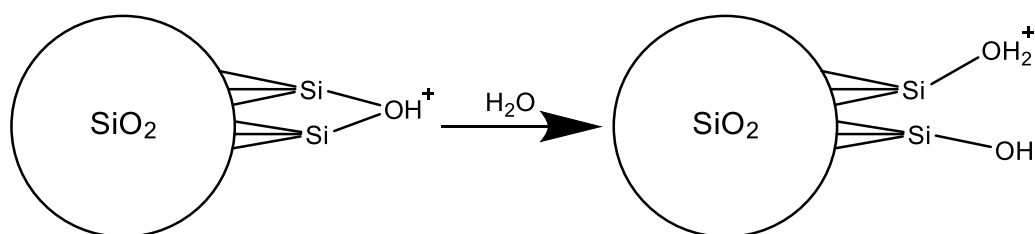
215 Spectra were recorded with an FTIR spectrometer (PerkinElmer Spectrum 100) equipped
216 with automated collection software (PerkinElmer Timebase) and a liquid nitrogen-cooled
217 MCT detector. A background spectrum was recorded in the absence of CO_2 and sample, and
218 was subtracted from all subsequent spectra. At this point, the spectrometer was moved into
219 position to allow the beam to pass through the transmission window and sample.
220 Automated spectral acquisition was initiated followed by expansion of CO_2 from the liquid
221 CO_2 reservoir into the FTIR cell. All spectra including background were recorded at 4 cm^{-1}
222 resolution with a minimum of 32 accumulated scans per spectrum across a range of 4500 –
223 500 cm^{-1}. Automated spectral acquisition software was set to record a spectrum every 36
224 seconds, which were subsequently subtracted from the first recorded spectrum of the
225 sample disc in air at the experimental temperature.
226
227 **3 Results & Discussion**
228 **3.2 Synthesis & characterisation of mineral analogues**
229 pH was monitored continuously during the ion-exchange synthesis procedure (Figure S1,
230 Supplementary Information). The first point was the pH of the dopant solution alone (pH
231 11.7) before a rapid decrease was seen 30 seconds after contact with amorphous silica. As
232 silica pH$_{pzc}$ = 4.1, (Schwarz et al., 1984) immersion in the above solution leads to
233 deprotonation of surface hydroxyl groups by modification of the equilibrium in Figure 2a.
234 Such deprotonation allows both non-specific and specific adsorptive interactions with
235 cations in solution; at low cation concentrations ion pairs are formed (Si-O$^-$: K$^+_{(aq)}$) before full
236 cation-exchange occurs at higher concentrations to form (Si-OK) as shown in Figure 2b.
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238 a)

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240 b)

241

242 c)

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SiO₂ ... Si—OH⁺ + H₂O → SiO₂ ... Si—OH₂⁺ / Si—OH

As the synthesis solution was 1.0 (mol K$^+$)·l^{-1} the specific cation-exchange interactions dominate and the maximum uptake as determined previously was achieved (Iordan et al., 1998). A similar dependence on *p*H is observed for sodium adsorption on silica, with weak interactions present at low *p*H and stronger adsorption possible through cation-exchange at high *p*H (Smit et al., 1978). After the initial rapid decrease the measurement was stable at *ca*. *p*H 10.9 for the duration of the mixing, indicating that the cation-exchange equilibrium and saturation population have been achieved, as both concentration and *p*H conditions as discussed above had been satisfied.

Surface area and porosity data is presented in Table 1 with the associated isotherms and pore distribution plots given in Figure S2, Supplementary Information. There was a clear drop in both surface area and pore volume after potassium doping and subsequent treatment at 450 °C. Isotherms conform to IUPAC Type IV classification, with Type H1 hysteresis loops present in all, indicating the presence of mesopores further evidenced in the pore size distribution plot (Figure S2, Supplementary Information). Excluded for brevity, the silica surface area after an identical treatment in Ultra-Pure Type I water was 252 m^2·g^{-1} indicating that the decrease in surface area during synthesis was due to phenomena associated with the cation-exchange procedure and not from physical agglomeration of silica particles.

Table 1 – Physical characteristics as determined by N₂ adsorption-desorption of fresh and potassium doped silicas as prepared and after treatment at 450 °C in air.

