Title: **Controls on CO_2 storage security in natural reservoirs and implications for CO_2 storage site selection**

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Abstract:

For carbon capture and storage to successfully contribute to climate mitigation efforts, the captured and stored CO_2 must be securely isolated from the atmosphere and oceans for a minimum of 10,000 years. As it is not possible to undertake experiments over such timescales, here we investigate natural occurrences of CO_2, trapped for 10^4 -10^6 yr to understand the geologic controls on long term storage performance. We present the most comprehensive natural CO_2 reservoir dataset compiled to date, containing 76 naturally occurring natural CO_2 stores, located in a range of geological environments around the world. We use this dataset to perform a critical analysis of the controls on long-term CO_2 retention in the subsurface. We find no evidence of measureable CO_2 migration at 66 sites and hence use these sites as examples of secure CO_2 retention over geological timescales. We find unequivocal evidence of CO_2 migration to the Earth's surface at only 6 sites, with inconclusive evidence of migration at 4 reservoirs. Our analysis shows that successful CO_2 retention is controlled by: thick and multiple caprocks, reservoir depths of >1200m, and high density CO_2. Where CO_2 has migrated to surface, the pathways by which it has done so are focused along faults, illustrating that CO_2 migration via faults is the biggest risk to secure storage. However, we also find that many naturally occurring CO_2 reservoirs are fault bound illustrating that faults can also securely retain CO_2 over geological timescales. Hence, we conclude that the sealing ability of fault or damage zones to CO_2 must be fully characterised during the appraisal process to fully assess the risk of CO_2 migration they pose. We propose new engineered storage site selection criteria informed directly from on our observations from naturally occurring CO_2 reservoirs. These criteria are similar to, but more prescriptive than, existing best-practise guidance for selecting sites for engineered CO_2 storage and we believe that if adopted will increase CO_2 storage security in engineered CO_2 stores.

Keywords:

CO_2 storage, CO_2 leakage, natural analogues; Geologic site screening

Highlights:

- The most comprehensive analysis of naturally occurring CO_2 reservoirs compiled to date
- CO_2 retention is controlled by CO_2 density & state, reservoir depth, and caprock integrity
- Migration to the surface occurs along faults and fracture zones
- New storage site selection criteria are proposed, based on secure natural reservoirs

1. Introduction

For successful widespread implementation of carbon capture and storage the long-term security of storage sites is vital. Migration of CO_2 to the surface would render storage ineffective, pose a human health risk, and negatively impact the public perception of CCS as a climate mitigation technology (Shackley et al., 2009; Roberts et al., 2011; L'Orange Segio et al., 2014). Indeed, fear of surface migration is a main driver of negative public opinion towards CCS and has led to the delay of storage project development and has driven storage operations offshore (Mabon et al, 2014). It is thus critical that the CO_2 storage security of potential sites is carefully assessed. Based on initial studies of natural analogues, experiences with pilot injection projects and the first industrial scale CO_2 storage sites, guidelines for minimizing risks associated with CO_2 storage and maximizing storage security have been developed over the last decade (Chadwick et al., 2008; IEA GHG, 2009; NETL, 2010; Det Norkse Veritas, 2010; Delprat-Jannaud et al., 2013). Key selection criteria include: depth, CO_2 state, and the presence of (open) fractures or faults. It is recommended that CO_2 is stored at depths which are greater than 800 m and most studies recommend storage of CO_2 in a supercritical state with reservoir temperatures in excess of 35 °C and reservoir pressure of more than 7.5 MPa (IEA GHG, 2009; CASSEM, 2011; Delprat-Jennaud et al., 2013) or over 1000 m (Chadwick et al., 2008). Sealing caprocks should be "laterally extensive" (NETL, 2010) with "minimal faulting" (CASSEM, 2011), effectively ruling out active faults. Additionally, the capillary entry pressure of caprocks should be greater than the pressure increase induced in the reservoir during CO_2 injection (Chadwick et al., 2008).

CO_2 derived from natural earth processes such as volcanism, mantle degassing, carbonate rock metamorphism or the degradation of organic matter (Wycherley et al., 1999) can naturally accumulate in subsurface rock formations and remain trapped for geological time periods. For example, known reservoirs in the US contain at least 310 Gt CO_2 (NETL, 2014), typically at concentrations of 85 to 99 % CO_2 (by volume), with the majority securely storing CO_2 for an excess of a million years (Sathaye et al, 2014) and in one case for 42-70 Ma (Gilfillan et al, 2008). These natural CO_2 stores can improve the understanding of the long-term behaviour and retention of CO_2 in the subsurface (Baines and Worden, 2004) and provide long-duration evidence of the interaction of CO_2 with the reservoir and caprock, which are difficult to reproduce in laboratory studies. In addition, natural sites can offer geological evidence of ancient or current migration of CO_2 out of the primary reservoir, and sometimes to the surface. Study of these sites provides insights into the mechanisms by which engineered sites may fail and thus inform the selection and management of secure CO_2 storage sites.

Hence, naturally occurring CO_2 reservoirs have been examined at a regional (tens of km) scale as analogues for saline aquifer carbon storage sites (Pearce et al, 1996; Stevens et al, 2001; Pearce et al, 2004; Dai et al, 2005; Holloway et al, 2005). These studies have concluded that CO_2 retention is extremely secure, and any upwards migration of CO_2 occurs mainly along fractures and faults that are conductive to fluid flow, and thus CO_2 migration is spatially restricted to fault zones (Frery et al., 2015). Fault zones, consisting of a fault core which accommodates most of the displacement and a surrounding damage zone which can be highly fractured, have long been recognised as fluid migration pathways in the subsurface and considerable research has been completed on the hydraulic properties, particularly on the predictability of the sealing properties of fault zones (Faulkner et al, 2010). However, to date only a few works have focused specifically on CO_2 retention in fault zones as the majority of published studies are focused on the sealing of faults to hydrocarbons (Yielding et al, 1997; Bretan et al, 2011).

