Assessment of the impact of CO_2 storage in sandstone formations by experimental studies and geochemical modeling: the case of the Mesohellenic Trough, NW Greece

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Abstract

Representative sandstone samples from Mesohellenic Trough (NW Greece) were selected to investigate the geochemical reactions that occur when they come in contact with CO_2 under representative in-situ conditions (T=70°C, P=150bar, 6 months reaction in batch experiments). Those sandstones consisted of predominant calcite and quartz, with lesser amounts of feldspars, chlorite, ankerite, dolomite, kaolinite, montmorillonite and muscovite. After reaction with CO_2, the brine became acidic and was enriched in cations as a result of mineral dissolution. Minor mineralogical changes were observed that involved: a) the dissolution of carbonate minerals and b) the incongruent dissolution of chlorite to form clays and silica. The results related to these, have been linked with geochemical modelling using the PHREEQC code. Simulation results for a 10 ka time period predicted that chlorite was expected to dissolve completely within 100 years, leading to boehmite growth and increasing the mass of dolomite. Feldspars were expected to react at a later stage in the reaction sequence. Sensitivity tests were run to access the effect of various adjustable parameters on the outcome results. The geochemical experiments and modelling lend support to the view that Pentalofos and Tsotyli sandstone formations of the Mesohellenic Trough are suitable for the long-term storage of CO_2 produced in the neighbouring lignite-fired power plants, at least in terms of mineralogy and geochemistry.

Key words: CCS, sequestration, geological storage, CO_2-brine-rock interactions PHREEQC

1. Introduction

Progressive industrialization and burning of fossil fuels has caused dramatic increases in emissions of carbon dioxide (CO_2) to the atmosphere in the past decades, leading to international concern about the potential for rapid climate change. CO_2 capture and underground storage (CCS) has been proposed as a workable method to reduce emissions to the atmosphere, and play a key role as we transition to low carbon energy supplies (IPCC, 2005).

Storage can be attained through injection of CO_2 into deep saline aquifers or depleted oil/gas reservoirs. In many geological settings, in-situ pressure/temperature conditions at greater than 1 km deep mean that CO_2 can exist as a stable supercritical phase (sCO_2, needs to be above 31.1°C and 7.39 MPa). Once injected, CO_2 is contained underground through a combination of capillary, structural, solubility or mineral trapping (De Silva et al., 2015; Wigand et al., 2008). However, the selection of suitable reservoirs and their caprocks is not trivial and detailed studies must be carried out to understand the geological conditions and structure of the whole basin (porosity, permeability, geometry, capacity, mineralogy etc.), before proposing it as a potential storage mean. The presence of sCO_2 in geological media can cause a number of geochemical reactions that can potentially change the reservoir integrity and trapping potential. Such changes include the acidification of pore waters, dissolution of primary minerals, precipitation of secondary phases, and changes in porosity and permeability (Black et al., 2014; Gaus, 2010). However, detailed assessment of individual formations is required to assess whether these changes result in overall increases or decreases in CO_2 storage potential.

Many experimental studies have been conducted in the laboratory (i.e. Alemu et al., 2011; García-Rios et al., 2013; Huq et al., 2012) or in situ (Wigand et al., 2008) to investigate the CO_2 trapping potential of various formations, such as sandstones and limestones (i.e. García-Rios et al., 2013), basalts (i.e. Van Pham et al., 2011), granites (i.e. Lin et al., 2008) and shales (i.e Sorensen et al., 2009). Many of these studies utilised ‘batch’-type reactors, where a fixed volume of solid and brine are placed into a vessel, pressurised with CO_2, and then allowed to react for a period of time (Lu et al., 2013; Rathnaweera et al., 2016). Analysis of extracted fluids and solids is used to determine the extent of CO_2-water-rock reaction (see comments in the experimental methods section below). This experimental approach has benefits of relative simplicity and ease of control of experimental parameters, and is good for assessing the types and directions of faster CO_2-water-rock reactions. However, it does not replicate the complex feedback processes that occur between kinetically-controlled dissolution/precipitation processes and fluid transport. These are better simulated in flow experiments (Bateman et al., 2005; Galarza et al., 2013; Huq et al., 2015; Luquot et al., 2012).

Sandstones are usually favoured, largely due to their widespread distribution, high permeability, favourable geochemical characteristics (i.e. better long-term pH buffer capacity), and presence of caprocks to keep the buoyant CO_2 within the reservoir rock. However that does not mean that other rock types are unsuitable, and carbonate-dominated rocks, as in the Weyburn case, can also be used (Wilson and Monea, 2005). The resultant alteration depends on the mineralogical composition of the rock sample used, the experimental conditions, and the duration of the experiments. Experimental studies have simulated a variety of in-situ pressure and temperature conditions, as those of the stored CO_2 will vary according to the depth of the target formations and local geothermal gradient. Together with the porewater composition (largely its salinity), these will dictate CO_2 solubility, and solution pH. A further factor that might control pH (and potentially redox state) will be the types and compositions of impurities in the CO_2-rich phase (e.g. oxygen, sulphur dioxide, hydrogen sulphide). Whilst the potential impact of impurities is beyond the scope of the experiments presented here, some recent studies have attempted to quantify CO_2-impurity-brine-rock reactions (i.e. Schoonen et al., 2012; Wilke et al., 2012). For most studies, formation water or simplified brine is usually used as the liquid medium (e.g. De Silva et al. 2015).

It is worth noting, that the reactions observed in laboratory experiments are not always the same as those seen in natural CO_2-rich settings or field injection operations, and care must be taken when extrapolating experimental results to field conditions. In part, these differences result from the very different durations over which reactions occur, with laboratory experiments capturing detailed information on short-term processes, and natural systems reflecting the end points of reactions which may have been ongoing for thousands or millions of years. Some investigators have used significantly elevated temperatures to increase the rates of CO_2-water-rock reactions (Kaszuba et al., 2003; Lu et al., 2013) and overcome sluggish reaction kinetics. Whilst this can be a useful approach to test models, potentially it risks the formation of secondary phases that would not be found within sedimentary used for CO_2 storage. Furthermore, the conditions in large scale field experiments are less controlled than in laboratory reactors, and factors such as fluid:rock ratio and fluid flow rates may vary greatly within different parts of a formation. Moreover, mineralogical and structural heterogeneities may mean that the (relatively small) rock samples used in the laboratory are not always representative of the whole formation. Indeed, samples used in laboratory experiments are typically pretreated (e.g. crushed, sieved and washed with acetone). Whilst this may increase homogenisation, and also increase surface areas to accelerate reaction rates (Huq et al., 2012), it will not reflect the often complex porosity/permeability of real rocks. Factors such as heterogeneity, permeability and porosity of the rock must be taken into account when extending the results of laboratory experiments to study the reaction and transport of sCO_2 and/or CO_2-saturated brine to field scales.

The Mesohellenic Trench has been attracted scientists' interest for further study unravelling the issues for potential CO_2 storage for many reasons. In particular, the area represents an appropriate geological environment of basin for CO_2 storage (Koukouzas et al., 2009). The size of the basin is remarkable, reaching up to 25000 km^2, having significant thicknesses of layers in a range of 1500-3500 m. Voluminous formations of sandstones and conglomerates are deformed in open anticline structures, representing possible porous reservoir rocks. In addition, marls and clays overlying the previous formations are excellent impermeable accumulations, forming the cap rocks of the whole stratigraphic succession. The tectonic stability characterizes the area, corresponding to a substantial factor favoring the storage of CO_2. Moreover, the proximity of the basin to significant CO_2 emission sources of the adjacent lignite power plants (there exist the largest of the Public Power Corporation's lignite-fired power plants are located representing 70% of the country's total power and heat production), as well as the possible existence of hydrocarbons (the 64% of the lignite reserves of the country (~2.8 Gt) are hosted in the same region) are two more criteria that lead us to a thorough study of the Mesohellenic Trench in such perspective (Koukouzas et al., 2009).

The aim of the present study is to investigate the potential mineralogical evolution of representative sandstone samples from the Mesohellenic Trough (NW Greece) exposed to a brine saturated with sCO_2. The current work included: a) laboratory experiments with crushed sandstone samples, and b) extending observed reactions to longer timescales using geochemical modelling. The fluid composition and sample mineralogy were studied before and after the reactions with the CO_2-saturated brine to investigate the geochemical reactions that may take place within a potential CO_2 storage reservoir. The experimental results were used to help define geochemical reactions which were extrapolated to longer timescales using the PHREEQC geochemical code. The ultimate goal is to predict the mineralogical evolution of the sandstones over long time-scales (i.e. 10 ka), in order to assess their potential for CO_2 geological storage.