Sample	Surface Area / m^2·g^{-1}	Pore Volume / cm^3·g^{-1}
SiO$_2$	257	1.72
K-SiO$_2$	69	0.46
K-SiO$_2$-450	51	0.38

The pore size distribution plots (Figure S2b) indicate that upon cation-exchange there was a general decrease in pore volume, accompanied by a subtle shift to a lower average pore width. Considering this fact alongside the high *p*H synthesis conditions, it is likely that the pore network has been partially dissolved. At high *p*H when the surface is negatively charged due to ionisation (Figure 2a), Si-O bonds are polarised and weakened, enhancing dissolution and consequently destroying the porous network (Brady and Walther, 1989). It has also been observed that the presence of cations enhances the rate of silica dissolution (Plettinck et al., 1994) and that there is a dissolution rate dependence on the particular alkali metal

cation, with sodium and potassium hydroxides or chlorides showing the greatest enhancement (Wijnen et al., 1990). At alkaline *p*H the effect is particularly strong for quartz dissolution in the presence of sodium, 200 times faster than in pure water (Rimstidt, 2015). It is known that protonation of silica increases the Si-O bond distance, in turn weakening the silica network and increasing reactivity with water. This reaction leads to the breaking of the silica network as shown in Figure 2c (Brown et al., 2014). If one substitutes the proton for the adsorption of potassium, it is reasonable to assume at least a similar effect.

An alternative scenario to explain this observation would be pore-blockage by the formation of a secondary oxide or hydroxide phase on the silica surface. Without evidence of the formation of a crystalline phase in X-ray diffractograms (Figure S3, Supplementary Information) this seems unlikely. However a disordered non-crystalline secondary phase would occupy a greater volume than the ordered crystalline equivalent which could explain the loss in porosity and surface area and thus cannot be ruled out entirely. A further smaller decrease in surface area and pore volume was apparent after treatment in air at 450 °C, which was possibly due to the onset of cristobalite or tridymite formation, enhanced at lower temperature in the presence of potassium (Iordan et al., 1998). Alternatively this could be due to the formation of crystalline potassium carbonate on the surface. The observation that the pore volume at around 500 Å was largely maintained at the expense of that at 200 Å during this transition would support the idea of formation of cristobalite or tridymite, as the initial loss of the smallest and consequently most unstable pores would be expected during crystallisation.

X-ray diffractograms are shown in Figure S3, Supplementary Information for both parent and potassium-doped silicas. The broad peak between 16 and 28° 2θ is indicative of amorphous silica and shows that after cation-exchange this amorphous nature is retained. Additional peaks at 30.1 and 31.2° 2θ were observed in the K-SiO$_2$-450 pattern but are not assignable to either K$_2$CO$_3$, quartz or cristobalite. They could be explained by a crystalline silica species e.g. tridymite (ICDD 42-1401) but as intensity of the signal was so low, it is likely arising from a very small amount of poorly crystalline material diluted in a large amount of amorphous silica. A conclusive identification was not possible and assertion of a positive identification would be misleading.
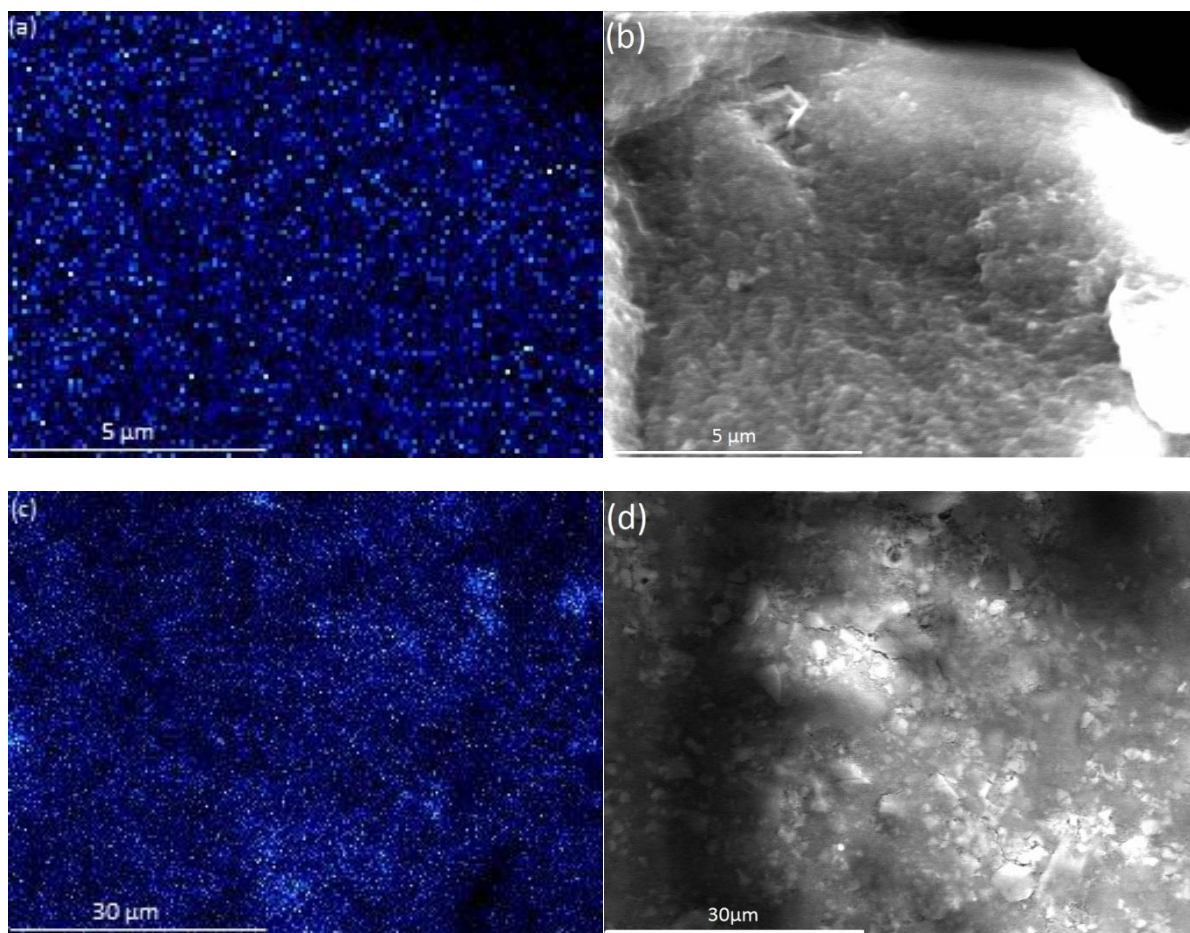
SEM images of K-SiO$_2$ (Figures 3a and b) and K-SiO$_2$-450 (Figures 3c and d) indicated the presence of amorphous silica aggregates throughout ranging from <1 to 30 μm, in agreement with the amorphous nature determined by XRD. EDX elemental maps of potassium within K-SiO$_2$ (Figure 4a) and K-SiO$_2$-450 (Figure 4c) collected from regions shown in Figure 4b and Figure 4d, respectively, showed that potassium was generally well dispersed within the sample, at different length scales, as-prepared and after treatment at high temperature. The cation loading appeared to be consistent across the surface, without the formation of concentrated regions of potassium indicative of a segregated secondary phase, consistent with the lack of K$_2$CO$_3$ observed in XRD. The results of the semi-quantitative EDX analysis (Table 2) indicated that potassium doping was significant with a level of 6.93 ± 0.03 wt% reached during synthesis and maintained after heat treatment. This was in excellent