Here, we build on this previous work by presenting the most comprehensive analysis of previously studied naturally occurring worldwide CO_2 reservoirs compiled to date, that are directly analogous to engineered CO_2 stores. We critically examine the characteristics of these reservoir systems to determine the geological criteria required for long-term CO_2 trapping in nature. These criteria are compared to site selection standards currently used to evaluate engineered storage sites, and we recommend improvements to these standards based on our findings.

2. Methods

We compiled a global dataset of 76 naturally occurring CO_2 reservoirs (Fig. 1; SI Tab. 1) extending a previous preliminary compilation of 49 sites (Miocic et al., 2013). All of the reservoirs have been investigated to some extent by previous published studies, and information about their geological characteristics is available (see SI Tab. 1 for specific details). The studied reservoirs have held CO_2 in high concentrations for geological time-scales within a clearly defined trap (structural, lithologic, or a combination of both) and can thus be viewed as analogues to engineered CO_2 storage sites. Reservoirs where no geological trap has been proven or that hold low (<20 %) CO_2 content have been disregarded. Naturally occurring CO_2 seeps which are not linked to a known reservoir structure containing free phase CO_2 at depth were also not included.

Data from national and local data repositories were retrieved and integrated to produce a comprehensive dataset of location, depth, temperature, pressure, CO_2 content, lithology of reservoir and sealing rocks for all reservoirs. The dataset also includes trapping structures, thicknesses of reservoir and CO_2 origin, and percentage composition where this information is available in well logs and published studies. Where in situ pressure data was not available (28 sites) we assume a hydrostatic pressure gradient of 10.0 kPa/m. Where temperature data was not available (9 sites), it is reconstructed using published regional and local temperature gradients (within 25 km of the reservoir extent). Where calculated information is used this is indicated (SI Tab. 1). These data are used to calculate CO_2 state and density for each case study using the equation of state developed by Huang et al. (1985) which is an extended Benedict-Webb-Rubin equation of state. In the following “dense phase CO_2” refers to supercritical and liquid state, i.e. excluding gaseous CO_2.

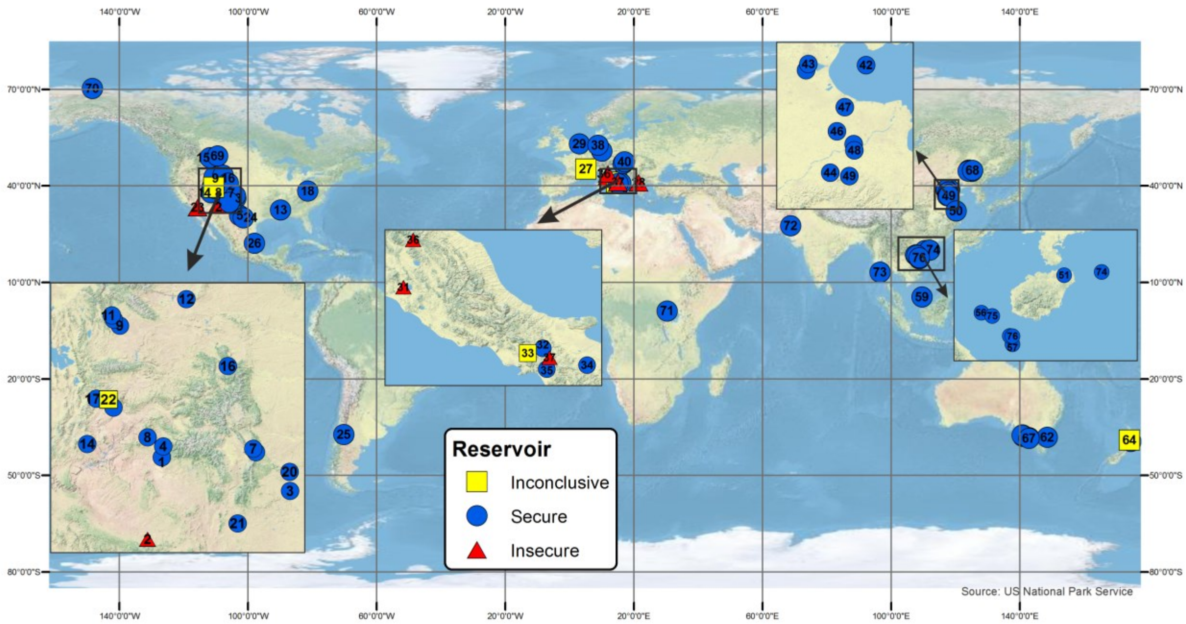

Fig. 1: Map showing the locations of naturally occurring CO_2 reservoirs included in this study. Note that the majority of the insecure reservoirs are found in tectonically active regions, such as the Apennine thrust belt in Italy or the Florina Basin in Greece.

Secure and insecure sites and reservoirs were determined using the following criteria to identify migration of CO_2 out of the reservoir: CO_2 occurrence at the surface within a 10 km radius of subsurface extent of the reservoir as determined from exploration data. This includes CO_2 rich springs, mofettes and diffusive degassing which indicates a present day migration of CO_2 to the surface. The precipitation of carbonate from springs to form travertine deposits at the surface may indicate the migration of dissolved CO_2. Thus, if travertine deposits are mapped within a 10 km radius of the known subsurface reservoir extent, we consider that these indicate CO_2 leakage, even if the travertine is historic and there is no evidence for current CO_2 migration. We use the 10 km radius based on an extensive study of natural CO_2 seeps in Italy by Roberts (2012) which conclusively found that surface seeps linked to deep free phase CO_2 reservoirs occurred with a 10 km radius of subsurface boreholes which encountered free phase CO_2.

In regions where natural CO_2 degassing occurs due to modern volcanic activity there has to be a clear connection from depth to the surface, in order for the reservoir to be classified as insecure. For example, a fault or geochemical evidence which directly links the proven subsurface CO_2 reservoir to the surface occurrence of CO_2 degassing. Reservoirs were classified as secure if no CO_2 is encountered above the primary seal and no indications for CO_2 seeps exist at the surface. Vertically stacked aquifers containing a proportion of CO_2 were regarded as secure reservoirs if, based on geological cross sections and well logs, it could be shown that the shallowest CO_2 holding aquifer was not in hydro-geological contact with the surface.

