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Mineralogical properties of the caprock and reservoir sandstone of the Heletz field scale experimental CO₂ injection site, Israel; and their initial sensitivity to CO₂ injection.

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1 Introduction

Concentrations of atmospheric CO₂ have increased by more than 35% since industrialisation began, UK Met Office (2010). To reduce the amount of CO₂ entering the Earth's atmosphere from increasing energy demands, Carbon Capture and Storage is being considered. CO₂ is separated from industrial emissions and injected in its supercritical phase into suitable deep geological formations. CO₂ saturated fluids and separated phase CO₂ are held in porous rocks sealed by overlying impermeable caprocks, Koide at al., (1992). The impermeable caprocks tend to be argillaceous mudstones, clays and shales which have a high sealing capacity due to their high capillary entry pressures, low permeability, high sorption capacity, high ion exchange capacity and potential swelling ability, IEAGHG, (2011). As scCO₂ is less dense and viscous than the saline formation fluids in the reservoir rock the injected CO₂ will experience an upwards buoyant force and migrate to accumulate against the underside of the impermeable caprock. Understanding the long term integrity of these caprock seals is a pre-requisite for CO₂ storage, DePaolo (2013), Bachu (2003), Busch et al. (2010), Li et al. (2005 & 2006), Class (2009), Ketzer et al. (2009), Fischer et al. (2010), Gaus (2010) and Amann et al. (2011).

During geological storage CO₂ is injected into the reservoir in its supercritical state (above 31.1°C and 7.3MPa or an 800m depth equivalent). CO₂ in its supercritical phase is lighter and less viscous that the formation brine making it more buoyant and mobile than the formation brine, even after injection has stopped, the CO₂ plume will continue to migrate in response to buoyancy and regional groundwater flow, Gaus (2010), Knauss et al. (2005). The collection of a reactive fluid like CO₂ saturate brine under the caprock and within the storage reservoir will result in chemical disequilibria and has the potential to initiate complex chemical dissolution and precipitation reactions within the caprock and reservoir rock minerals that may impact on the injectivity or the storage reservoir and security of the caprock integrity, Rochelle et al. (2004). A number of different CO₂ / formation brine / rock interactions are encountered as the plume migrates upwards towards the caprock, Kampman et al (2014), Fitts and Peters (2013), Michael et al (2010), Gaus (2010) and Griffith et al. (2011), Figure 1.



Figure 1 Cartoon of the primary CO_2 / brine / caprock contacts and interactions

At the leading edge of the CO_2 plume, the CO_2 will displace the formation brine in a drainage process and some CO_2 will dissolve into the formation brine, Duan and Sun (2003), Duan et al., (2006). When CO_2 gas dissolves in water, it lowers the pH of the formation fluid, through the production of carbonic acid (H₂CO₃), and its subsequent dissociation to bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻), which releases protons (H⁺), through the following reaction:

$$CO_2(aq) + H_2O \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{2-} + 2H^+$$
(1)

This lowered pH may enhance the dissolution of minerals; altering permeability or causing potential breakdown of the rock (or cement) matrix, Czernichowski-Lauriol et al. (2006) and Bensen et al. (2005). The rate and extent of mineral dissolution is dependent on the chemical composition of the fluid, the mineralogy of the rock, pressure, temperature and the kinetics of reaction, DePaolo (2013), which is in turn dependant on the reactive surface area, Landrot et al. (2012) and the mechanisms of dissolution. In general CO₂-acidified brines cause the dissolution of carbonate minerals (with relatively fast reaction rates, reaching equilibrium within a few hours, Rosenbauer et al. (2005)), and silicate minerals, in particular alumina-silicate minerals such as clays and feldspars, (with slow reaction rates of up to several thousands of years, Rosenqvist et al., (2014)). The presence of CO₂ can also lead to the dehydration of salts and clays leading to the shrinkage of clay minerals through the loss of interlayer water, Loring et al., (2013). If these reactions occur in the Heletz storage caprocks, the associated permeability and porosity changes may decrease the integrity of the caprock and reduce the security of CO₂ storage, Nogues et al (2013). If they occur within the reservoir storage rock, they may change the porosity, permeability and mechanical integrity of the reservoir leading to a change in the injectivity or induce wellbore collapse or sanding.