322 agreement with the original publication which determined a loading of 6.9 wt% K^+ using a
323 1.01 (mol K^+)·l^{-1} solution of K_2CO_3 (Iordan et al., 1998).
324

325 Considering the Kiselev-Zhuravlev value of 4.6 (least-squares) or 4.9 OH·nm^{-2} (arithmetical
326 mean), which gives the number of hydroxyl groups per unit surface area when the degree of
327 hydroxylation is at a maximum, one can determine a surface coverage of potassium by also
328 using the surface area and potassium loading determined by EDX (Zhuravlev, 2000). Using
329 the surface area of the water treated sample (252 m^2·g^{-1}) a surface coverage of 92.1 or
330 86.4% was determined by using the least-squares and arithmetical mean respectively. Detail
331 of the calculation is given in the Supplementary Information. It is important to consider the
332 limitations of a model that uses maximum hydroxylation when the cation-exchange
333 procedure relies on extensive dihydroxylation. However, as the silica used for synthesis was
334 not dried or heat treated before exposure to the dopant solution, the conclusions
335 surrounding coverage are valid.

336

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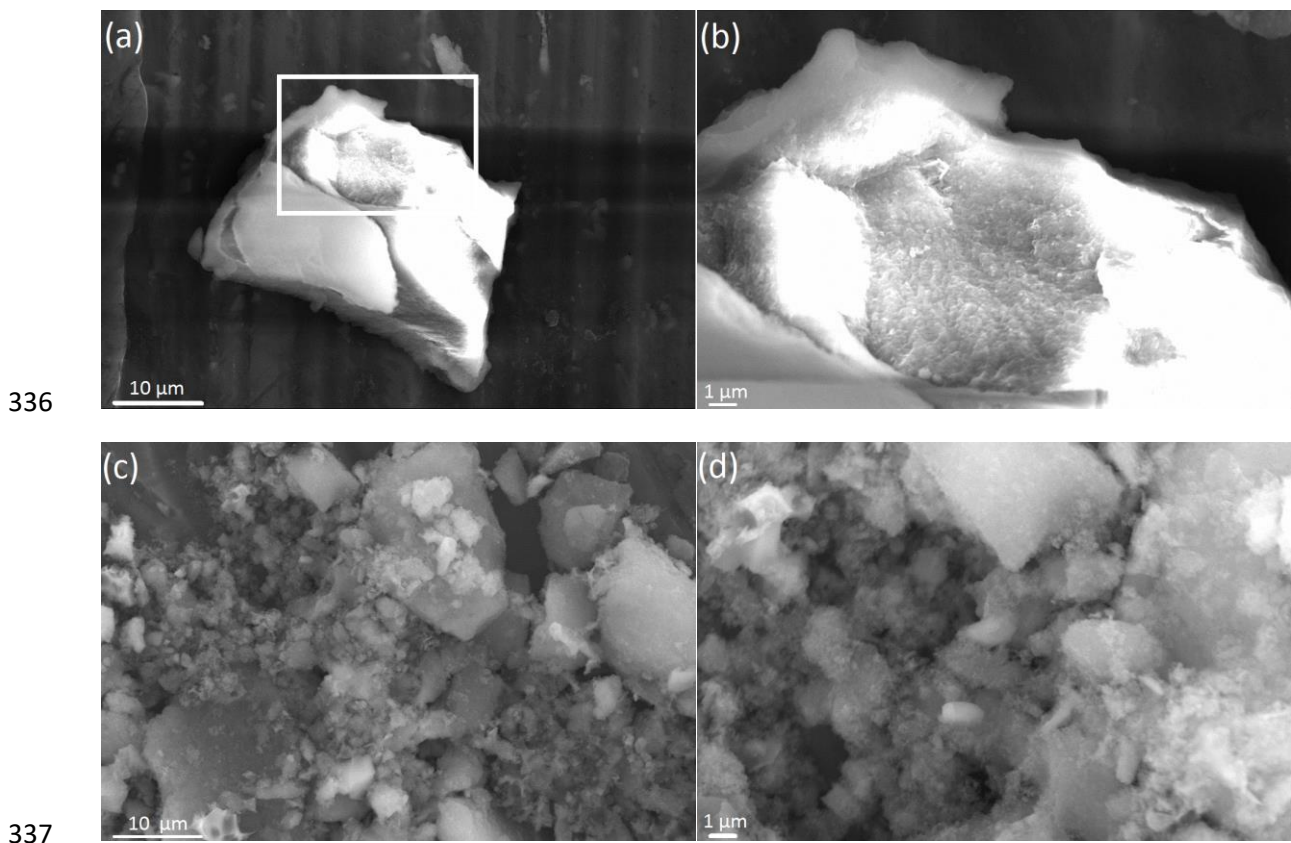
338 **Figure 3 – SEM images of K-SiO₂ at (a) 5000x and (b) framed section in (a) at 15000x magnification as prepared**
339 **and at (c) 5000x and (d) 15000x magnification after treatment at 450 °C in air. Aggregates of amorphous silica**
340 **are visible in all images.**

341

342

| Sample	Si / wt%	O / wt%	K^+ / wt%
SiO₂	43.99 ± 0.45	56.01 ± 0.45	
K-SiO₂	39.01 ± 0.28	54.06 ± 0.32	6.93 ± 0.03
K-SiO₂-450	36.79 ± 0.12	53.82 ± 0.16	7.41 ± 0.04

349

350 Carbon dioxide is routinely used in surface chemistry studies to probe the nature of Lewis
351 acid sites through electronic σ-donation *via* the oxygen lone-pair or Lewis base sites through
352 reactive adsorption to form carbonate, bicarbonate or formate species, respectively (Busca
353 and Lorenzelli, 1982). Characteristic absorption bands are used to differentiate surface
354 complexes. Therefore regarding the *in-vacuo* FTIR investigation, the formation of surface
355 carbonates (as opposed to bulk carbonates) on K-SiO₂ surface was evidenced (Figure 5) by
356 growth of bands due to vibrations in the range $1750 - 1275$ cm^{-1} as a function of CO_2
357 pressure. This was an initial indication that the loading of potassium had been successful and
358 implied that it was located on the surface, consistent with the sub-monolayer coverage
359 calculations above. Based on changes in intensity during outgassing (not shown for brevity),
360 peaks at 1633/1345 cm^{-1} and 1663/1401 cm^{-1} were assigned as associated pairs. Upon