Six of the 76 reservoirs show clear evidence of CO_2 migration to the surface while 66 reservoirs (86 %) are classified as secure, and thus successfully trap CO_2. Four reservoirs exhibit inconclusive evidence for either migration or retention and could thus not be conclusively defined as secure or insecure. Montmiral in SE France, which is used as a secure example by Pearce et al. (2004), has many CO_2 rich springs within a 10 km radius of the field which provide evidence for CO_2 migration to the surface. However, it is currently unclear if the CO_2 originates from the reservoir or is sourced from elsewhere. The Monte Taburno reservoir in central Italy is located just 1.6 km from a thermal spring with a small CO_2 content and since there is no further geochemical information about the spring or the CO_2 reservoir, the relationship between the two is unclear (Roberts, 2012). The Paritutu reservoir offshore New Plymouth, NZ, is shallow and there is a vent at the surface degassing CO_2 (Lyon et al, 1996). However, the distance between the reservoir penetrating well and the vent is unknown, as are the possible CO_2 migration pathways. For the reservoir of Farnham Dome, US, Kampman et al. (2012) reported that “surface calcite debris fields attest to leakage in the recent geological past” but did not identify a direct link between the reservoir and the debris fields. This is in contrast to previous reports where the reservoir was classified as secure (Morgan and Chidsey, 1991; Allis et al., 2001).

Thus, for the following analyses, we present few examples of breached reservoirs. This is to be expected as we focus on reservoirs which have been charged with CO_2 over geological time and it is probable that structures which do not securely retain CO_2 are not preserved over such timescales. Numerous previously published studies have focused on sites which are actively degassing CO_2 in the form of springs, mofettes, travertines and diffusive degassing (Gal et al., 2011; Schütze et al., 2012; Burnside et al, 2013). Significantly, in the vast majority of areas of active CO_2 degassing subsurface CO_2 reservoirs are rare. For example in Italy there are 308 dominantly CO_2 seeps degassing at the surface (Roberts et al., 2015), yet only seven subsurface CO_2 reservoirs have been identified. This is also the case on the West coast of the USA, namely in Washington, Oregon and California where some 92 CO_2 rich springs have been recorded, with only four subsurface wells encountering free-phase CO_2 in California and no natural CO_2 accumulations having been discovered in any of the three states (Irwin and Barnes, 1982). This is despite extensive CO_2 exploration efforts driven by the desire for CO_2 for enhanced oil recovery (Irwin and Barnes, 1982). Hence, whilst it is impossible be certain that our secure stores are truly 100% secure, with absolutely no diffuse CO_2 leakage occurring, the mere fact that they still retain large amounts of CO_2 without recorded CO_2 degassing or detrimental environmental effects nearby makes them suitable analogues for engineered CO_2 stores. Based on the assumption that these reservoirs exhibit the desirable characteristics required for long term CO_2 retention, as evidenced by their current existence, we believe that the conclusions we draw from studying these reservoirs in this work are valid.

3. Properties of naturally occurring CO_2 reservoirs

Reservoir fluid composition: The CO_2 contained in the studied reservoirs is mainly sourced from mantle degassing and igneous processes (32 of the 45 reservoirs for which stable carbon isotope and noble gas geochemical data is available; SI Tab. 1), with the remainder being sourced from the thermal breakdown of marine carbonates and/or organic matter. The CO_2 saturations (vol-%) range from 20 % to >99 % with 41 reservoirs having minimum concentrations which are 90 % or higher. Other frequently trapped gases include, in order of decreasing abundance; methane, nitrogen, helium and hydrogen sulphide. There are no notable differences between the CO_2 composition or origin between secure and insecure reservoirs, with insecure reservoirs exhibiting CO_2 concentrations ranging from 90 % to >99 %.

Rock type and stratigraphic column: We find no relationship between successful CO_2 retention and the lithology of the reservoir or caprock in reservoirs for which this geological information is available (64 of 76 reservoirs). Naturally occurring CO_2 reservoir rocks are commonly siliciclastic (37 reservoirs) or carbonate (24 reservoirs), or interlayered (11 reservoirs). Silicate mudstones and shales (43 reservoirs) are the dominant caprock lithology, with fewer cases of evaporite-bearing caprocks (12 reservoirs), or interlayered carbonate and siliciclastic seals (3 reservoirs). Thickness of the primary seal appears to influence the security of CO_2 storage. Caprocks directly above sealing reservoirs are on average nearly twice as thick as caprocks above insecure reservoirs, albeit based on a small dataset for insecure reservoirs for the reasons previously discussed (SI Fig. 1). Furthermore, stacked reservoirs enhance storage security, since at least a third (21 out of 66) of the secure reservoirs consist of layered compartments with up to five different reservoir horizons each with corresponding multiple caprocks. In contrast, only one of the insecure reservoirs has layered compartments (No. 2 in SI Tab. 1).