This paper presents an overview of the geological setting of the Heletz site and its depositional history, and the first mineralogy results from nine Heletz caprock and reservoir sandstone samples from Heletz wells H-2 and H-18, obtained through X-Ray Diffraction (XRD). It also presents the results from limited "cook and look" bench experiments that were conducted on the Heletz caprock and reservoir sandstone samples to identify if there was any immediate mineral reactivity within the caprock or reservoir sandstone on exposure to CO₂ that would change the permeability and cause concerns during well completion and initial injection of CO₂ at Heletz. This was achieved by exposing caprock and reservoir rock chips to CO₂ saturated brine under in-situ reservoir temperature and salinity in a reaction vessel and testing for any changes in mineralogy that are products of dissolution such as decreases in carbonates, alumiosilicates or kaolinite or an increase in illite over and above that of the rocks natural variability.

1.1 Heletz geological setting

The Heletz site is located in the Southern Mediterranean Coastal Plain of Israel and is currently a test site for the EU FP7 MUSTANG pilot injection experiment, where CO₂ injection under realistic storage site conditions provides important evidence of the processes which will influence the storage behaviour and caprock integrity, Niemi et al. (2012). The Heletz structure is an anticline fold with a crest of about 2 km by 4 km and a vertical closure of 70 m, Shtivelman at al. (2010), Figure 2. The structure is gently dipping to the east, truncated by a pinch-out line to the west, Figure 3. The anticline was a result of tectonic activity during the Upper Cretaceous Syrian Arc folding system that created the symmetrical Heletz anticline.

The Heletz reservoir consists of three Lower Cretaceous sand layers; 'K', 'W' and 'A' separated by shales of various thicknesses deposited within sequences of repeated regressive – transgressive (marine – nearshore - coastal) depositional sequences, Amireh (1996), Eppelbaum and Katz, (2011). CO_2 Injection is into the reservoir layer 'W' where the reservoir sands have a maximum thickness of 21m in the South-East and pinch out to the West where the sands are replaced by shales. The caprock has a thickness increasing from 23 m in the North to 54 m in the South. δO^{18} values suggest a maximum burial temperature of around 60° C and a burial depth of around 1200 - 1400m, Levy, (1981).

Core samples have been provided from two wells (Figure 2), H-2 drilled and cored sometime between 1955 and 1960 and H-18 drilled and cored in 2013, Niemi at al. (2016).



Figure 2 The Heletz location map and structure (from Shtivelman at al. 2010)



Figure 3 Heletz reservoir cross section (from Shtivelman at al. 2010)

2 Heletz mineralogy methods and results

Seven Heletz caprock samples and two Heletz reservoir sandstone were available for mineralogical and experimental testing from wells H-2 and the newly drilled Well H-18 (Figure 2). Their depths and images are presented in Table 1 and Figure 4.

Table 1 Heletz sam	ple nomenclature.	depth and	vear drilled	and cored
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Sample name	Depth (m)	Year drilled and cored
Heletz H-18 (sample A)	1596.00	2013
Heletz H-18 (sample B)	1596.04	2013
Heletz H-18 (sample C)	1596.08	2013
Heletz H-18 (sample D)	1596.39	2013
Heletz H-18 (sample E)	1596.43	2013
Heletz H-18 (sample F)	1596.47	2013
Heletz H-2 (sample A)	Unknown but higher up the anticline and shallower	Between 1955 and 1960
	than the H-18 deposits	
Heletz H-18 Sandstone 1	1634.00	2013
Heletz H-18 Sandstone 1	1634.00	2013







Heletz H-18 (sample A) Heletz H-18 (sample B)





Heletz H-18 (sample C)

Heletz H-18 (sample D)

Heletz H-18 (sample E)





Heletz H-2





Heletz H-18 Sandstone 1 Heletz H-18 Sandstone 2

Figure 4 Heletz caprock samples from Well H-18 and H-2, plus two reservoir sandstones from Well H-18.