361   coordination to a surface, carbonate ion symmetry is lowered and consequently the
362   degenerate v_3 asymmetric carbon-oxygen stretch at 1415 cm^{-1} is split into pairs. As first
363   proposed by (Nakamoto et al., 1957), the magnitude of the splitting indicates whether the
364   surface species is ionic (< 50 cm^{-1}), monodentate (100 cm^{-1}), bidentate (300 cm^{-1}) or bridged
365   (≥ 400 cm^{-1}). The bands in Figure 5 had a Δv_3 of *ca.* 288 and 262 cm^{-1}, respectively which
366   implied a bidentate coordination to the potassium cation.
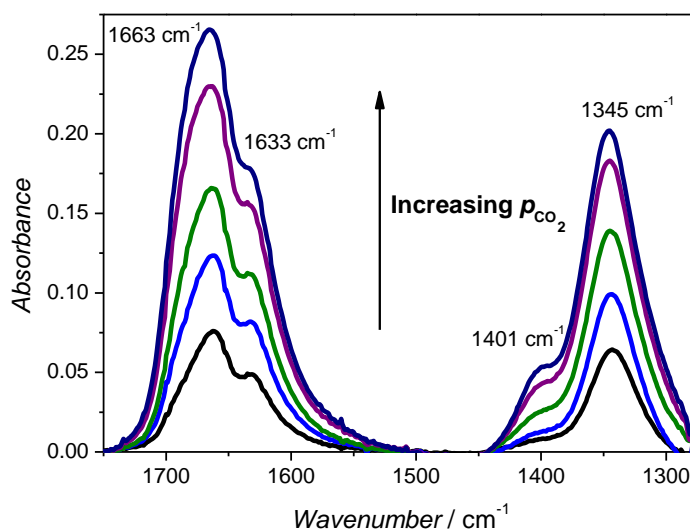
Figure 5 – Evolution of bands assigned to bidentate carbonates on K-SiO$_2$ at 1750 – 1275 cm^{-1} as a function of CO$_2$ pressure from 0.025 – 20.8 mbar. Spectra were recorded at room temperature and are plotted as difference spectra relative to K-SiO$_2$ after treatment *in-vacuo* at 400 °C.

3.3 High pressure *in-situ* FTIR spectroscopy

372   Figure 6 shows typical FTIR spectra of CO$_2$ at conditions relevant to this work, in both the
373   liquid and supercritical state. Broad bands at *ca.* 3700 cm^{-1} and 2350 cm^{-1} were assigned to a
374   band due to a combination mode ($v_1 + v_3$) and the asymmetric stretch respectively. The
375   narrow band around 2075 cm^{-1} was attributable to a combination of symmetric bend and
376   symmetric stretch. Weak bands visible in the liquid CO$_2$ spectrum included a band due to a
377   combination mode at 3012 cm^{-1} from the symmetric bend and asymmetric stretch, a band at
378   1949 cm^{-1} from symmetric bend and symmetric stretch combination and a peak at 1610 cm^{-1}
379   attributed to the OH bending vibration of water. Bands at 1388 and 1282 cm^{-1} which are
380   enhanced by Fermi resonance were suppressed during the transition from liquid to
381   supercritical CO$_2$. These served as a good example of the general loss in intensity of many of
382   the bands observed during this transition, with the most intense broad bands at 3700 and
383   2350 cm^{-1} narrowing also. Two bending modes of CO$_2$ at 666 cm^{-1} were not visible due to the
384   cut-off of the optical windows. Band assignments for CO$_2$ are given in (Yagi et al., 1993) and
385   for carbonates from (Busca and Lorenzelli, 1982)
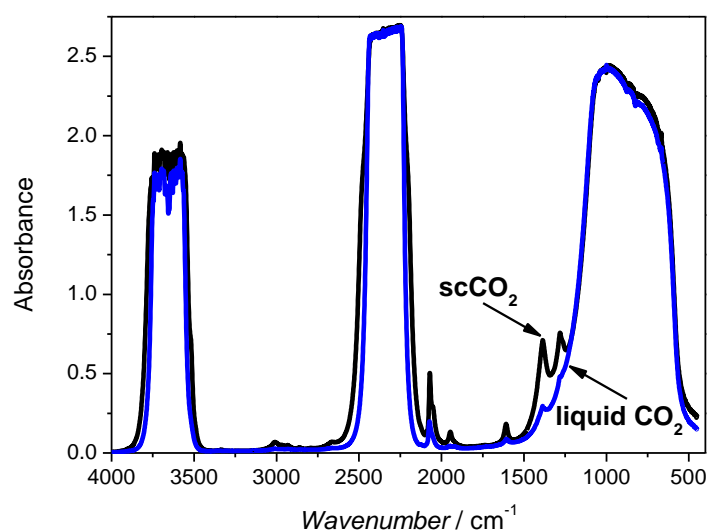
Figure 6 – FT-IR spectra of liquid carbon dioxide (black) at 19 °C and supercritical carbon dioxide (blue) at 50 °C after isochoric heating. The intensities of most of the vibrational bands decrease upon transition from liquid to supercritical phase, or in the case of the most intense bands, narrow slightly.