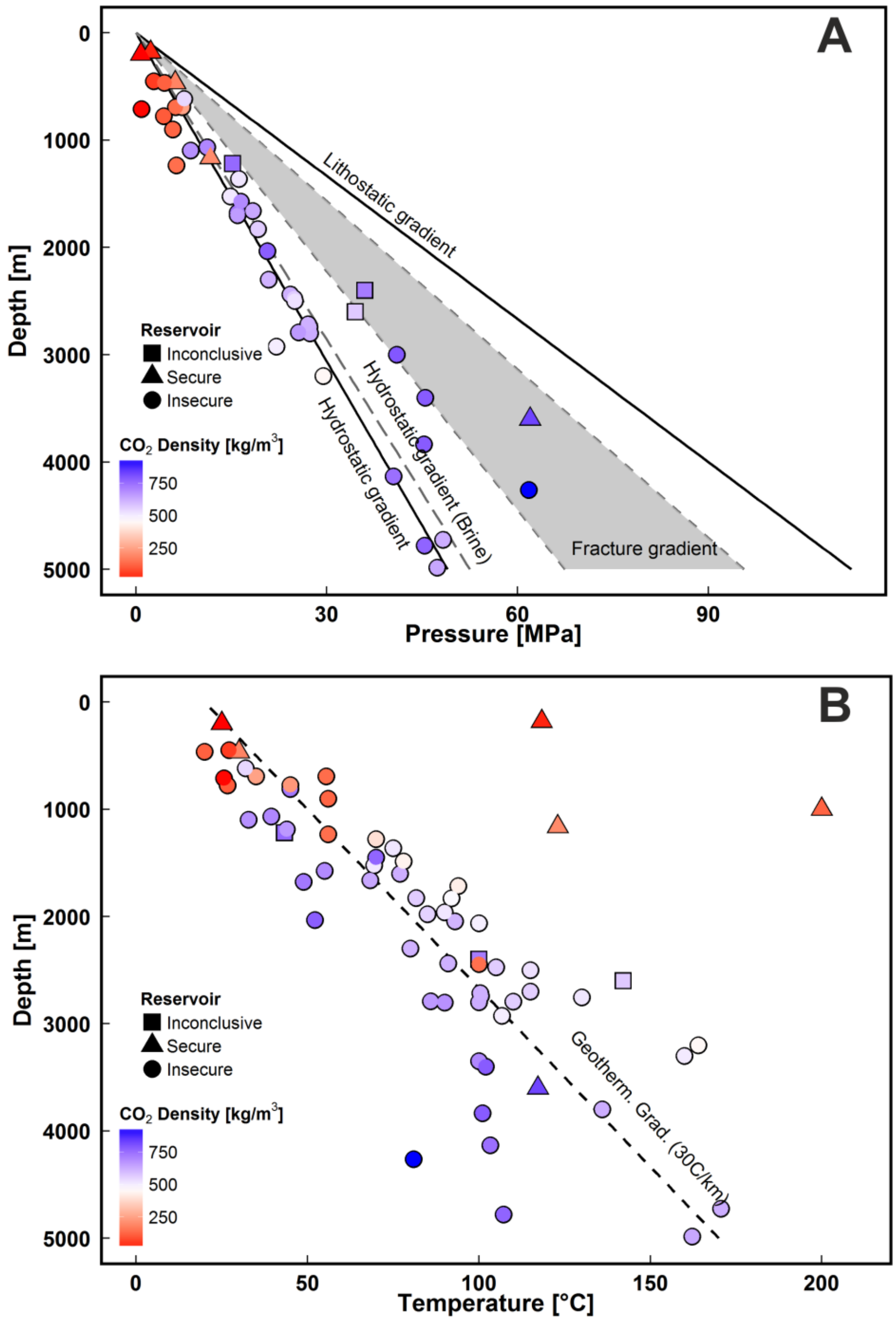

Fig. 2 (A) Depth versus pressure plot of naturally occurring CO_2 reservoirs with in situ pressure data. Note that insecure and inconclusive reservoirs are mainly shallow (<1200 m) or within the fracture gradient regime. Fracture gradients tend to range from 60-90 % of lithostatic stress and depend on the sedimentary basin and tectonic regime. The deep, insecure reservoir with reservoir pressure in the fracture gradient regime is Pieve Santo Stefano, Italy (No. 36, SI Tab. 1). (B) Depth versus temperature plot of naturally occurring CO_2 reservoirs, based on in situ data. Note that a high geothermal gradient is associated with migration of CO_2 in shallow reservoirs.

Reservoir depth and fluid pressure: Our dataset shows that naturally occurring CO_2 reservoirs around the globe exhibit a range of depths below the ground surface, from shallow (180 m, No. 23 in SI Tab. 1.) to very deep (7250 m, No. 12 in SI Tab. 1). Significantly, insecure reservoirs are, with one exception, located at depths shallower than 1200 m below surface (Figs. 2A & 3). Reservoir fluid pressures range from 0.5 MPa to >60 MPa and Fig. 2A shows that successful CO_2 trapping may be controlled to some extent by reservoir fluid pressure. Shallow CO_2 reservoirs (<1200 m depth below surface) that are sealing are hydrostatically pressured, whereas insecure reservoirs at these depths exhibit pressures both above and below hydrostatic. Some sealing reservoirs that are deeper than 1200 m below surface show excess pressures 40-50 % above hydrostatic. In contrast, insecure and inconclusively insecure reservoirs at these depths all exhibit pressures significantly greater than hydrostatic despite ongoing CO_2 migration, and thus being connected to the Earth's surface (Fig. 3). These pressures are within 60-90 % of lithostatic pressure, which is the typical range for fracture pressure of caprocks in the North Sea (Moss et al., 2003), and in other sedimentary basins where the rock fractures (Hillis, 2003). Indeed, the only insecure reservoir which is at a depth of over 1,200 m exhibits reservoir fluid pressures within the fracture envelope (Fig. 2A).

CO_2 fluid properties: Reservoir temperatures range from 20 to 200°C (Fig. 2B), with insecure reservoirs having either "normal" (30°C per km) or very high geothermal gradients. At pressures and temperatures below the critical point (7.38 MPa, 31.1 ºC) CO_2 will be gaseous and exhibit densities of <470 kg/m^3 while at conditions above the critical point it will be supercritical and shows a wide range of densities (<200-1000 kg/m^3). Calculated CO_2 densities based on reservoir pressures and temperatures range from 15 to 919 kg/m^3 (Fig. 4). CO_2 is therefore securely contained in subsurface reservoirs in gas (8 out of 76 reservoirs) and supercritical CO_2 phases; not as a liquid. It also exists as a dissolved phase, which has been shown to be a significant CO_2 trapping mechanism in natural CO_2 reservoirs by several studies (Gilfillan et al., 2009, Sathaye et al., 2014). Insecure reservoirs typically contain CO_2 in a gaseous state (with an average density of 110 kg/m^3) (Fig. 4B). Reservoirs containing CO_2 in a gaseous state are more prone to migration than reservoirs containing supercritical CO_2 (Fig. 4A): 27 % (3 out of 11) of reservoirs with gaseous CO_2 showing evidence for CO_2

migration, while only ~5 % (3 out of 65) of deeper reservoirs containing CO_2 as a supercritical phase exhibit CO_2 evidence for migration to the surface.