2. Materials and Methods

2.1. Materials

The sandstone samples used in the current experimental work come from the molassic formations of Mesohellenic Trough (MT). The MT is a basin with a length of over 200 km and a width of 30-40 km in NW Greece and it was developed between Middle Eocene to Late Miocene and has a NNW-SSE orientation (Figure 1, modified after Brunn, 1956).

Insert Figure 1

The sedimentary formations of the basin include deltaic conglomerates, alluvial scree, sandstones and clays of turbiditic and deltaic origin, floodplain and sandy shelf sediments, with a maximum thickness of 4,000 meters. The Tsotyli and Pentalofos Formations, correspond to potential local caprock and reservoir respectively. The Tsotyli Formation (23-21 Ma) consists of turbiditic conglomerates, sandstones and shales. The Pentalofos Formation (25-23 Ma), consists mainly of loam and fine-grained sandstones (Vamvaka, 2009; Zelilidis et al., 2002). The two sandstone samples that were used in the experiments came from surface outcrops of the Tsotyli (TS) and Pentalofos (PS) Formations respectively.

2.2. Experimental set up and procedure

Each sandstone sample was gently crushed and sieved to give 3 size fractions (<250, 250-500 and >500 μm). The 250-500 μm fraction was selected for use in the experiments. This was largely as a compromise between being fine enough to have a high enough surface area to cause sufficient reaction on an experimental timescale, and coarse enough to facilitate mineralogical observations. The grains were rinsed with acetone to remove fine particles, and filtered using a Buchner funnel containing a Whatman no.1 filter paper. 20g of this granulated and cleaned sandstone was mixed with 200 ml of ~0.5M NaCl solution (simplified porewater) (fluid/rock mass ratio 10:1). To minimise corrosion and potential contamination issues, the reaction vessel consisted of lower and upper wetted parts made of titanium, and these were held together with a 316 stainless steel retaining ring. A Viton O-ring was used as a pressure seal. A magnetic stirrer was used to ensure good mixing between fluid and solid. However, in order to minimise mechanical damage to the solid grains, this stirrer was held in a small cage just above the bottom of the vessel. A titanium dip tube to the bottom of the reaction vessel allowed for the withdrawal of aqueous samples. Once assembled, the vessels were heated in a fan-assisted Binder oven to 70 ^{o}C (manufacturer's data show temperature fluctuations less than ± 0.5°C). The salinity chosen (approximate seawater salinity) has also been applied by a number of authors in their experiments (Baraka, 2015; De Silva et al., 2015; Zhang and Pu, 2011). In order to ensure good rock-fluid mixing, it was stirred via a magnetic stirrer for 2 minutes every 4 hours. Periodic, rather than continuous, stirring ensured that the sandstone powder did not suffer too much mechanical abrasion, but also ensured that the reactants were well mixed during the experiment.

For the initial 37 days of the experiment the sandstone and solution were allowed to partially equilibrate under CO_2-free conditions, with 15 bar (1.5MPa) pressure of inert nitrogen in the headspace of the reaction vessel to aid sampling of the brine. Prior to aqueous sample collection, 1-1.5 ml was withdrawn and discarded in order to clean the sampling lines. The volume of the collected sample was typically 10 ml. By day 37 the brine had been sampled twice, and this was followed by depressurisation and flushing of the headspace (at 70°C) with excess CO_2 to remove the nitrogen. Once flushed, the CO_2 pressure was raised, and thereafter maintained at a pressure of 150 bar (15 MPa - super-critical CO_2 conditions) for the rest of the experiment using a Teledyne ISCO 500D pump running in constant pressure mode. Eight further brine samples were taken between then and the end of the experiment, whilst the experiment was under CO_2-pressurised conditions. During sampling, the CO_2-rich brine was allowed to degas into a sterile syringe. The collected samples were pre-filtered through an Acrodisc NYLON 0.2 μm filter. The associated loss of CO_2 will have an unavoidable impact on very rapidly-responding geochemical parameters - such as pH. However, after sampling the solutions were rapidly analysed for Eh and dissolved bicarbonate, as these would change if the solutions were left for some time. Other subsamples were immediately preserved for the accurate determination of reduced iron using 2,2-dipyridyl, and major and trace cations using a 1% addition of concentrated nitric acid. The addition of acid prevented the possible precipitation of solids which might occur during storage once the samples were fully degassed. Immediately prior to analysis, the fluid samples were checked visually, and no precipitates were observed. It has been our experience that collection of several subsamples in this way, together with the immediate analyses of key parameters, gives an accurate representation of most in-situ fluid compositional parameters. The main exceptions to this are: a) total dissolved inorganic carbon, as much of the dissolved CO_2 (CO_{2aq}) will degas, b) pH, as this will be influenced by the amount of dissolved CO_2 in solution. However, geochemical modelling can be used to effectively ‘titrate’ the lost CO_2 back into solution.

A total of ten fluid samples (having an accurately-known volume between 10-15 ml) were collected from each vessel. Pressure stayed relatively constant within the vessel during the sampling procedure because the CO_2 pump ran in constant pressure mode, and added extra CO_2 as brine was withdrawn. The periodic sample extraction led to modification of the liquid/solid ratio from 10:1 to approximately 4:1 at the end of the experiment. The impact of this changing fluid:rock ratio would have been an apparent increase in the rate of reaction, and would thus have helped drive the reactions closer to steady-state conditions. This was advantageous to this study in order to assess dissolution/precipitation processes and overall reaction directions. However it makes quantification of rates of mineral reactions more difficult.

After a total duration of 184 days (6 months) as much as possible of the remaining brine was drained from the experiment via the ‘dip tube’ that reached close to the bottom of the vessel. It was then slowly depressurized and dismantled to allow the collection of the solid material. Removal of brine prior to depressurization was done to minimize the potential for unintended carbonate mineral precipitation (Figure 2).

Insert Figure 2

2.3. Mineralogical analysis

Quantitative mineralogical analysis of the samples before and after the reaction with CO_2 was achieved by powder X-Ray Diffraction analysis (XRD) using a SIEMENS D5005 instrument (CuKa radiation operating at 40kV and 40mA), with 2θ angle ranging from 5^o to 70^o, step 0.01^o, time per step 5sec, at ambient conditions. Mineralogical evaluation was conducted using the Siemens DIFRAC PLUS v2.2 software by Siemens and data were processed using the Rietveld method by the BRUKER TOPAS Software. The morphology of the samples was examined by scanning electron microscopy (SEM) using a JEOL JSM-5600 instrument, operating at 25-30 kV.

2.4. Chemical Analysis

Each sample was sub-sampled and prepared for analysis of pH, Eh (redox), anions, cations, alkalinity and iron (II) using the following methods. pH on depressurised (i.e. largely CO_2 degassed) solutions was measured at room temperature and pressure by an Orion bench top meter and glass pH electrode calibrated using NBS-traceable pH buffers of 4, 7 and 10 prior to sample analysis. The calibration of a Ag/AgCl Eh electrode was checked using Zobell’s solution prior to analysis of Eh. Alkalinity was measured using potentiometric titration as soon as possible after sampling (usually within 1-3 days). The remainder of the subsamples were first pre-filtered through a 0.2 μm nylon Acrodisc filter. Subsamples destined for cation analysis were preserved by acidification with 1% concentrated nitric acid. Subsamples for anion analysis could not be preserved, but were diluted to 25% concentration with deionised water to minimise the potential for precipitation prior to analysis. The cation, anion and iron (II) samples were stored in a fridge at 4°C prior to analysis. Cations were analysed using ICP-MS (dilution 1:10 for Ca, Mg, Na and K), anions by ion chromatography and reduced iron by UV-visible spectrophotometry.

2.5. Geochemical modelling and reaction rates

The PHREEQC v.3.3 geochemical code was employed to simulate the reactions in the solid/liquid interface between the sCO_2-saturated brine and the sandstone samples The LLNL database was used (compiled by Lawrence Livermore National Laboratory) which employs the Truesdell-Jones model to calculate the activity coefficeints at high ionic strengths (up to 2) (Delany and Lundeen, 1991; Parkhust and Appelo, 1999).

Insert Figure 3

Reaction rate parameters for each mineral were defined and solved by CVODE solver for stiff ordinary differential equation (ODE) systems. The methodology followed is summarized in Figure 3. Speciation calculations were conducted on the basis of measured final solution composition regarding the major ions (total Ca, Mg, Na, K, Al, Si, Fe) and total inorganic carbon, taking into account the loss in solution mass and the degassing effects due to sampling. Kinetic and equilibrium models accounted for possible changes in total mass of the solids during the experiment.

Reaction dissolution and precipitation rates were calculated using the Transition State Theory (TST) (Lasaga, 1984) and presented in detail in Appendix A. The thermodynamic parameters and kinetic rate data of the selected minerals are compiled and presented in Appendix A. Most of them are included in llnl.dat database. The composition of ankerite chosen in the present work was a solid solution consisting of 40% dolomite and 60% ankerite as end-members, giving the formula $CaFe_{0.6}Mg_{0.4}(CO_3)_2$ and the thermodynamic data used, were taken from Van Pham et al. (2012).