Immediately upon immersion in $scCO_2$ at 50 °C and 4.92 MPa, $K-SiO_2$ formed bidentate carbonates (Figure 7) comparable with those formed *in-vacuo* (Figure 5). Plotted as difference spectra relative to $K-SiO_2$ at 50 °C in air before expansion of liquid CO_2 into the cell, the black (before venting) spectrum was recorded 10 minutes after expansion into the cell. The blue spectrum (after venting) was recorded following 48 h immersion under the conditions above and subsequent venting of the $scCO_2$, indicating that the formed carbonates remained stable in the absence of the fluid phase $scCO_2$. In order to investigate the evolution of the carbonate bands, automatic acquisition software was employed to record spectra immediately following expansion into the high pressure cell. It was observed (Figure 8) that at 50 °C and 5.29 MPa the development of bidentate carbonate was rapid with bands at $1750 - 1300$ cm^{-1} showing uniform growth against time. In both sets of spectra (Figure 7 and Figure 8) it was observed that Δv_3 was consistent with the results *in-vacuo* and thus it was assumed that the relationships between pairs of degenerate bands were unchanged. If a position of 1680 cm^{-1} is taken for the highest frequency band (Figure 7 and Figure 8), Δv_3 value for the 1615/1372 cm^{-1} band pair in (Figure 7) was 243 cm^{-1} and the 1680/1403 cm^{-1} band pair was 277 cm^{-1}. In Figure 8 the Δv_3 value for the 1601/1373 cm^{-1} band pair was 228 cm^{-1} and the 1680/1417 cm^{-1} band pair was 263 cm^{-1}. Thus in both the low pressure and high pressure regimes, the species formed upon exposure to $scCO_2$ are bidentate carbonates for $K-SiO_2$.

These findings are comparable with those of (Loring et al., 2011) who studied the carbonation of forsterite (Mg_2SiO_4) in $scCO_2$ at 50 °C and 180 atm, evidencing the growth of a magnesium carbonate precipitate through an increase in v_3 C-O stretching modes at 1480 and 1425 cm^{-1}. A similar conclusion was drawn in the case of the inosilicate mineral wollastonite ($CaSiO_3$) where features due to carbonate at 1410 cm^{-1} with a broad shoulder at 1460 cm^{-1} indicated the formation of potentially hydrated metastable amorphous calcium carbonate phase (Miller et al., 2013). The shoulder appeared to decrease with increasing

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water saturation of the $scCO_2$ phase, indicating a change in the speciation of the surface carbonate. It is pertinent to highlight in these two former studies bulk carbonate formation was evidenced, whereas in the current study we show surface carbonate formation. The importance of water was also highlighted, by a lack of reaction in anhydrous $scCO_2$ (Miller et al., 2013). This issue is overcome in the present study by both trace amounts of water in the liquid CO_2 and those remaining post-synthesis. Zhuravlev defined the removal of physisorbed water from amorphous silica as being complete at 190 ± 10 °C, with subsequent weight loss due to the removal of surface hydroxyl groups (Zhuravlev, 1993, 1989). From the TGA measurements (Figure S4, Supplementary Information), the water content of $K\text{-}SiO_2$ was established as 3.57% (Table S1, Supplementary Information), by taking the numerical average of weight loss at 190 ± 10 °C for the triplicate measurements. $scCO_2$ is highly efficient at extracting water from amorphous silica (Tripp and Combes, 1998) and therefore the water content of the silica is critical in determining the water content of fluid phase, and as above, the applicability to various stages of CO_2 injection. Considering the ca. 20 mg discs used in the HP/HT *in-situ* FTIR experiments and the quantity of $scCO_2$ present determined from the volume and experimental thermodynamic conditions (Span and Wagner, 1996), the amount of water present in the $scCO_2$ was calculated and confirmed we are operating in a wet CO_2 regime. Detail of the calculation is given in the Supplementary Information. Furthermore the supercritical line for water-CO_2 mixtures is severely depressed in terms of pressure as compared to pure CO_2 (Jager et al., 2013). Considering the pressures reported for the HP/HT *in-situ* FTIR experiments and that the quantity of water present can only be increased by trace (<20 ppm v/v) water present in the liquid CO_2 as purchased, this is further evidence that we are operating within a wet CO_2 regime. Greater detail on the importance of the presence of water on carbonation reactions is found in (Thompson et al., 2013) where the bicarbonate anion present in the thin water film on the surface of silicate minerals is shown by *in-situ* FTIR. This is a key reaction intermediate, highlighting the advantages of FTIR in elucidating reaction mechanism in wet CO_2 (Thompson et al., 2013).
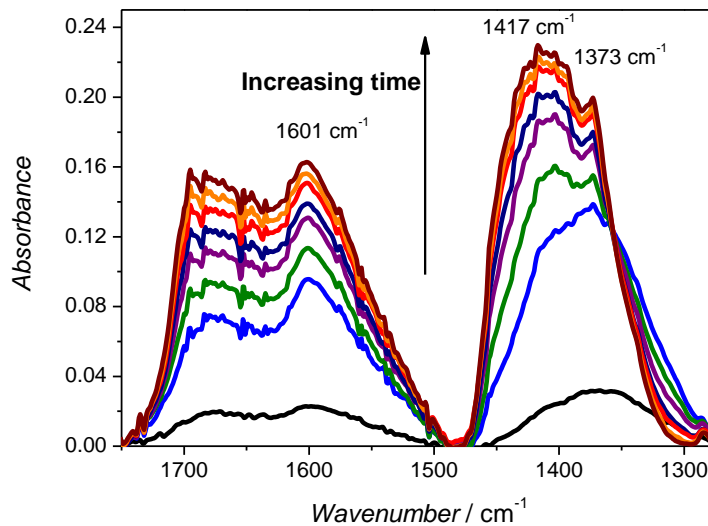
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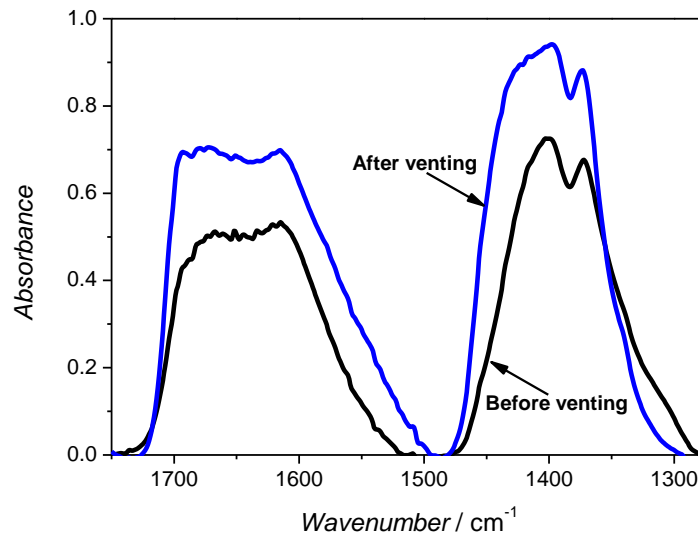
Figure 7 –Bands due to bidentate carbonate at 1750 – 1275 cm^{-1} following scCO$_2$ exposure at 50°C and 4.92 MPa (black) and after venting of scCO$_2$ following 48 hours immersion under above conditions (blue), plotted as difference spectra relative to K-SiO$_2$ at 50 °C in air.