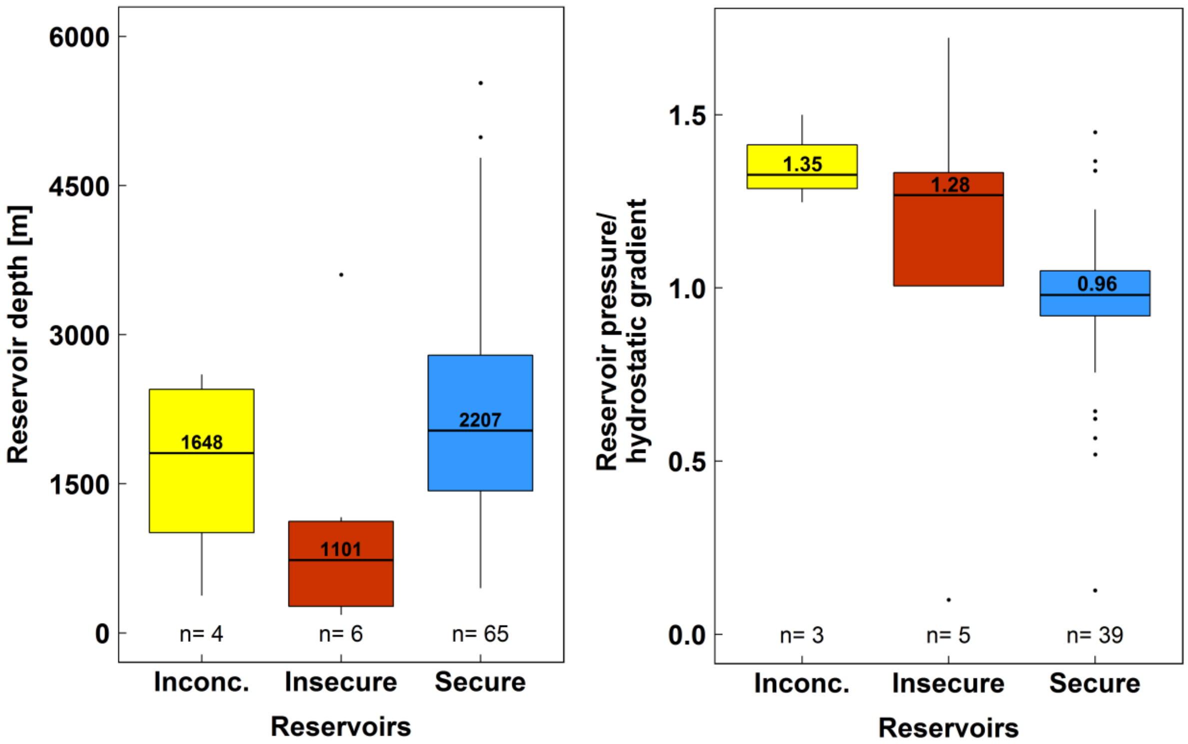

Figure 3: Left: Boxplot of reservoir depth of naturally occurring CO2 reservoirs against inconclusive (inconc.), insecure and secure reservoirs. Note that insecure reservoirs are mainly found in shallow depths (median of 1101 m) while secure reservoirs are generally deeper (2207 m). Right: Boxplot of reservoir pressure/hydrostatic gradient of naturally occurring CO_2 reservoirs against inconclusive (inconc.), insecure and secure reservoirs. Note that inconclusive and insecure reservoirs tend to be overpressured (reservoir pressure/hydrostatic gradient > 1) while secure reservoirs show a wide range of pressures. The box plot shows the median (black horizontal line) and the interquartile range. The whiskers (black vertical line) depicts the 1.5 inter-quartile range.

Geological structure: Where data are available for the 21 multi-layered CO_2 reservoirs, we observe CO_2 is migrating between these stacked formations via faults or fractures (e.g. Huangquiao CO_2 field, China). For 5 of the 6 insecure CO_2 reservoirs, the migrating CO_2 emerges at the surface as CO_2 rich springs and travertine deposits within 5 km to the surface traces of faults, showing the influence of faults on crustal fluid flow, in the near surface at least. However, over half of the secure reservoirs are fault bound structural traps, and several more are located in structurally complex and faulted provinces, indicating that faults more often inhibit CO_2 migration rather than permit it. Importantly, the majority of the insecure reservoirs are found in tectonically active regions, such as the Apennine mountain belt in Italy or the Florina Basin in Greece (Fig. 1).