Moreover, some additional phases were tracked in the model to investigate their potential for formation. These phases include magnesite, siderite, dawsonite, boehmite, $Fe(OH)_3$, goethite, gibbsite and illite. As kinetic data for ankerite and dawsonite could not be identified in the literature, the respective parameters of another carbonate phase, dolomite, were taken as being similar, and were used instead. Respectively, siderite data were used for magnesite, boehmite for hydro-oxides and kaolinite for clays (Marty et al., 2015; Palandri and Kharaka, 2004; Van Pham et al., 2011).

3. Results & Discussion

3.1. Mineralogy of the reactant and produced solids

Both of the sandstone samples are arenites and mainly consist of well-rounded, fine-grained quartz and feldspars grains. These lie within a diagenetic carbonate cement that consists of both calcite and dolomite, with calcite being the more abundant (Figures 4 & 5).

Insert Figure 4

The silicate grains of the Tsotyli Formation (TS) sample are anhedral and smaller than 100μm. The phyllosilicate minerals detected are chlorite and muscovite having narrow flaky grains of about 50μm long. Calcite and dolomite appear in the form of relatively large anhedral crystals. Opaque minerals appear as rare and small-sized grains. Limited fossil fragments were found and identified to be Operculina sp..

The sample of the Pentalofos Formation (PS) is a poorly to moderately sorted sandstone that consists of larger silicate (200-500μm) and carbonate (50-500 μm) grains. These lie within an authigenic matrix of clay minerals including illite, kaolinite and smectite (10-50μm). It exhibits a wide range of sizes, mostly with angular grains although few are subrounded. Phyllosilicate grains vary in size between 10 and 500μm. Feldspar minerals include both alkali feldspars as well as plagioclase. Additional mineral phases include biotite, partly altered to chlorite, muscovite, as well scarce small olivine grains.

Insert Figure 5

Insert Figure 6

XRD analysis confirmed the microscopic observations, that both samples exhibit a common mineralogical composition (Figure 6 & Table 1). The bulk of the samples are composed mainly of calcite, quartz and feldspars, with the phyllosilicates of lower abundance in the sandstones. The main differences in the mineralogy of the two samples are (a) the presence of ankerite in the TS sample and montmorillonite in the PS sample, and (b) the high calcite content in the TS sample.

Table 1: *Quantitative X-ray analysis (wt%) of the samples before and at the end of the interaction with CO_2-saturated brine, as well as the expected percentages calculated by the kinetic reaction models of Section 3.3.3.*

Sample	**Pentalofos Sandstone (PS)**			**Tsotylli Sandstone (TS)**		
Minerals	**Unreacted**	**CO_2-**	**Kinetic**	**Unreacted**	**CO_2-**	**Kinetic**

	Sample	reacted sample	model results	Sample	reacted sample	model results
Albite	15	13	15.6	~9	~9	9.4
Calcite	38	35	35.6	58	58	57
Clinochlore	7	6	6.6	4	2.5	3.2
Dolomite	4	2	3.6	<0.5	2	0.12
Kaolinite	<0.5	<0.5	0.5	1	1	1.1
Montmorillonite	3	4	3.1	-	-	-
Muscovite	~2	~2	1.8	~0.5	<0.5	0.4
Orthoclase	10	10	10.7	5	5	5
Quartz	~21	~28	22.4	17	17	17.7
Ankerite	-	-		6	5	6.1

The interaction of the samples with CO_2-saturated brine only resulted in minor mineralogical changes over the duration of the experiments. This is not entirely surprising given the relatively slow reaction kinetics at the experimental temperatures. Changes observed include decreasing of feldspars' quantity and a relative change in the proportion of carbonate phases. Minor changes were also observed in the amounts of chlorite and muscovite. Those minor changes may be due to the incongruent dissolution of feldspars and phyllosilicates leading to clay formation (Black et al., 2014; Kaszuba et al., 2013). However, SEM observation of the powder fraction that was used in the experiments was unable to confirm those mineralogical changes. The magnetic stirrer bar from sample PS attracted some iron bearing grains, which could also be of primary origin. No new secondary phases (such as Fe/Al hydro/oxides dawsonite, magnesite, etc.) were identified by XRD or SEM analysis. Although dawsonite formation is favoured in some feldsparic rather than in quartz sandstones (Tremosa et al., 2014), its absence in experimental studies is in line with other studies. The dissolution/transition among the carbonate minerals and the incongruent hydrolysis of aluminosilicates, mainly feldspars, to clays have been well documented in other CO_2-water-rock reaction studies (Kaszuba et al., 2013; Lu et al., 2013; Wigand et al., 2008). In the Wekerdam gas field, the mineralogical study concluded that feldspar hydrolysis promoted the transformation of kaolinite to illite, whereas dolomite and siderite are the main carbonate precipitates (Koenen et al., 2013). When sandstone samples from the Songliao Basin in China were subjected to laboratory experiments simulating reservoir conditions (T=100°C, P=24MPa), complete dissolution of calcite and partial hydrolysis of feldspars occurred, together with enrichment in quartz and clays (Yu et al., 2012). Although our study considers temperatures at <100°C, the importance of CO_2-feldspar reaction and resultant clay formation is also highlighted by higher temperature work at up to 200°C involving both sandstones (Kaszuba et al., 2003; Lu et al., 2013) and granite (Lin et al., 2008).

None of the above studies reported the precipitation of dawsonite, although it is a possible precipitate coming from hydrolysis of feldspars in sodium-rich solutions (De Silva et al., 2015):

$$NaAlSi_3O_8 + CO_2 + H_2O \rightarrow NaAlCO_3(OH)_2 + 3SiO_2$$

Albite *Dawsonite* *"amorphous"*

Dawsonite has been considered an important secondary phase in modelling studies, largely because its relatively large molar volume might have an impact on porosity/permeability (Johnson et al., 2004). Indeed, it has been reported in some sandstone formations that have come into contact with CO_2 under elevated pressure and temperature (Worden, 2006; Zhou et al., 2014). In some cases its formation was also related to alkaline Na-HCO_3 waters (Kampman et al., 2014), though in others to acidic high-salinity brines (Worden, 2006). However, its formation has been questioned because of its absence in many natural settings (Hellevang et al., 2011) and general absence in laboratory experimental studies even when it was expected to be found, including when a pure feldspar sample was used (Alemu et al., 2011; Gaus et al., 2005; Huq et al., 2012; Van Pham et al., 2011; Wigand et al., 2008). There is thus some uncertainty as to why dawsonite does not form in some environments, but possible reasons could include kinetic constraints, temperatures being too high, or pH being too low (Hellevang et al., 2011; Lu et al., 2013).

3.2. Fluids chemistry

The concentrations of major ions and selected trace elements for both experiments are presented in Table 2 for the starting brine composition, N_2-saturated brine (0-37 days), and also CO_2–saturated brine (37-184 days). The pH and Eh of the starting solution drop after addition of CO_2:

$$CO_2 + H_2O = HCO_3^- + H^+$$

However, it is noted that the measured pH values refer to solutions that have been largely degassed.

The major element chemical evolution of the extracted fluid samples is presented in Figure 7 and Table B.1 (Supplementary Material). Complete chemical analyses of the fluid samples are available in Appendix B. Initial brine-sandstone interaction leads to a slight increase in ion concentrations in the solution of both sandstones (Ca~70-110mg L^{-1}, Mg~7-12mg L^{-1}, K~5-12mg L^{-1}, HCO_3^- ~60-100 mg L^{-1}), likely due to dissolution of carbonates and possible ion exchange effects on clay surfaces (Table 2). Si reaches 7-8 mg L^{-1} and Al 20-100 μm L^{-1} respectively, as a result of minor dissolution of the alumino-silicates, especially muscovite and clinochlore. The TS sample exhibits higher dissolved Fe concentrations (up to 3.5 mg L^{-1}) due to dissolution of ankerite.

Once CO_2 enters the reaction vessel, ion concentrations increase abruptly. Ca, and bicarbonate concentrations reach ~1200 mg L^{-1} and ~1500 mg L^{-1} within the first 3 days, as a result of the brine acidification and calcite/dolomite dissolution. K reaches 6 mg L^{-1} and 16 mg L^{-1} in the TS and PS sample experiments respectively, considered mainly due to muscovite hydrolysis. Magnesium was increasing steadily in both samples, whereas aluminum and silica contents increased only to a small extent, as hydrolysis reactions are relatively slow, making them hard to quantify over low temperature experimental time-scales of just a few months (Gaus, 2010).