The mineralogy of the Heletz samples was determined using X-Ray diffraction (XRD) in a Bruker D8 Advance with Sol-X Energy Dispersive detector, in conjunction with the Bruker Diffrac.EVA software utilising the currently available International Centre for Diffraction Data (ICDD) database. Quantitative analysis is available using the TOPAS 3.0 Rietveld analysis software. The rock sample was placed in a tungsten carbide crushing mill to create chips. The chips were then placed in a Tema orbital mill for 2-3 minutes to create the powdered sample. For the sandstone, it was necessary to hand grind the powder to obtain the desired grain size of 50µm. The powdered samples were then placed in a glass mount making sure the surface was completely flat before being placed in the XRD instrument for quantitative Rietveld analysis. Extra care was taken not to over flatten the top layer of powder to ensure a fresh grain surface for analysis. Five different aliquots of each powdered sample were analysed which involved remounting the samples to get a fresh alignment of minerals on the top surface. This was in order to increase the precision of the results and to get an indication of the sampling and instrumental errors involved.

Table 2 and Figure 5 present the XRD mineralogy results for all the Heletz caprock samples. It can be seen that for all of the H-18 Heletz caprock samples the dominant mineral is K-feldspar (average 41wt%) followed by plagioclase feldspar (average 15wt%), kaolinite (average 11wt%), muscovite (average 8wt%) and illite (average 7% wt%) with minor chlorite and calcite (both average of 5wt%), quartz (average 3wt%), ankerite and pyrite (both with average 2wt%) and trace dolomite and siderite. Heletz well H-2 is dominated by kaolinite (23wt%) followed by K-feldspar (17wt%), illite and

muscovite(both with 11wt%), quartz (9wt%), plagioclase and chlorite (6wt%), calcite (5wt%) and pyrite (2.5wt%) with minor siderite, dolomite and ankerite.

There is a degree of variability of mineral distribution between the caprock samples. Figure 6 is a box and whisper plot for the caprock sample mineralogy and shows that in particular there is variability within the aluminosilicates followed by the clays and calcite; all of the minerals most likely to react with the CO_2 saturated brine.

Looking in more detail at the difference between the H-2 and H-18 caprocks, it can be identified that the H-2 caprock has a higher quartz, illite and kaolinite composition and a lower plagioclase feldspar and potassium feldspar composition than H-18 caprocks. The lower feldspar and increased kaolinite combined with the increased illite and quartz contents of the H-2 caprocks may indicate that the H-2 caprocks have undergone more diagenetic alteration than the H-18 caprocks.

Group	Mineral	Heletz						
		H-18	H-18	H-18	H-18	H-18	H-18	H-2
		(Sample A)	(Sample B)	(Sample C)	(Sample D)	(Sample E)	(Sample F)	(Sample A)
Silicates	Quartz	1.6	1.9	5.1	3.6	3.2	0.3	9
	Plagioclase Feldspar	11.2	12.2	12.6	17.8	17.4	16.1	6.2
	K-feldspar	35.7	33.8	29.0	54.8	48.2	46.1	17.1
Clays	Illite	5.1	11.6	10.0	2.5	4.4	6.7	11.4
	Kaolinite	8.7	14.3	12.2	7.3	11.6	12.1	23.3
Mica	Muscovite	8.9	10.9	10.0	2.1	4.9	9.9	11.6
Chlorite	Chlorite	3.2	5.3	6.1	2.3	6.7	4.9	6.8
Carbonates	Calcite	19.1	3.6	4.9	0.6	0.0	0.0	4.9
	Dolomite	0.3	2.0	1.9	1.6	0.0	0.0	1.5
	Siderite	0.4	0.4	0.1	0.2	0.3	0.6	1.59
	Ankerite	2.3	1.7	2.4	3.3	1.1	0.8	0.1
Sulphides	Pyrite	2.2	2.3	3.0	3.2	1.4	2.2	2.45
	Gypsum	1.4	0.0	2.6	0.6	0.7	0.3	1.81

Table 2 Heletz H-18 and H-2 caprock XRD mineralogy results



Figure 5 Heletz H-18 and H-2 caprock XRD mineralogy results



Figure 6 Box and whisper plot showing the variability within the mineralogy of the Heletz caprock samples

Table 3 and Figure 7 present the XRD mineralogy results for the reservoir sandstone samples. These Heletz sand 'W' reservoir sandstones are primarily quartz (average 70wt%) and K-feldspar (average 12wt%) with plagioclase feldspar (average 4wt%) kaolinite (average 3.2wt%), illite (average 2.6wt%) and pyrite (average 2wt%) with minor ankerite, chlorite, muscovite, dolomite, siderite and calcite. There is very little variability within the mineralogy between samples, Figure 8, with only quartz and kaolinite showing limited variability.