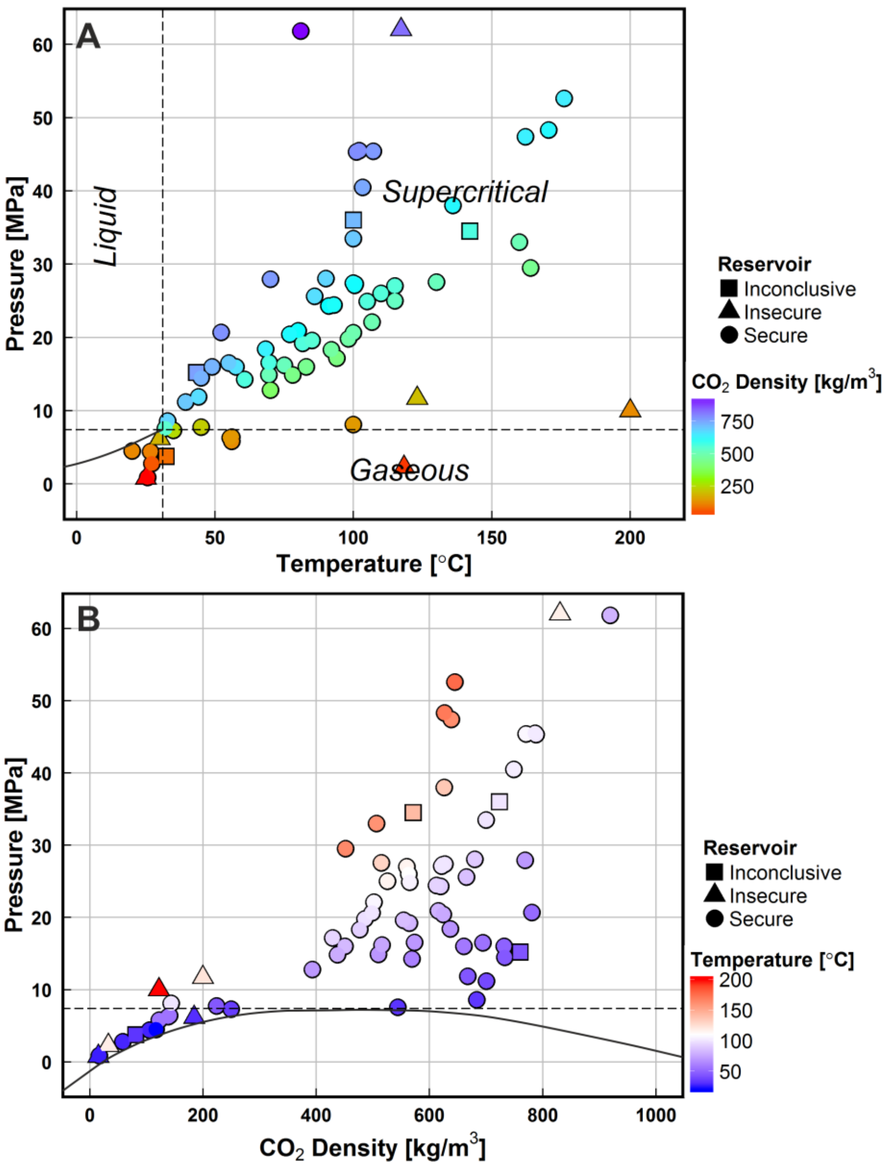

Fig. 4: CO_2 state diagrams of the studied naturally occurring CO_2 reservoirs. Dashed lines indicate critical pressure (7.38 MPa) and temperature (31°C), the thick black line represents the vapour curve. (A) Pressure versus temperature plot highlights that reservoirs holding gaseous CO_2 are more likely to be insecure than reservoirs holding supercritical CO_2. (B) Pressure versus CO_2 density plot illustrating that the majority of insecure reservoirs hold CO_2 with a low (<250 kg/m^3) density.

4. Controls of CO_2 retention in naturally occurring reservoirs

From our study of naturally occurring CO_2 reservoirs, we have observed that insecure CO_2 reservoirs tend to be shallow (<1200 m depth, Fig. 3), contain gaseous or supercritical CO_2

with a low (<200 kg/m^3) density (Fig. 5), exhibit reservoir pressures which are significantly above hydrostatic (Fig. 3), and that migration occurs along faults. Sealing reservoirs tend to be close to hydrostatic pressure, contain supercritical CO_2 with a density of >250 kg/m^3 and present faults are vertically sealing. Three key mechanisms are believed to control whether CO_2 is securely retained in the subsurface or migrates out of the reservoir: diffusion through caprocks, capillary flow through caprocks and fault rocks, and flow of CO_2 through fractures and faults (Gilfillan et al., 2009; Song and Zhang, 2013). The latter could be via existing structural elements, or induced by fracturing due to elevated fluid pressures (Rutqvist and Tsang, 2002).

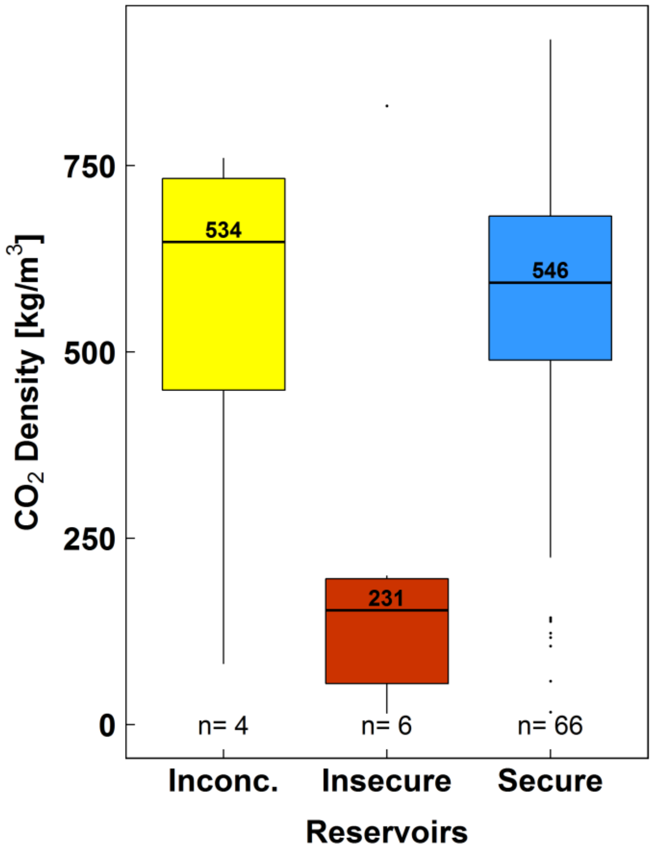

Figure 5: Box plot of CO_2 density in naturally occurring CO_2 reservoirs against inconclusive (inconc.), insecure and secure reservoirs. Note that insecure reservoirs hold low density CO_2 (231 kg/m^3) while secure reservoirs on average have a higher density (546 kg/m^3). The box plot shows the median (black horizontal line) and the interquartile range. The whiskers (black vertical line) depicts the 1.5 inter-quartile range.