Insert Figure 7

The overall concentration of ions released reached approximate steady state within the first ~50 days of the experiment, similar to those reported by Wigand et al. (2008) (~33 days at T=60°C, P=150 bar) and Kaszuba et al. (2003) (~55 days at T=200°C, P=200bar). Only Mg shows a significant steady increase in concentration with time. It is noted that the reduction of brine:rock ratio due to constant fluid extraction may help contribute to the Mg, K, TIC and Si enrichment of the final solution because of condensation.

The time-dependent trend of selected variables was examined through Pearson correlation analysis according to their correlation coefficient R given by the equation (Eq. 1):

$$r = \frac{\sum x_i y_i - n\overline{xy}}{\sqrt{(\sum x_i^2 - n\overline{x}^2)}\sqrt{(\sum y_i^2 - n\overline{y}^2)}} \qquad (1)$$

Bicarbonate and Ba-Sr-Mn (R>0.8) shows a strong dependence of these elements with dissolution/precipitation of carbonate minerals. Moreover, the relationship between Co-Ni-Mn (R>0.9) can be attributed to either the ophiolithic protolith mineral phases that contribute to the sandstone composition, or the presence of Mn hydroxides (Wigand et al., 2008). Fe is not correlated to any of the major or trace elements analyzed for. Iron could be present in the lattice of carbonates, or originate from chlorite and olivine, but neither case was included in the proposed models. The presence of olivine grains was confirmed in SEM images, although in trace amounts.

Sodium exhibits different behavior between the two samples, showing positive correlation to Si (R=0.9) in the TS experiment and negative correlation in the PS experiment (R=-0.9), which can be attributed to the minor differences in mineralogy of the sandstones. For the PS sample, incongruent dissolution of albite releases sodium that could be bound into a montmorillonite precipitate, unlike the TS sample that lacked any major clay components (Table 2).

Table 2: ***Chemical analysis of the extracted fluids***

		TS		**PS**	
Analyte	**Starting solution**	**Brine with N_2 after 37 days**	**Brine with sCO_2 after 184 days**	**Brine with N_2 after 37 days**	**Brine with sCO_2 after 184 days**
pH (at 20°C)[a]	8.96	7.51	6.68	7.48	6.71
Eh (mV at 20°C)	137.4	109.4	43.5	91.3	13.6
(mg L^{-1})					
Ca	<10	84	1195	108	1052
Mg	<0.8	9.5	102	12.3	223
Na	12940	11676	12395	13538	11943
K	1.2	4.8	6.4	12.3	15.4
HCO_3^-	-	157	2714	90	2894
Cl^-	17230	17546	18589	16972	18758
TIC	0	31	534	18	570
Si	<1.7	8	40	8	108
Balance (%)	7	1	-9	10	-12
(µm L^{-1})					
Ba	<5	122	567	53	233
Sr	9	805	4639	200	879
Mn	<7	99	870	115	2033

Total Fe	<42	1546	1930	3344	2062
Li	<37	65	96	46	88
Al	<18	23	48	19	<18
Ti	<0.6	<0.6	1.1	<0.6	1.1
V	<3	<3	4	<3	5
Cr	<1	<1	2	<1	6
Co	<0.4	17.7	37.1	3.8	83.9
Ni	0.8	668	696	147	1397
Cu	4.2	4.2	20	23.7	3
Zn	20	23	40	23	43

[a]pH values refer to degassed solutions after sampling

Combining the mineralogical and chemical data of the samples, the proposed reactions include:

i. <u>Dissolution of carbonates:</u>

In PS sample both calcite and dolomite dissolved releasing Ca and Mg.

$$CaCO_3 + CaMg(CO_3)_2 + 3H^+ \rightarrow 2Ca^{+2} + Mg^{+2} + 3HCO_3^-$$

Calcite Dolomite

In TS sample, dissolution of calcite was not observed (at least, not detected according to Rietveld method). Instead, ankerite transition into dolomite was proposed as:

$$CaFe_{0.4}Mg_{0.6}(CO_3)_2 + 0.8H^+ \rightarrow 0.4Ca^{+2} + 0.4Fe^{+2} + 0.6CaMg(CO_3)_2 + 0.8HCO_3^-$$

Ankerite Dolomite

As Ca reached a steady state very quickly (within ~4 days after CO_2 injection) in both samples, it was assumed that the respective Mg concentration at equilibrium should not exceed ~40 mg L-1, and thus the excessive amount had a different origin.

ii. <u>Hydrolysis of phyllosilicates (clinochlore/muscovite):</u>

The excess Mg amount was attributed to clinochlore hydrolysis, as testified by numerous researchers (e.g. Alemu et al., 2011; Black et al., 2014; Luquot et al., 2012). Gaus (2010) proposed that chlorite may interact with calcite and CO_2 to form siderite, dolomite, kaolinite and amorphous silica:

$$Fe_{2.5}Mg_{2.5}Al_2Si_3O_{10}(OH)_8 + 2.5CaCO_3 + 5CO_2 \rightarrow$$

Chlorite calcite

$$2.5FeCO_3 + 2.5CaMg(CO_3)_2 + Al_2Si_2O_5(OH)_4 + SiO_2 + 2H_2O$$

Siderite Dolomite Kaolinite “chalcedony”

In our study, calcite dissolved along with dolomite in PS sample. Siderite was not observed and kaolinite mass remained the same. Even if the proposed reaction would have occurred, the small mineral amounts produced, would not be detected by the deployed methods (XRD or SEM).

Potassium may have come from minor muscovite corrosion from the brine. The almost fixed concentration during CO_2 diffusion suggested no further interaction of the phase with the solution.

iii. Precipitation of montmorillonite:

In some studies montmorillonite was directly associated with the hydrolysis of albite (Fischer et al., 2011; Huq et al., 2012; Wigand et al., 2008) and a simplified reaction can be expressed as:

$$2NaAlSi_3O_8 + 2CO_2 + 2H_2O \rightarrow Al_2Si_4O10(OH)_2 + 2Na^+ + 2SiO_2 + 2HCO_3^-$$

Albite Montmorillonite

Montmorillonite growth occurred only in PS sample, where albite mass showed some decrease. On the contrary, is absent in TS sample, where albite mass remained constant. Thus, it was assumed that montmorillonite was a byproduct of albite hydrolysis.

The above reactions were confirmed both experimentally and numerically and were consistent with those refereed in the literature concerning siliciclastic formations (Horner et al., 2015; Huq et al., 2015).

3.3. Geochemical Modelling

3.3.1. Fluid speciation

Based on the chemical evolution of the analyzed brine samples, saturation indices were calculated for the mineral phases within the rocks, plus some possible secondary precipitates. The measured pH values of the brine samples extracted during the CO_2-pressurised part of the experiments were recalculated by equilibrating them with CO_2 ($logP_{co_2} = 2.17$) to reproduce the experimental conditions. Thus, the pH values calculated in this manner, do not exceed 4.8, and the saturation indices were calculated using these values (Figure 8).

Insert Figure 8

Prior to CO_2 injection, the analyzed fluids appear undersaturated with respect to all major mineral phases. After interaction with the brine, calcite, dolomite, chlorite, and quartz are close to equilibrium, with saturation index (SI) values ranging from -0.6 to 0.6. When the sCO_2 entered the system, the analyzed fluids become oversaturated in respect to kaolinite (SI>2), montmorillonite (SI>1) and muscovite (SI>2) and undersaturated with respect to feldspars (SI>-2). This trend reflects the incongruent dissolution of chlorite discussed previously, as well as the minor hydrolysis of albite to montmorillonite (in PS sample), and is in line with previous models (Gunter et al., 1997, 1993). Muscovite precipitation would never occur, however it could be considered as substitute for illite precipitation.

The fluid samples from both experiments are almost equilibrated with calcite, quartz and dolomite.

The saturation state of some possible secondary precipitates was also calculated. Both experiments were close to equilibrium with respect to boehmite, gibbsite, magnesite and siderite, prior to CO_2 injection. When CO_2 entered the system, the fluids became oversaturated with respect to boehmite (SI~ 1.5), illite (SI~ 0-2), Fe-hydro/oxides (SI>2.5) and dawsonite (SI>1.5), and undersaturated in respect to magnesite (SI> -1.5) and siderite (SI> -3). These phases were also included in the kinetic models.

3.3.2. Model input parameters

Mineral reaction kinetics depends on a number of parameters, of which some were calculated or measured experimentally, whilst others were available in the existing literature (i.e. Marty et al., 2015; Palandri and Kharaka, 2004; Van Pham et al., 2011).