Group	Mineral	Heletz H-18	Heletz H-18
		(Sandstone 1)	(Sandstone 2)
Silicates	Quartz	73.4	66.0
	Plagioclase Feldspar	3.4	4.4
	K-feldspar	11.1	12.9
Clays	Illite	2.0	3.3
	Kaolinite	1.3	5.0
Mica	Muscovite	1.1	1.3
Chlorite	Chlorite	0.7	2.0
Carbonates	Calcite	0.0	0.1
	Dolomite	1.8	0.3
	Siderite	1.0	0.5
	Ankerite	2.1	1.5
Sulphides	Pyrite	1.8	2.3
	Gypsum	0.4	0.4

Table 3 Heletz H-18 sandstone XRD mineralogy results



Figure 7 Heletz H-18 sandstone XRD mineralogy results



Figure 8 Box and whisper plot showing the variability within the mineralogy of the Heletz reservoir sandstone samples

3 Experimental methodology

Samples of Heletz caprock and sandstone were exposed to CO₂ saturated brine in simple "cook and look" bench experiments for 3 months that were designed to identify if there was any immediate mineral reactivity within the caprock or reservoir sandstone on exposure to CO₂ that could serve to alter permeability which may raise concerns during well completion and initial injection of CO₂ at Heletz.

The experimental equipment comprises a 3 arm conical flask, Ludwig condenser, heating mantle, thermometer and CO_2 inlet, Figure 9 which facilitated the exposure of Heletz rocks to CO_2 saturated brine under conditions of reservoir temperature and salinity. The experimental conditions were:

- Conical 3-arm flask containing 100g of 5mm diameter rock chip samples.
- Temperature of 55°C. Satrinsky (1974) indicates a maximum temperature of 50-60°C at 1500-1800m for the Heletz reservoir.
- Brine of 35,000ppm NaCl. The logging report for Heletz well H-38 provided a salinity defined by DST of 35,000 40,000ppm at 1050m depth and of 22,113ppm Cl at 1555m.
- Ambient pressure.
- Gas phase CO_2 is continually bubbled through the brine at around 0.5ml/min to ensure a consistently CO_2 saturated brine.
- The experiment is static, with no stirring or agitation of the rock chip samples.

- Two identical experimental set-ups are run in tandem. One is run without CO₂ as a reference to identify the changes brought about by reactivity with brine so that any changes due to CO₂ can be identified.
- The experiments were run for 3 months.

There were two analytical strategies used during the experiments:

- Before the experiment half of the rock chips to be used in each of flasks were taken for bulk XRD analysis to obtain the bulk mineralogy before the experiment. The other half of the chips were added to each of the flasks for the bench experiments. At the end of the experiment the remaining rock chips from each of the flasks were taken for bulk XRD analysis to identify if there was any bulk mineralogical changes after 3 months.
- As there was an absence of fluid analysis equipment available at the time of the experimental program, Scanning Electron Microscope (SEM) analysis of the surfaces of the rock chips was undertaken for the duration of the experiments. A single Heletz caprock chip was removed from both of the flasks every week for SEM analysis to identify if there are any distinct mineralogical changes within the Heletz caprock and reservoir rock on exposure to CO₂.

The sampling of different chips to identify any change in the rocks due to exposure to CO_2 will be influenced by the variability of the rock samples as highlighted in Figures 6 and 8. This is due to the compositional variability / heterogeneity within the rock samples themselves. This was minimised by selecting the most homogeneous rock from which to take the chips. The bulk XRD analysis at the beginning and end of the experiments will also provide average end member mineralogy which will not be so vulnerable to sample variability sensitivity.