Experimental investigations of CO_2 diffusion through caprocks have shown that loss of CO_2 from reservoirs by this process is negligible at storage conditions (Chiquet et al., 2007; Angeli et al., 2009; Wollenweber et al., 2010). Migration of CO_2 by capillary flow will occur when the pressure in the reservoir exceeds that of the capillary entry pressure of pores in the caprock (Finkbeiner et al., 2001). The pores in low permeability rocks are so small that they require very high capillary entry pressure for flow to occur. Such high pressures could be achieved by reservoir fluid overpressure, or by very high buoyancy pressure. The density contrast between CO_2 and brine in the reservoir decreases with increasing depth because density and phase conditions of CO_2 are dependent on pressure and temperature. For this reason, CO_2 buoyancy pressure exerted on the caprock is more likely to be greater in shallow accumulations (<1000 m depth) and this more likely to approach or overcome capillary entry pressure. However, the CO_2 buoyancy will also be affected by the geothermal gradient and the column height of CO_2 accumulation, as controlled by geological setting and structure. Despite this, migration at the shallow reservoirs in this study is associated with fractures and fault damage zones, illustrating that capillary flow through unfractured caprock is not the primary CO_2 migration mechanism from these natural reservoirs. Roberts at al. (2015) studied migration from breached CO_2 reservoirs in Italy and were able to show that the rate of surface seepage greatly exceed the rates physical possible from CO_2 migration by capillary flow or diffusion through intact mudrocks showing that fracture-related rock permeabilities are necessary to permit such flow rates. For these reasons we can also identify that free-phase CO_2 (as gas or supercritical phase) will be more prone to vertical migration due to gravitational forces than brine with dissolved CO_2, which tends to be heavier than CO_2 free pore-fluids. At only one of the 76 reservoirs included in this study, the St. Johns Dome reservoir in Arizona (No. 2, SI Tab. 1), a connection between migrating dissolved phase CO_2 and a subsurface reservoir could be documented (Gilfillan et al., 2011; Keating et al., 2014). This means that solubility trapping is also a critical control in secure CO_2 retention as previously suggested (Gilfillan et al., 2009).

Many of the leaking reservoirs are overpressured with respect to the hydrostatic pressure gradient, suggesting that mechanisms of fluid escape could be enhanced by elevated pressures. Hydraulic fracturing and/or frictional failure along optimally oriented pre-existing fractures of the caprock can occur if pore pressure in the reservoir exceeds both the pore pressure in the caprock and the tensile strength of the caprock - including any differences in confining stress due to different elastic properties (Finkbeiner et al, 2001; McDermott et al, 2013). Both mechanisms can lead to migration of CO_2 from the reservoir through the caprock by flow in the induced fractures (Shukla et al., 2010). Hydraulic fracturing only occurs when the fluid pressure exceeds the least principal stress of the caprock (Hillis, 2003). The pore pressure required to form dilatant joints is less than that required to overcome the capillary entry pressure of a mudstone caprock (Busch et al., 2010), and so caprocks are more likely to fail before CO_2 can overcome capillary entry pressures.

There is evidence for CO_2 migration through faulting related fractures at several insecure reservoirs in this study. CO_2 seeps are frequently located close to faults, some of which, but not all, having been recently seismically active (Irwin and Barnes, 1980; Shipton et al., 2004). Thus fractures in the fault damage zone appear to be important fluid pathways for CO_2 migration to surface. The role of fracture networks/corridors for CO_2 rich fluid migration in natural systems (e.g. on the Colorado Plateau, USA; Latera Caldera, Italy) has been studied and highlighted by several authors (Faulkner et al., 2010; Annunziatellis et al., 2008; Shipton et al., 2005). Dockrill and Shipton (2010) found that CO_2 fluid flow at the northern end of the Paradox Basin (Utah) is localised and focused within the damage zone of faults. Further, they found evidence of several episodes of fluid flow, illustrating that such pathways have the potential to support long-term fluid migration from depth to the surface. Fieldwork in the same area enabled Ogata et al. (2014) to reinforce that extensive fracture networks/fracture corridors are the main pathways for (CO_2 rich) fluid migration from depth to the surface. They were able to classify three fracture corridor types that bypass local sealing units: (1) fractures related to the damage zone of faults; (2) fractures related to the tip of faults; and (3) fractures related to the crest of folds. This is also the case at St. Johns Dome, Arizona, where ongoing migration of dissolved phase CO_2 is concentrated along fracture networks at the fault tip of, and along fracture zones related to a large fault in the region (Gilfillan et al., 2011, Keating et al., 2014). This aligns with the conclusions of from Roberts (2012) studying the geological controls on natural CO_2 systems in Italy. These three types correspond with the different structural settings at which CO_2 migration is observed at the insecure natural analogues of this study and may thus be useful to predict potential fluid migration pathways at CO_2 storage sites.

The introduction of CO_2 into the subsurface reservoirs may have increased the reservoir fluid pressure and led to fracture opening, reactivation or even to hydraulic fracturing of the caprocks, which could explain our observation that several insecure reservoirs are currently overpressured, despite ongoing CO_2 migration from them. This is perhaps indicative of ongoing CO_2 charge of the reservoirs, or perhaps the slow rate of pressure leak-off from CO_2 migration. While buoyancy may be the driving force of CO_2 migration at some reservoirs, pressure gradients in excess of hydrostatic can also cause upwards flow, even in the absence of buoyancy forces. Thus the pressure difference between reservoir and caprock is important: If the pressure within the caprock is higher than the reservoir pressure, no fluid migration from the reservoir into the overlying caprock will occur as the caprock will act as a hydraulic barrier (Reveillere & Rohmer, 2011).

The critical need to understand fracture networks and the potential of fracture reactivation and/or hydromechanically fracturing of caprock due to the injection of CO_2 has been highlighted by experiences at existing industrial CO_2 storage projects. At the Sleipner storage site, located in the Norwegian sector of the North Sea, where more than 15 Mt of CO_2 has been injected into a saline aquifer at a depth of 800-1000 m since 1996, fractures in thin shale layers seem to control the size and extent of the CO_2 plume (Cavanagh and Haszeldine, 2014). At the storage site of In Salah, Algeria, where between 2004 and 2011 around 4 million tons of CO_2 were injected into an anticlinal structure at ~1,800 m depth, high injection pressures resulted in hydraulic fracturing of the reservoir and lower caprock units and potentially reactivated pre-existing fracture networks and small scale faults (Rutqvist et al., 2010; White et al., 2014). Experiences from both Sleipner and In Salah thus coincide with our observations from naturally occurring CO_2 reservoirs that flow of CO_2 through fractures and fault damage zone related fracture networks is the controlling mechanism for migration of CO_2 within the subsurface. The two other modes of CO_2 migration, diffusion and capillary flow through unfractured caprock, have not been found to play a significant role in leakage to the surface from naturally occurring CO_2 reservoirs.