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Figure 8 – Evolution of bands due to bidentate carbonate at 1750 – 1275 cm^{-1} during the first 5 minutes of reaction upon scCO$_2$ exposure at 50°C and 5.29 MPa. The temporal acquisition software recorded each spectrum at an interval of 36 seconds and spectra are plotted as difference spectra relative to K-SiO$_2$ at 50 °C in air.

As carbon storage is envisaged for geological formations, the influence of depth (and thus temperature) is important. It has been shown (Hur et al., 2013) that cation type and the presence of water is important in determining carbonate formation as above. It was also shown that upon moving from liquid to supercritical CO$_2$ the carbonate formation reaction at the internal surfaces became possible due to the lower viscosity and higher diffusivity achieved in the supercritical regime. Carbonates formed on calcium exchanged montmorillonite but not in sodium exchanged clay, with the speciation of carbonates as

15

determined by FTIR changing depending on the phase of CO_2 present. Thus the influence of temperature on the carbonation of $K-SiO_2$ was investigated (Figure 9a) at 50 °C and 5.84 MPa (blue), 70 °C and 5.98 MPa (green) and 90 °C and 6.09 MPa (purple). Due to the design of the cell, both temperature and pressure are inherently linked and therefore discrimination of the effect of each parameter was not possible. Initially it appeared that the magnitude of carbonation decreased with increasing temperature (Figure 9a), but upon investigation across the spectral region attributable to surface hydroxyl groups (Figure 9b), it can be seen that in fact the sample was being dried, due to a combination of increased temperature and the well-known drying effect of $scCO_2$ (Kim et al., 2012; Tripp and Combes, 1998). Upon removal of water from $K-SiO_2$, the transmission properties of the sample improved and thus the apparent absorption across the whole spectrum decreased, leading to the false assumption that the carbonate population was decreasing.

It is interesting to note that there is no change in the carbonate coordination to the surface as it has been shown previously in forsterite that water concentration directly impacted carbonate coordination (Loring et al., 2015). Below a threshold value of 76 (μmol H_2O)$\cdot$m^{-2} carbonate complexes were formed, with bidentate coordination observed at the lowest water concentrations. Considering the current results where bidentate coordination was observed throughout the experiment, this would imply that we began with a minimal amount of adsorbed water (< 76 (μmol H_2O)$\cdot$m^{-2}) and subsequent drying thus had no impact on the coordination of the adsorbed carbonate species. Considering the water content determined by TGA, the surface area of $K-SiO_2$ and the average pellet mass, the adsorbed water present before experiment was 29 (μmol H_2O)$\cdot$m^{-2}, in excellent agreement with the spectroscopic findings. Detail of the calculation is given in the Supplementary Information. Generally, considering the small changes in absorption, it is likely that the magnitude of carbonation was unaffected by the small change in temperature. However it is important to comment on the changes observed in the hydroxyl group region, as it is known that wettability directly influences plume migration and residual trapping (Bourg et al., 2015). It is accepted that changes to the hydrophilicity, particularly at the pore scale, have significant impact on wettability and thus geological storage of CO_2 (Chen et al., 2015) and these results suggested that to study them at high pressure and high temperature, *in-situ* FTIR may be a suitable tool. Indeed inaccessible hydroxyl groups on silica are accessible in $scCO_2$ (McCool and Tripp, 2005) and therefore CO_2 is regarded as being highly effective at removing water from silica (Dickson et al., 2006), consistent with our observations.