Figure 9 CO₂ saturated brine bench experiment equipment

4 Results and discussion

Considering the mineralogy of the Heletz caprock and reservoir rocks, Tables 2 and 3, some of the reactivity dissolution markers include, Velde, (1995):

- A decrease in calcite (or dolomite CaMg(CO₃)₂) as a result of carbonate reactivity: CaCO₃ (calcite) + H+ ⇒ Ca²⁺ + HCO₃⁻
- A decrease in k-feldspar and increase in illite as a result of the digenetic breakdown of the aluminosilicate K-feldspar: 3KAlSi₃O₈ (*K-Feldspar*) + 2H⁺ + 12H₂O ⇒ 2K⁺ + 6Si(OH)₄ ⁰ + KAl₃Si₃O₁₀(OH)₂ (*illite*)
- A decrease in Kaolinite and increase in illite as a result of the reactivity of kaolinite: kaolinite + cation $(K^*) \rightleftharpoons$ illite + quartz + water.

4.1 Heletz H-2 caprock / CO₂ saturated brine reactivity

Table 4 and Figure 10 present the bulk XRD mineralogy of the Heletz H-2 shale caprock before testing, after the three months of exposure to brine only and CO_2 saturated brine at 55°C.

Group	Mineral	Heletz H-2	Heletz H-2 (brine and	Heletz H-2 (brine,
		(before testing)	temperature only)	temperature and CO ₂)
Silicates	Quartz	9.0	6.0	1.5
	Plagioclase Feldspar	6.2	8.4	4.5
	K-feldspar	17.1	15.3	16.3
Clays	Illite	11.4	11.2	23.0
	Kaolinite	23.3	24	22.7
Mica	Muscovite	11.6	15.1	9.2
Chlorite	Chlorite	6.8	9.0	10.3
Carbonates	Calcite	4.9	4.6	3.5
	Dolomite	1.5	0.0	1.2
	Siderite	1.6	1.6	1.6
	Ankerite	0.1	1.0	0.0
Sulphides	Pyrite	2.4	1.1	0.2
	Gypsum	1.8	2.4	6.0





Figure 10 Heletz H-2 mineralogy before and after CO₂ exposure

4.1.1 Reactivity of the Heletz H-2 caprock carbonate minerals

The bulk XRD analysis indicated that there was a slight decrease in the carbonate minerals within the Heletz H-2 caprock on exposure to CO_2 saturated brine over 3 months, with calcite reducing from 4.9 to 3.5 wt% and dolomite reducing from 1.5 to 1.2 wt%. SEM investigations revealed a lack of calcite minerals within the samples exposed to CO_2 for 3 months which had been observed at the beginning of the experiment, Figure 11.



Figure 11 Calcite minerals identified at the beginning of the experiment but absent after 3 months exposure to CO_2 saturated brine.

There is a high percentage of calcite in one of the Heletz H-18 caprocks (Sample A, Table 2) with all the other samples having low amounts of calcite (average of 2.3wt%), therefore permeability reduction due to carbonate dissolution is not likely to be a risk to the integrity of the Heletz caprock during drilling and initial injection.

4.1.2 Reactivity of the Heletz H-2 caprock alumina-silicate / clay minerals

The bulk XRD analysis indicated that there was an observed increase in illite in the samples exposed to brine and CO₂ for 3 months, from 11.4 wt% to 23wt%, which could be a result of the breakdown of K-feldspar to illite or the breakdown of kaolinite to illite. Both k-feldspar and kaolinite do show a decrease in weight percentage from 17.1 to 16.3 and 23.3 to 22.7 respectively, however this does not balance with the amount of illite increase. The SEM investigations during the experiments did not reveal any wispy authigenic illite crystals on the chip surfaces that would indicate the diagenetic breakdown of K-feldspar or kaolinite to illite and the surfaces become weathered and amorphous, Figure 12. In addition looking at the natural variability between samples of Heletz caprock of k-feldspar, kaolinite and illite, Table 2 and Figure 6, the analysis reveals a variability of weight percentage of K-feldspar to be between 17.1% and 54.8%, kaolinite to be between 7.3% and 23.3%, and illite between 2.5% to 11.6%, for the Heletz caprock, which confirms a reasonable degree of variability of k-feldspar, kaolinite and Illite distribution within the Heletz caprock samples, however it should not be discounted that there is the possibility of a net illite precipitations within the caprock and an associated decrease in permeability and change in caprock properties.