Mineral surface areas S_A ($m^2\ g^{-1}$) were calculated assuming that all grains were spherical (i.e. geometric areas, and done for reasons of simplicity, though we acknowledge that this is not truly realistic for phyllosilicate minerals) and their grain diameter was estimated from SEM images (Appendix A) (Tester et al., 1994). This is a simplistic approach, as there is no account for surface roughness, and thus our assumption will tend to minimize surface areas. On the other hand, only the more reactive surface sites will actually undergo dissolution. The role of reactivity of the surface area was accessed through a number of sensitivity simulations given in Section 3.4.2. The effective diameter, d_e, (calculated using equation A6, in Appendix A according to (Tester et al.,

1994) and mass amount in moles, n, is shown in Table 3. Reactive fraction λ was set to 1 for all aluminosilicates, assuming that the small grain size of the solids and their unconsolidated form, allows for the whole grain surface to come in contact with the solution. However, this value initially led to overestimation of Ca and Mg concentrations, and λ was subsequently set to 0.001 for carbonate phases.

Table 3*: *Mineral parameters for the kinetic modelling

		PS			**TS**		
Mineral	**ρ (g cm^{-3})** (Smyth and McCormick, 1995)	**moles**	**d_e (μm)**	**S_A (m^2 g^{-1})**	**moles**	**d_e (μm)**	**S_A (m^2 g^{-1})**
Albite	2.62	0.0113	327	0.007	0.0068	72	0.0317
Orthoclase	2.56	0.0073	327	0.007	0.0036	72	0.0325
Calcite	2.71	0.0763	195	0.011	0.1159	144	0.0153
Dolomite	2.65	0.0038	195	0.012	0.0004	144	0.0136
Montmorillonite	2.35	0.0016	25	0.103	-	-	-
Kaolinite	2.60	0.0004	25	0.093	0.0008	72	0.0320
Muscovite	2.82	0.0010	195	0.011	0.0003	72	0.0295
Clinochlore	2.65	0.0025	195	0.012	0.0014	72	0.0314
Quartz	2.62	0.0699	72	0.032	0.0566	72	0.0317
Ankerite	3.05	-	-	-	0.0058	144	0.0136

The effect of ion exchange was also considered in the modelling, although the CEC of the samples was not measured experimentally. The relative ion exchange capacity was calculated using literature CEC values (meq kg^{-1}) for each mineral phase present (kaolinite, montmorillonite, chlorite) and their relative abundance in the samples (Appelo and Postma, 2005). The calculated CEC range from 31 to 67 meq kg^{-1} for the PS sample and from 4 to 16 meq kg^{-1} for the TS sample. The average values used are 50 meq kg^{-1} (5 mmol L^{-1}) and 10 meq kg^{-1} (1 mmol L^{-1}) for the PS and TS samples respectively.

All simulations took into consideration the experimental conditions. The fugacity coefficient and solubility of CO_2 in 0.5M NaCl were calculated as 0.57 and 0.78 mol/kg H_2O respectively (Duan & Sun 2003; Duan et al., 1995).

3.3.3. Equilibrium and kinetic modelling

Whilst we recognize that the six-month experiment duration was a relatively short period of reaction time, it is informative to undertake these calculations to ascertain which reactions may have neared steady state conditions. An ‘equilibrium model’ was used to simulate reactions of the rocks with the brine (for up to day 37 of the experiments). It considered equilibrium with calcite, dolomite, chlorite and quartz, and was based upon their respective SI values. Cation exchange capacity was also used to study the effect of the clay content of the samples in the chemistry of the fluids. Some degree of secondary precipitation (e.g. boehmite for both the PS and TS simulations, and $Fe(OH)_3$ for TS simulations) was allowed, to counterbalance the increased concentrations of Al and Fe ions in the simulated fluids. Furthermore, a kinetic model was used to simulate geochemical reactions after the injection of CO_2. CEC and λ values remained stable. The model assumed a constant CO_2 pressure of 150 bar (15 MPa). Calibration of both models was done by comparing the simulated concentrations of major ions with those measured in the sampled fluids.

The measured and calculated ion concentrations are shown in Figure 7, and the models were able to broadly reproduce the measured cation concentrations. At a more detailed level however, the model more accurately represented the PS compared to the TS experiment, in which Mg and Si contents were slightly overestimated.

The chemical evolution of the fluids reflected the respective mineralogical changes in each sample (Figure 9, Table 1). In general terms, as CO_2 was added to the system, calcite and chlorite were readily dissolved, releasing magnesium and calcium (Figure 9a, b). Dissolution of dolomite (in the PS experiment) or ankerite (in the TS experiment) was inferred by rising magnesium concentrations, but was hard to confirm experimentally due to the low mineral content. Feldspars showed little reaction on these timescales. Overall, both systems reach approximate steady state after 50 days of reaction (Figure 9c, d).

Insert Figure 7

Excessive chlorite hydrolysis during the simulations gave Al concentration values far greater than those measured. The formation of aluminium colloids which were removed from the fluid samples during filtration could be the explanation for the low Al concentrations measured. This increase was counterbalanced by equilibration with boehmite in both models for both solids. The rest of the secondary phases used (i.e. gibbsite, magnesite, dawsonite, illite, etc.) were included in the model with kinetic control. Simulations results suggest that boehmite, gibbsite and $Fe(OH)_3$ should precipitate in both sandstone samples (Figure 9e,f). However, the amounts predicted fall under the 1% detection limit of the XRD analysis, explaining their apparent absence from XRD patterns. Potential secondary carbonate phases (dawsonite, siderite and magnesite) were also included in the proposed models, but the fluids were undersaturated with respect to these phases.

The samples also exhibit similar trends with regard to the cation distribution among the exchangeable sites (Figure 9g, h). Sodium occupies 93-95% of the sites at the start of the experiment, which is gradually replaced mainly by Ca, but also by Mg and K. After addition of CO_2, the rapid enrichment of Ca ions in solution enhances replacement of Na ions on the solid surface. Under steady-state conditions, the exchangeable sites consist of 55-59% Na, 37-40% Ca and 4-5% Mg.

3.3.4. Prediction model

The kinetic model above was extended to simulate potential longer-term reactions with CO_2 – in this case 10 ka. Similar predicted timescales have been used previously by several researchers (e.g. Hellevang et al., 2013; Mohd Amin et al., 2014; Van Pham et al., 2012). We recognize that this extends an experimentally-derived model far in excess of its validated time period, and the results should be seen as tentative. However, this can be a useful exercise, as it helps identify a possible scenario for the long-term fate of stored CO_2 and its potential impact on the rock types studied.

The geochemical reactions predicted for both sandstone samples proceeded very slowly, and in a similar manner (Figure 10a-d). The main reaction was chlorite hydrolysis which enriches the solution in Mg (up to 500 mg L^{-1}), until the chlorite was exhausted at 100 years of simulated time. The predicted Mg released within the first 10 years, enabled minor quantities of calcite to transform into dolomite, whilst the Al and Si released contributed to the formation of boehmite (Figure 10e,f). Muscovite reacted slowly, whereas feldspars initially remained stable. However, K-feldspar was predicted to react after 100 years of simulated time, when chlorite was removed from the system. There was potential for Fe hydro-oxides to be formed in the TS sample due to the relatively large amounts of Fe released from ankerite breakdown (Figure 10e,f). K gradually replaced Ca in the exchangeable sites (Figure 10g, h).

Insert Figure 8

Numerous previous experimental and modelling studies have concluded that carbonates are the first phases to react upon addition of CO_2, and saturation is quickly attained. Incongruent hydrolysis of aluminosilicates then becomes the main rate-limiting reaction. Moreover, the aluminosilicate:carbonate ratio should be initially larger in order to maintain long-term acid consumption capacity (Allan et al., 2011). In our case, chlorite (and in a lesser extend muscovite) is the main consumer of the generated acid. Phyllosilicates exhibit high surface area and are succeptible to alteration. Their incongruent dissolution provides divalent cations, especially K and Mg, which promotes the precipitation of secondary phases. This is in accordance with observations made by Carroll et al. (2013) who found that phyllosilicate hydrolysis is the rate-limiting reaction, when micas are present. Moreover, a sandstone experiment conducted for 1.5 years (P=10MPa, T=40°C, NaCl 20%) by Rathnaweera et al. (2016) showed dissolution of calcite, siderite and quartz.

The predicted geochemical reactions were compared to paragenetic sequences observed in sandstones from existing oil and gas fields. In the Werkendam gas field (Netherlands), the mineralogical assemblage consists of kaolinite which reacted with K-feldspar to form illite and quartz, whereas dolomite and siderite are the main carbonates (Koenen et al., 2013). CO_2 has been accumulating in Montmiral Triassic Sandstone since 15 Ma ago, leading to the formation of kaolinite at the expense of K-feldspar, corrosion of ankerite and precipitation of barite, and ankerite/dolomite phases as secondary products. Dawsonite was not observed (Czernichowski-Lauriol et al., 2006). The simulated geochemical sequences were in accordance with observations from UK oilfields, where carbonates and feldspars are not equilibrated with the current CO_2 of the reservoir (Haszeldine et al., 2005).