5. Implications for storage site selection

Our analysis of a global dataset of naturally occurring CO_2 reservoirs has highlighted the importance of fault related fracture networks in causing the migration of CO_2 from subsurface reservoirs to the surface. We also identify that shallow reservoirs with low density (<250 kg/m^3) gaseous or supercritical CO_2 are less likely to securely retain CO_2 over the timescales required for geological storage and we propose that this could be in part controlled by CO_2 buoyancy. Carbon stores are more likely to be secure if they are selected to have thick (>150 m) caprocks.

Table 1: Table comparing site selection criteria for geological CO_2 storage from previous recommendations and our study results.

Criteria	CASSEM (2011)	Chadwick (2008)	IEA (2009)	This Study
Fluid Properties				
CO_2 State	-	Dense	-	Supercritical or liquid
CO_2 density (kg/m3)	-	-	-	>250
Reservoir				
Structure	Minimal faulting, with trapping structure	Small or no faults	Low faulting frequency, multi layered system	Vertically sealing faults, multi layered systems
Depth (m)	>800 <2500	>1000 <2500	>800	>1200
Temperature	-	-	Minimum temperature of 35 °C	Geo-thermal gradient of max. 30°C/km
Pressure (MPa)	-	-	>7.5	~10kPa/m (ideally close to hydrostatic)
Caprock				
Thickness (m)	>100	>100	>10	>150
Continuity	-	Uniform	Extensive	Low fracture density

Tab. 1 shows how the results of this study compare with the previously published guidelines for site selection to minimize the risks associated with geological storage of CO_2. If existing site selection criteria were applied to the six insecure reservoirs in this study, these reservoirs would be deemed unsuitable for CO_2 storage (Tab 2). This gives confidence that the current site selection recommendations for engineered storage sites are effective in selecting sites which will be able securely retain CO_2 for the timescales required. However, based on our observations from naturally occurring CO_2 reservoirs we have identified a number of controls on CO_2 storage security that are currently not addressed sufficiently in the existing site selection criteria. We find that the density of CO_2, which governs the density contrast between CO_2 and reservoir fluid, has a higher impact on reservoir security than storage depth or CO_2 state (Fig. 5). Previous site selection criteria do not include recommendations for CO_2 density, only the CO_2 state. Based on our findings we recommend that CO_2 should be stored in a dense phase at the pressure and temperature conditions of the proposed storage reservoir, or, at the minimum, density should be no less than 250kg/m^3 so as to minimize the density contrast between the CO_2 and the brine, and thus minimise the CO_2 buoyancy forces acting on the reservoir seal.

Table 2: Table highlighting that insecure CO_2 stores would have been identified using the site selection criteria listed in Tab. 1. Bold indicates where the reservoirs would have failed the selection criteria. Three of the insecure reservoirs hold CO_2 in gaseous state with low densities due to their shallow depths. Two of the insecure reservoirs are located in suitable depths and hold supercritical CO_2 but exhibit low densities due to very high temperature gradients. One insecure reservoir is located at a much greater depth and retains supercritical CO_2 but is significantly overpressured.

Site	St. Johns Dome (USA)	Imperial (USA)	Messo-kampos (Greece)	Latera Caldera (Italy)	Pieve Santo Stefano (Italy)	Frigento Field (Italy)
Depth (m)	**465**	**180**	**200**	1000	3600	1163
Temperature (°C)	30	118	25	**200**	117	**123**
Pressure (MPa)	6.2	2.3	0.8	-	**62**	11.7
CO_2 state	**Gaseous**	**Gaseous**	**Gaseous**	Sc	Sc	Sc
CO_2 density (kg/m^3)	**184**	**33**	**15**	**122**	830	**200**

Faults and associated fracture networks are the only migration pathways observed at naturally occurring analogues, perhaps enhanced by elevated fluid pressure. For secure engineered CO_2 storage, any faults must be vertically sealing and thus preventing vertical fluid migration. This can be determined by subsurface pressure analysis, and fault seal analysis, which we strongly recommend to be part of the screening process for potential storage sites regardless of the vertical extent of the faults present. Particular attention should be paid to the in-situ stress regime in order to assess the threat of fault/fracture network reactivation during CO_2 injection. The potential for CO_2 migration laterally across faults must also be assessed. The extent of lateral movement across faults is unclear in the natural analogues we studied here. CO_2 storage in tectonically active regions should be avoided since critically stressed fracture networks are more permeable and thus CO_2 can migrate along active faults from great depths to the surface. We also recommend that selection criteria increase the minimum caprock thickness to 150 m. Potential fracture networks within the caprock should be considered in order to focus leakage monitoring efforts to these areas. Multiple caprock layers have been proven to be beneficial for a secure storage site.

Most of the proposed site selection criteria for secure storage sites (Tab. 1) can be applied during site scoping where only limited subsurface data is available. Reservoir depth will be known in the order of 10s of meters and basin specific temperature and pressure gradients should also be readily available. With this information an estimate of CO_2 state and density at reservoir conditions is possible and unsuitable sites can be ruled out quickly. However, a fault seal analysis at suitable sites requires detailed in situ information such as stress field data, reservoir pressure, and 3D subsurface structure which will rely on the existence of well and seismic data. For site scoping arbitrary limitations on site selection criteria such as caprock thickness, reservoir depth or CO_2 density, may potentially be disadvantageous as otherwise suitable storage sites could be ruled out (Hannon and Esposito, 2015). These limitations risk making site selection prescriptive when actually the process must take many formation characteristics that influence storage and sealing viability into account. However, the lack of such subsurface data at the first screening makes good site selection criteria (Tab. 1) crucial even if they may occasionally exclude suitable storage sites.

The selection of secure sites for geological carbon storage is one of the greatest challenges for a successful implementation of this climate mitigation technology. Here we have identified controls for retention and migration of CO_2 in the subsurface by analysing naturally occurring CO_2 reservoirs. We find that insecure natural CO_2 reservoirs would not pass current storage site selection criteria, though we also present new site selection criteria based on our results. Adopting these criteria would increase confidence in geological carbon storage site selection (Tab. 1).

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