(B) Matrix detail after 3 months CO₂ / brine / heat exposure.

Figure 12 SEM of caprock matrix surface before and after CO₂ exposure

4.1.3 Reactivity of the Heletz H-2 caprock quartz.

The bulk XRD analysis indicated that these was an observed decrease in quartz in the caprock samples exposed to brine and CO_2 for 3 months from 9wt% to 1.5wt%. The timescales and experimental conditions of these experiments rule out the alteration of quartz and the difference is most likely due to the variability within the sample. Figure 6 and Table 2 shows the weight percentage of quartz within the Heletz caprock samples ranges from 0.3% to 9%, which confirms this high degree of variability of quartz distribution within the Heletz caprock samples. SEM investigations, Figure 13, show little evidence for any surface changes on the quartz crystals, with no obvious changes in the angles of the edges or in pits on exposure to CO_2 .



(A) Quartz crystal after 3 months brine / heat exposure



(B) Quartz crystal after 3 months CO₂ / brine / heat exposure

Figure 13 SEM investigation into potential quartz reactivity

4.2 Heletz H-18 reservoir sandstone CO₂ reactivity

The Heletz H-18 sandstone is relatively soft and although consolidated, there were indications that it would not withstand the bench experiments. So prior to breaking the Heletz H-18 (sandstone 2) into chips it was placed in a beaker of Heletz brine and the sample completely disintegrated into its component parts, Figure 14.

This meant that the sandstone samples were not tested in the bench experiments and the disintegration findings were directly communicated to the Heletz drilling team as a potential risk during completion and injection. To a certain degree this was observed in the field. Well H-18 was cemented and after cementation the wells were flushed with fresh water and the well perforated. A few months later a pump test was performed and the test revealed that the well was clogged due to mixing between the freshwater in the borehole and the formation water resulting in clay swelling, Fe hydroxides and other chemical processes, Luquot et al., (2016). Injectivity was restored by injecting KCL into the well and performing 20 swab-suctions.



Figure 14 Heletz H-18 sandstone before and after saturation in synthetic Heletz brine.

4.3 Further discussions

The "cook and look" experiments were undertaken with at ambient pressure and elevated temperature where the CO_2 is in its gas phase. The Heletz storage site depth and temperature means that the CO_2 will be in its supercritical state. Previous work on the interaction of scCO₂ and fractured caprock by the author, Edlmann et al., (2013) indicated little or no reactivity and as such the findings from these investigations will hold under the Heletz site storage conditions.

5 Conclusions

It can be seen that for all of the H-18 Heletz caprock samples the dominant mineral is K-feldspar followed by plagioclase feldspar, kaolinite, muscovite and illite with minor chlorite and calcite, quartz, ankerite and pyrite and trace dolomite and siderite. Heletz well H-2 is dominated by kaolinite followed by K-feldspar illite and muscovite, quartz, plagioclase and chlorite, calcite and pyrite with minor siderite, dolomite and ankerite. The H-2 caprock has a higher quartz, illite and kaolinite composition and a lower plagioclase feldspar and potassium feldspar composition than H-18 caprocks. The lower feldspar and increased kaolinite combined with the increased illite and quartz contents of the H-2 caprocks may indicate that the H-2 caprocks have undergone more diagenetic alteration than the H-18 caprocks.

While there are some minor observed changes in the mineralogy on exposure to CO_2 saturated brine these observations were within the natural variability between the Heletz caprock samples and as such the "cook and look" bench experiments revealed that there is no significant mineral reactivity that would alter permeability in the Heletz caprock that could cause concerns during well completion and initial injection of CO₂ at Heletz.

The Heletz H-18 sandstone became completely unconsolidated when exposed to Heletz brine and this reactivity was also observed in the field. During completion of Well H-18 loss of injectivity occurred clay swelling, Fe hydroxides and other chemical processes, which was restored by injecting KCL into the well and performing 20 swab-suctions.

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