3.4. Sensitivity tests and model limitations

The proposed model partially reproduced the experimental data. The kinetic models predicted the broad trend of the reactions, but failed to reproduce the exact amount of reacting phases (quantitative mineralogical analysis of the solids after reaction with CO_2 gave values lower than those calculated by the models. Moreover, the calculated aluminium contents were much higher than those analysed in the sampled fluids. These discrepancies could be minimized by taking into account some identified uncertainties:

- Firstly, the model used the chemistry and thermodynamic data of ideal mineral phases. However, some phase involved may not be pure. So, for example, it is possible that chlorite and calcite could contain some iron, explaining its concentration in the analyzed fluids.
- Secondly, ion exchange capacity and surface areas were not measured, but approximated by the mineral content and grain size. In order to simplify calculations, these values remained constant, although both mineral mass and size were changed during the dissolution/precipitation reactions.
- Lastly, the reactive fraction λ was a fitting parameter in order for the model to match the experimental data. As we lack a more detailed series of experiments to determine the actual solid fraction that reacted with the brine, this parameter would add to the uncertainty of the proposed models.

The role of the above uncertainties on the viability of the model results was evaluated by running sensitivity tests considering the cation exchange capacity, the reactive surface areas, and formation of possible precipitates.

3.4.1. Effect of cation exchange capacity

Cation exchange capacity was used mainly to simulate the initial fast increase of Ca, Mg and HCO_3^- during the reaction of the solids with the N_2-saturated brine. The importance of cation exchange was represented using CEC values from zero to a maximum according to the mineralogy of the samples. All other parameters remained unchanged.

The concentrations of Ca, Mg and HCO_3^- were the most affected by the different CEC values tested, and thus the amounts of the minerals involved. The use of CEC value affected mainly the reaction behavior of carbonates, the incongruent dissolution of K-feldspar and chlorite, and formation of boehmite and silica (Figure 11). Calcite and chlorite were dissolved and the released magnesium enabled the precipitation of dolomite. The maximum amount of dolomite was achieved when no CEC was used, whereas more calcite was dissolved at the highest CEC value. However, predicted steady-state was reached after 100 years. On the other hand, chlorite and K-feldspar dissolved, releasing silica regardless of the tested exchange capacity. It was concluded that cation exchange was an important process occurring during equilibrium, which was overwhelmed by the kinetically induced reactions between the solids and the dissolved CO_2.

Insert Figure 11

3.4.2. Effect of reactive surface area

The determination of reactive surface area is a rather difficult task. Even if a surface area value had been measured (i.e. by BET measurements), its reactivity depends on the anomalies and dislocations on the surface of the grains. If λ is equal to 1, the whole grain is reacting with the solution, and reaction rate is maximized. The lower the λ value, the more that reactivity is minimized. Sensitivity test was run using λ values from 0.00001 (practically smooth surface) to 1 (a rough surface) (Figure 12, 13).

The main reactive phases in the PS sample were the carbonates, muscovite, chlorite and quartz. The amounts of feldspar dissolution and clay precipitation were less than 1μmol, and so they were omitted from the figures. When a smooth surface was used (Figure 12a,b & 13a,b), the rate-limiting reaction was aluminosilicate dissolution, which occurred after 10 years, along with a change in the carbonate phases. When λ was increased by two orders of magnitude, carbonate transformation was brought forward up by approximately 5 years, and chlorite hydrolysis prevailed (Figure 12c, d & 13c, d). For simulations with a fully reactive surface area (Figure 12e, f & 13e, f), chlorite was completely dissolved within 100 years, and K-feldspar hydrolysis became the rate-limiting step. The predicted excessive Mg content during the first 100 years promoted dolomite precipitation over calcite in the PS simulation. None of the simulations predicted the formation of dawsonite, magnesite or siderite.

Insert Figure 12

Insert Figure 13

3.4.3. Effect of secondary precipitates

In the proposed model the fluid was equilibrated with boehmite to counterbalance the high Al content extracted from the simulations. Most of the other selected secondary phases (i.e. magnetite, siderite, gibbsite, illite, etc) did not kinetically form under the simulated conditions (perhaps the kinetic data used do not represent the occurring reaction rates). The importance of these phases in the evolution of the primary mineralogy of the samples was assessed via a semi-kinetic model, where kinetic reactions were used for the primary phases with CO_2-saturated brine and equilibrium reactions for all the secondary precipitates.

The CO_2-brine-rock system was equilibrated with boehmite (SI=0). The other secondary phases were either allowed or forced to attain equilibrium. In the first case, dawsonite, gibbsite, magnesite, illite, goethite, and $Fe(OH)_3$ freely reacted (dissolved/precipitated) until SI=0 (Figure 14a-d). Under these assumptions, dawsonite was formed instantaneously (consuming the Al required for boehmite growth), though the kinetic model did not predict its formation. This was also the case in simulations conducted by Hellevang et al. (2013). In the second case, the aforementioned phases were forced to reach the over- or undersaturation using the indices calculated in Session 3.4.1.This resulted in the formation of gibbsite as the main precipitate (Figure 14e-h). Illite and boehmite were predicted to form at the very start of all simulations, during the first decade. Siderite growth resulted from ankerite dissolution after 1000 years of simulated reactions.

In either case, the overall mass transfer as discussed in the base case scenario of Section 3.3.4 and presented in detail in Figure 11 (diagrams e & f), shows that the semi-kinetic approach does not affect the kinetic reactions of the primary phases. However, it fails to predict accurately the formation of the secondary phases, as some of them are favoured and expected under equilibrium conditions. Thus, the kinetic modelling approach would be more realistic if it is important to describe in detail the mineral phases that help CO_2 trapping. However, if the main concern is the overall mineralogical evolution of the reservoir, the use of a semi-kinetic (i.e. equilibrium and kinetic) model would provide adequate levels of detail.

Insert Figure 14

Conclusions

Representative sandstone samples from Mesohellenic Trough (NW Greece) were tested to investigate the geochemical reactions that occur when they come in contact with CO_2-saturated brine (~0.5M) under representative in-situ conditions. A PHREEQC-based geochemical model was used, and for shorter timescales was calibrated using mineralogical and chemical results from lab experiments.

Geochemical reactions that occurred within the sandstone-brine-CO_2 system were limited and the absence of noticeable changes in the sandstone samples indicated that the proposed reactions proceeded very slowly, but included (a) mass transfer among carbonate phases, and (b) the incongruent dissolution of phyllosilicates. No secondary carbonates were observed at the end of the experiments. However, simulation results for a 10 ka time period predicted that chlorite was expected to dissolve completely within 100 years, leading to boehmite growth and increasing the mass of dolomite. Feldspars were expected to react at a later stage in the reaction sequence.

A number of key uncertainties were identified, such as reactive surface area, cation exchange capacity, and secondary mineral growth. The impact of these on the simulations was assessed using sensitivity tests, and these showed that the silicate hydrolysis is the rate-limiting reaction on the system. Furthermore, the growth of secondary precipitates was favored under local equilibrium conditions.

The geochemical experiments and modelling lend support to the view that Pentalofos and Tsotyli sandstone formations of the Mesohellenic Trough are suitable for the long-term storage of CO_2 produced in the neighbouring lignite-fired power plants, at least in terms of mineralogy and geochemistry. Continued optimization of the model used, combined with more information on the structural properties of sandstone formations of a sedimentary basin such as the Mesohellenic Trough (porosity, permeability, etc.), could help in their further evaluation as a potential storage structure for CO_2.

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Appendix A. Supplementary data

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Assessment of the impact of CO_2 storage in sandstone formations by experimental studies and geochemical modeling: the case of the Mesohellenic Trough, NW Greece

SUPPLEMENTARY CONTENT

APPENDIX A: REACTION RATES AND THERMODYNAMIC DATA

Reaction dissolution and precipitation rates were calculated using the Transition State Theory (TST) (Lasaga, 1984) (Eq. A1):

$$r_n = \pm k_n RS_A \left|1 - \Omega_n^p\right|^q \qquad \text{(A1)}$$

where k_n corresponds to the reaction rate constant (mol m^{-2} s^{-1}), RS_A to the reactive surface area (m^2 g^{-1}) and Ω_n to the saturation state and where p,q are constants. Positive and negative r_n values refer to dissolution and precipitation reactions respectively.