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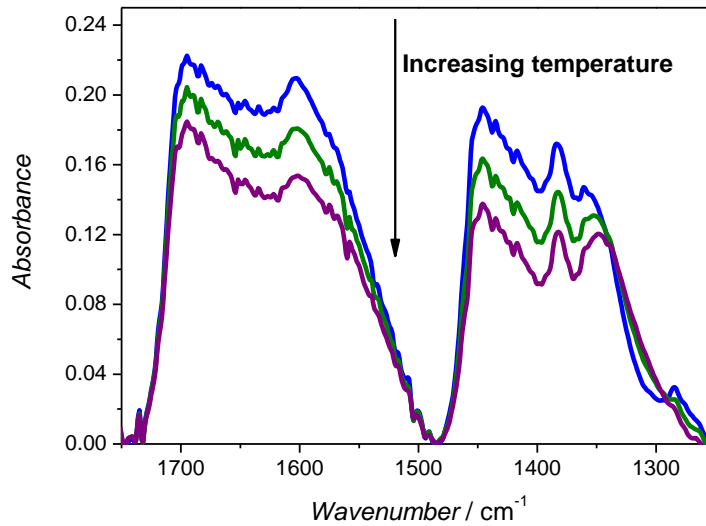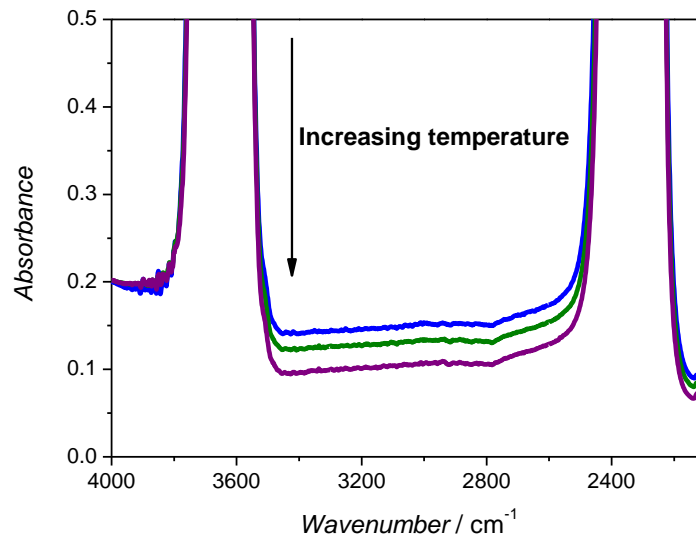
Figure 9 – (a) Changes in carbonate band intensity (1750 – 1275 cm^{-1}) at 50 °C and 5.84 MPa (blue), 70 °C and 5.98 MPa (green) and 90 °C and 6.09 MPa (purple). (b) Changes in OH region during same experiment showing drying of K-SiO$_2$ with increased temperature and pressure, 50 °C and 5.84 MPa (blue), 70 °C and 5.98 MPa (green) and 90 °C and 6.09 MPa (purple).

4   Conclusions

In this paper, it was shown that through the preparation of cation-doped silica, one can produce a model system that facilitates fundamental understanding associated with chemical changes to host mineralogy during carbon sequestration. An investigation of surface chemistry changes occurring during exposure to scCO$_2$ has been performed in a custom high pressure/high temperature FTIR cell and was shown to be comparable with more conventional surface chemistry high vacuum FTIR methods. The carbonation of potassium doped silica, as a simple model system for the surface of silicate minerals, was possible in pressure and temperature conditions relevant to geological sequestration of carbon dioxide, with potential implications for mineral dissolution. In all cases the

17

508 carbonation reaction produced bidentate carbonates on the surface of potassium doped
509 silica indicating sufficient reactivity for the mineralisation of scCO$_2$. As the surface of a
510 mineral or the interfacial region between scCO$_2$ and mineral will be the initial point of
511 contact during EOR or CCS, it is of fundamental importance to understand the nature of
512 reaction products. Furthermore the nature of the ligand is known to influence the
513 dissolution rate of minerals during CCS and therefore obtaining carbonate speciation/cation
514 coordination is of importance. Further work is ongoing to determine the role of cation and
515 the presence of water on the speciation of formed carbonates. In general it has been shown
516 that FTIR can be used to understand EOR and CCS processes in challenging environments.

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