The reaction rate constant k_n depends on the reaction temperature and pH of the solution according to Arrhenius law (Eq. A2):

$$k_n = k_0^{nu}\, exp\left[\frac{-E_a^{nu}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] + k_0^{acid}\, exp\left[\frac{-E_a^{acid}}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] a_H^{n(acid)} + k_0^{base}\left[\frac{-E_a^{base}}{R}\left(\frac{1}{T} \quad \frac{1}{298.15}\right)\right] a_{OH}^{n(base)} \qquad \text{(A2)}$$

where k_0 is the intrinsic kinetic constant at 298K (in mol m^{-2} s^{-1}), R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (in K), Ea is the reaction activation energy (in kJ mol^{-1}), a is the ion activity and n is a constant. The acid part of the equation corresponds to the $[H^+]$ influence, whereas the base part to the $[OH^-]$, (or $[HCO_3^-]$ when carbonates are involved).

The saturation state Ω_n depends on the Gibbs free energy of the reaction (Eq. A3):

$$\Delta G_r = -RTln\Omega \qquad \text{(A3)}$$

The reactive surface area RS_A of a mineral corresponds to the fraction of the total surface area that is subject to dissolution or precipitation (Eq. A4).

$$RS_A = \lambda mMS_A \qquad \text{(A4)}$$

where n and M are the mineral moles and molar weight respectively, S_A is the specific surface area and λ the reactive fraction. The fraction λ equals to 1 when the whole surface area is reactive, and was estimated by the model. The surface area of a mineral is measured using BET methods, or calculated geometrically, using the relations (A5) and (A6):

$$S_A = \frac{6}{d_e \rho} \qquad \text{(A5)}$$

$$d_e = \frac{d_{max} - d_{min}}{\ln\left(\frac{d_{max}}{d_{min}}\right)} \qquad \text{(A6)}$$

where d_e, d_{max} and d_{min} are the effective, the maximum and the minimum particle diameter respectively and p the mineral density (Tester *et al.*, 1994).

In our study, the mineral moles n were calculated on the base of the wt% analysis of the samples. The effective diameter, d_e, of the solid particles and their reactive surface area, RS_A, were calculated for the 250-500 µm particle size, assuming a spherical shape of the grains.

The thermodynamic parameters of the selected minerals are presented in Table A.1. Most of them are included in llnl.dat database. Ankerite data were taken from Krupka et al. (2010). Moreover, some additional phases were selected to investigate their possible formation by the model. These phases include magnesite, siderite, dawsonite, boehmite, $Fe(OH)_3$ and gibbsite. Kinetic dissolution and precipitation parameters are presented in Tables A.2 & A.3 (Palandri and Kharaka, 2004; Van Pham *et al.*, 2011; Marty *et al.*, 2015). As kinetic data for ankerite, dawsonite could not be identified in the literature, the respective parameters of another carbonate phase, dolomite, were taken as being similar, and were used instead. In the same manner, siderite data were used for magnesite, and boehmite for gibbsite and $Fe(OH)_3$.

Table A.1: Thermodynamic data of the selected sandstone minerals at 25°C, used in the geochemical models (llnl.dat)

Mineral	**Formula**	**Dissolution reaction**	**$Logk_0$ (25°C)**	**ΔH_r (kJ mol^{-1})**
Albite	$NaAlSi_3O_8$	$NaAlSi_3O_8 + 4H^+ = Al^{3+} + Na^+ + 2H_2O + 3SiO_2$	2.76	-51.85
Orthoclase	$KAlSi_3O_8$	$KAlSi_3O_8 + 4H^+ = Al^{3+} + K^+ + 2H_2O + 3SiO_2$	-0.27	-23.94
Calcite	$CaCO_3$	$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$	1.85	-25.71
Dolomite	$CaMg(CO_3)_2$	$CaMg(CO_3)_2 + 2H^+ = Ca^{2+} + Mg^{2+} + 2HCO_3^-$	2.51	-59.96
Montmorillonite	$Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2$	$Na_{0.33}Mg_{0.33}Al_{1.67}Si_4O_{10}(OH)_2 + 6H^+ = 0.33Mg^{2+} + 0.33Na^+ + 1.67Al^{3+} + 4H_2O + 4SiO_2$	2.48	-93.22
Kaolinite	$Al_2Si_2O_5(OH)_4$	$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2SiO_2 + 5H_2O$	6.81	-151.78
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	$KAl_3Si_3O_{10}(OH)_2 + 10H^+ = K^+ + 3Al^{3+} + 3SiO_2 + 6H_2O$	13.59	-243.22
Clinochlore	$Mg_5Al_2Si_3O_{10}(OH)_8$	$Mg_5Al_2Si_3O_{10}(OH)_8 + 16H^+ = 2Al^{3+} + 3SiO_2 + 5Mg^{2+} + 12H_2O$	67.24	-612.38
Quartz	SiO_2	$SiO_2 = SiO_2$	-3.99	32.95
[a]Ankerite	$CaFe_{0.4}Mg_{0.6}(CO_3)_2$	$CaFe_{0.4}Mg_{0.6}(CO_3)_2 + 2H^+ = Ca^{2+} + 0.4Fe^{3+} + 0.6Mg^{2+} + 2HCO_3^-$	-19.59	-42.96
Dawsonite	$NaAlCO_3(OH)_2$	$NaAlCO_3(OH)_2 + 3H^+ = Al^{3+} + HCO_3^- + Na^+ + 2H_2O$	4.35	-76.35
Magnesite	$MgCO_3$	$MgCO_3 + H^+ = HCO_3^- + Mg^{2+}$	2.29	-44.49
Siderite	$FeCO_3$	$FeCO_3 + H^+ = Fe^{+2} + HCO_3^-$	-0.19	-32.53
Gibbsite	$Al(OH)_3$	$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	7.75	-102.79
Fe(OH)3	$Fe(OH)_3$	$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$	5.65	-84.08
Goethite	$FeOOH$	$FeOOH + 3H^+ = Fe^{+3} + 2H_2O$	0.53	-61.93
Boehmite	AlO_2H	$AlO_2H + 3H^+ = Al^{3+} + 2H_2O$	7.56	-113.28

[a] *Thermodynamic data from* (Van Pham, Aagaard and Hellevang, 2012)

Table A.2 : Dissolution kinetic parameters used in the geochemical models

	Acidic term			**Neutral term**		**Base term**		**n** **(base)**	**p**	**q**	**Reference**
Mineral	**k_0^{acid}** **(mol m^{-2} s^{-1})**	**E_a^{acid}** **(J mol^{-1})**	**$n^{(acid)}$**	**k_0^{neu}** **(mol m^{-2} s^{-1})**	**E_a^{neu}** **(J mol^{-1})**	**k_0^{base}** **(mol m^{-2} s^{-1})**	**E_a^{base}** **(J mol^{-1})**				
Albite	$8.50x10^{-11}$	58000	0.34	$5.10x10^{-20}$	57000	$1.40x10^{-10}$	56000	0.32	1.00	1.00	Marty et al. (2015)
Orthoclse	$1.70x10^{-11}$	31000	0.27	$1.00x10^{-14}$	31000	$1.40x10^{-10}$	31000	0.35	1.00	1.00	Marty et al. (2015)
^{a} **Calcite**	$5.01x10^{-01}$	14400	1	$1.55x10^{-06}$	23500	$3.30x10^{-04}$	35400	1.00	1.00	1.00	Palandri & Kharaka (2004)
^{b} **Dolomite**	$2.80x10^{-04}$	46000	0.61	$1.10x10^{-08}$	31000	-	-	-	0.16	2.10	Marty et al. (2015)
Montmorillonite	$5.30x10^{-11}$	54000	0.69	$9.30x10^{-15}$	63000	$2.90x10^{-12}$	61000	0.34	0.17	10.34	Marty et al. (2015)
Kaolinite	$7.50x10^{-12}$	43000	0.51	$1.10x10^{-14}$	38000	$2.50x10^{-11}$	46000	0.58	1.00	1.00	Marty et al. (2015)
Muscovite	$1.41x10^{-12}$	22000	0.37	$2.82x10^{-14}$	22000	$2.80x10^{-15}$	22000	-0.22	1.00	1.00	Palandri & Kharaka (2004)
Clinochlore	$8.20x10^{-09}$	17000	0.28	$6.40x10^{-17}$	16000	$6.90x10^{-09}$	16000	0.34	1.00	1.00	Marty et al. (2015)
Quartz	-	-	-	$6.40x10^{-14}$	77000	$1.90X10^{-10}$	80000	0.34	1.00	1.00	Marty et al. (2015)
^{b}**Ankerite**	$2.80x10^{-04}$	46000	0.61	$1.10x10^{-08}$	31000	-	-	-	0.16	2.10	Marty et al. (2015)

^{a} *Base term in respect to [HCO_3^-]*

^{b} *Disordered (sedimentary) dolomite dissolution data were used.*

Table A.3: Precipitation rate parameters

	Precipitation Rates (Marty, et al., 2015)						
	Precipitation term		**Additional term**			**p**	**q**
Mineral	**k_0^{pre} (mol m^{-2} s^{-1})**	**E_a^{pre} (J mol^{-1})**	**k_0^{add} (mol m^{-2} s^{-1})**	**E_a^{add} (J mol^{-1})**	**n(add)**		
Quartz	3.20×10^{-12}	50000	-	-	-	4.58	0.54
[a] **Calcite**	1.80×10^{-07}	66000	1.90×10^{-03}	67000	1.63	0.5	2
Dolomite	9.50×10^{-15}	103000	-	-	-	1	1
[b] **Ankerite**	9.50×10^{-15}	103000	-	-	-	1	1
[b] **Dawsonite**	9.50×10^{-15}	103000	-	-	-	1	1
[c] **Magnesite**	1.60×10^{-11}	108000	-	-	-	1	1
[d] **Montmorillonite**	5.50×10^{-13}	66000	-	-	-	0.06	1.68
Kaolinite	5.50×10^{-13}	66000	-	-	-	0.06	1.68
[d]**Illite**	5.50×10^{-13}	66000	-	-	-	0.06	1.68
Boehmite	-	-	3.1×10^{-06}	0	1	1	1
[e] **$Fe(OH)_3$**	-	-	3.1×10^{-06}	0	1	1	1
[e] **Gibbsite**	-	-	3.1×10^{-06}	0	1	1	1

[a] *Additional term in respect to [HCO_3^-]*

[b] *Dolomite precipitation data used for ankerite and dawsonite*

[c] *Siderite precipitation parameters used for magnesite*

[d] *Kaolinite precipitation data used for montmorillonite and illite*

[e] *Boehmite presipitation data used for $Fe(OH)_3$ and gibbsite. Additional term in respect to [OH^-]*

APPENDIX B: Chemical analysis of the fluid samples

Table B.1: Fluid chemistry data for the batch experiment of Tsotyli Sandstone (TS) sample[a]

Sampling date	Sample Code	pH	Eh	Ca	Mg	Na	K	HCO_3^-	Cl^-	Balance	TIC (from alk)	Si	Al
		at 20°C	mV at 20°C	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	%	mg L^{-1}	mg L^{-1}	µg L^{-1}
27/5/14	Brine	8.96	137.4	<10	<0.8	12940	1.2	ND	17230	7	0	<1.7	<18
5/6/14	1683/1	7.33	205.5	77	7.2	11898	5.3	97	17790	1	19	7	106
3/7/14	1683/2	7.51	109.4	84	9.5	11676	4.8	157	17546	1	31	8	23
7/7/14	1683/3	6.74	46.7	1140	41.7	12423	6.2	1119	17579	2	220	20	58
15/7/14	1683/4	6.73	6.4	1112	42.5	12159	6.2	1522	17100	1	300	22	50
22/7/14	1683/5	6.67	53.7	1211	46.8	12237	6.1	1404	18918	-3	276	24	58
28/7/14	1683/6	6.63	39.1	1018	49.1	12143	6.1	1494	17133	-1	294	25	<18
14/7/14	1683/7	6.66	33.7	1282	58.7	12421	6.4	1949	17271	-2	384	28	61
8/9/14	1683/8	6.79	52.1	1354	74.8	13388	6.8	1786	17766	2	352	34	48
20/10/14	1683/9	6.68	43.5	1258	83.2	12890	7.5	2154	17550	-2	424	36	36
25/11/14	1683/10	6.68	26.9	1195	102	12395	6.4	2714	18589	-9	534	40	48

Table B.1 (cont.)

Sampling date	Sample Code	Total Fe µg L^{-1}	Oxidised Fe µg L^{-1}	Reduced Fe µg L^{-1}	Li µg L^{-1}	Ti µg L^{-1}	V µg L^{-1}	Cr µg L^{-1}	Co µg L^{-1}	Ni µg L^{-1}	Cu µg L^{-1}	Ba µg L^{-1}	Sr µg L^{-1}	Mn µg L^{-1}	Zn µg L^{-1}
27/5/14	Brine	<42	<37.1	<4.9	<37	<0.6	<3	<1	<0.4	0.8	4.2	<5	9	<7	20
5/6/14	1683/1	<42	<42.3	0	86	<0.6	10	3	0.5	39	217	113	694	23	47
3/7/14	1683/2	1546	1325	221	65	<0.6	<3	<1	17.7	668	4.2	122	805	99	23
7/7/14	1683/3	1335	1157	178	69	<0.6	4	47	24.8	724	48.2	449	4094	1040	81
15/7/14	1683/4	3792	3270	522	70	1.4	4	10	23.6	715	38.7	450	4190	897	70
22/7/14	1683/5	579	505	75	71	1.1	4	5	24.9	624	65.1	481	4366	1004	100
28/7/14	1683/6	827	717	110	71	1.3	3	6	21	621	44.8	513	4215	576	47
14/7/14	1683/7	1274	1130	144	74	0.8	5	9	29.9	679	45.3	537	4602	1134	77
8/9/14	1683/8	1152	1061	91	77	0.8	6	5	34.3	724	59.5	543	4952	1111	61
20/10/14	1683/9	1101	996	105	84	<0.6	4	3	35.7	723	73.8	528	4834	1058	50
25/11/14	1683/10	1930	1802	128	96	1.1	4	2	37.1	696	20.0	567	4639	870	40

Table B.2: Fluid chemistry data for the batch experiment of Pentalofos Sandstone (PS) sample[a]

Sampling Date	**Sample Code**	**pH** at 20°C	**Eh** mVat 20°C	**Ca** mg L^{-1}	**Mg** mg L^{-1}	**Na** mg L^{-1}	**K** mg L^{-1}	**HCO_3^-** mg L^{-1}	**Cl^-** mg L^{-1}	**Balance** %	**TIC (from alk)** mg L^{-1}	**Si** mg L^{-1}	**Al** µg L^{-1}
5/6/14	1684/1	7.31	187	114	11.3	13193	11.4	59	17685	7	12	7	64
3/7/14	1684/2	7.48	91.3	108	12.3	13538	12.3	90	16972	10	18	8	19
7/7/14	1684/3	6.74	-8.1	1136	40.5	12968	15.6	1152	17626	3	227	22	28
15/7/14	1684/4	6.67	27.8	1153	55.5	13258	18.4	1151	17461	5	227	33	19
22/7/14	1684/5	6.61	4.6	1145	68	13014	16.5	1492	17043	3	294	41	20
28/7/14	1684/6	6.49	39.1	1013	77.2	12832	16.5	1677	17411	0	330	47	<18
14/7/14	1684/7	6.76	9	1248	104	12616	16.4	1886	17555	-1	371	63	30
8/9/14	1684/8	6.78	32.7	1202	142	13030	17.3	1770	17088	2	348	78	<18
20/10/14	1684/9	6.71	22.1	1180	170	12574	16.7	1977	17325	-1	389	87	21
25/11/14	1684/10	6.71	13.6	1052	223	11943	15.4	2894	18758	-12	570	108	<18

Table B.2 (cont.)

Sampling date	**Sample Code**	**Total Fe** µg L^{-1}	**Oxidised Fe** µg L^{-1}	**Reduced Fe** µg L^{-1}	**Li** µg L^{-1}	**Ti** µg L^{-1}	**V** µg L^{-1}	**Cr** µg L^{-1}	**Co** µg L^{-1}	**Ni** µg L^{-1}	**Cu** µg L^{-1}	**Ba** µg L^{-1}	**Sr** µg L^{-1}	**Mn** µg L^{-1}	**Zn** µg L^{-1}
5/6/14	1684/1	85	81	4	48	<0.6	45	2	0.6	31.2	1155	81	174	42	50
3/7/14	1684/2	3344	2934	410	46	<0.6	<3	<1	3.8	147	23.7	53	200	115	23
7/7/14	1684/3	7111	6199	912	54	<0.6	4	13	52.4	1185	120	186	863	1904	73
15/7/14	1684/4	2136	1863	273	65	0.8	4	11	57.6	1227	172	213	950	1490	75
22/7/14	1684/5	5334	4653	681	60	0.8	4	10	64.2	1361	217	204	956	1441	68
28/7/14	1684/6	2273	1976	298	59	<0.6	4	7	53.7	1276	199	219	940	961	93
14/7/14	1684/7	2949	2646	303	70	<0.6	7	6	82.1	1458	131	221	932	2289	68
8/9/14	1684/8	2606	2379	227	75	0.8	4	9	88.7	1540	198	231	943	1891	39
20/10/14	1684/9	2062	1846	216	72	<0.6	5	4	93.5	1543	77.5	218	926	2033	41
25/11/14	1684/10				88	1.1	5	6	83.9	1397	3.0	233	879	1058	43

NO^{2-}, NO^{3-}, HPO_4^{-2}, Br^-, SO_4^{-2} were below the detection limit