Natural CO$_2$ sites in Italy show the importance of overburden geopressure, fractures and faults for CO$_2$ storage performance and risk management

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Abstract: The study of natural analogues can inform the long-term performance security of engineered CO$_2$ storage. There are natural CO$_2$ reservoirs and CO$_2$ seeps in Italy. Here, we study nine reservoirs and establish which are sealed or are leaking CO$_2$ to surface. Their characteristics are compared to elucidate which conditions control CO$_2$ leakage. All of the case studies would fail current CO$_2$ storage site selection criteria, although only two leak CO$_2$ to surface. The factors found to systematically affect seal performance are overburden geopressure and proximity to modern extensional faults. Amongst our case studies, the sealing reservoirs show elevated overburden geopressure whereas the leaking reservoirs do not. Since the leaking reservoirs are located within <10 km of modern extensional faults, pressure equilibration within the overburden may be facilitated by enhanced crustal permeability related to faulting. Modelling of the properties that could enable the observed CO$_2$ leakage rates finds that high-permeability pathways (such as transmissive faults or fractures) become increasingly necessary to sustain leak rates as CO$_2$ density decreases during ascent to surface, regardless of the leakage mechanism into the overburden. This work illustrates the value of characterizing the overburden geology during CO$_2$ storage site selection to inform screening criterion, risk assessment and monitoring strategy.

Carbon capture and storage (CCS) could significantly reduce anthropogenic CO$_2$ emissions from large industrial sources of CO$_2$. However, to be an effective climate change mitigation strategy, the injected CO$_2$ must remain in the subsurface for timescales of multiple thousands of years (Shaffer 2010). Leakage of CO$_2$ out of a reservoir could compromise the long-term emission reductions achieved by a CCS project (EU CSS Directive 2009; Zwaan & Gerlagh 2009), and if leaked CO$_2$ then migrates to the surface or into aquifers there may be local environmental and human health impacts (Jones *et al.* 2015). Unintended leakage to surface in the early phase of technology roll-out could compromise the public acceptability of future CCS, as well as the economic feasibility due to remediation expenditure and liability pay-out (Zwaan & Gerlagh 2009; Heptonstall *et al.* 2012), and, in the EU, possible fines for CO$_2$ emissions (Dixon *et al.* 2015). Thus, any incidence of leakage from engineered stores may have ramifications for the CCS industry on a global scale.

For these reasons, it is important that the storage site characterization and selection process maximizes the likelihood that injected CO$_2$ will be securely retained in the subsurface for the timescales intended (thousands of years). Characterization and selection criteria must be applicable in a range of geological settings, and without imposing excessive financial costs. In addition to geological, technical and economic considerations, siting is also constrained by the proximity of the CO$_2$ source, permitting procedures and public perception. Sites selected for storage do not, therefore, have to be the most geologically favourable (Hannon & Esposito 2015) but must comply with selection criteria. To ensure that CO$_2$ leakage is avoided, these criteria must be guided by a thorough understanding of the geological characteristics that are most relevant to site integrity. Table 1 summarizes the site selection criteria from guidelines published to date (Miocic *et al.* 2016), which are intended to maximize the likelihood of long-term CO$_2$ containment. The site selection process must characterize the risks of

Table 1. *A summary of published CO$_2$ storage site selection criteria*

	Feature	Criteria/Requirement	Source
CO$_2$ properties	CO$_2$ state	Dense phase	Chadwick *et al.* (2008)
Reservoir properties	Structure	No faults, or small faults. Low faulting frequency Multilayered system	Chadwick *et al.* (2008), IEA-GHG (2009), Smith *et al.* (2011) IEA-GHG (2009)
	Depth (m)	Between 800 and 2500 m 800 m minimum depth	Chadwick *et al.* (2008), IEA-GHG (2009), Smith *et al.* (2011) IEA-GHG (2009)
	Temperature	>35°C	IEA-GHG (2009)
	Pressure (MPa)	>7.5	IEA-GHG (2009)
Cap-rock property	Thickness (m)	Between 10 and 100 m	Chadwick *et al.* (2008), IEA-GHG (2009), Smith *et al.* (2011)
	Continuity	Uniform (laterally) Extensive	Chadwick *et al.* (2008) IEA-GHG (2009)

These criteria are recommended to minimize the risks of CO$_2$ leakage. Adapted from Miocic *et al.* (2016).

geological storage, and understanding how CO$_2$ could move out of a reservoir and potentially through the overburden and to the surface is critical for constraining and managing risk.

Natural CO$_2$ reservoirs cannot serve as direct analogues to engineered CO$_2$ storage sites. The latter are specifically selected for characteristics that minimize leakage, and are charged from a point source at rates and for timescales that are unlikely to mimic any natural process. However, instances of CO$_2$ migration to the surface from naturally occurring reservoirs provide an opportunity to assess the conditions required for leakage from the reservoirs and to understand the crustal fluid pathways for migration from depth (Annunziatellis *et al.* 2008; Wilkinson *et al.* 2009; Dockrill & Shipton 2010; Kampman *et al.* 2010). Similarly, instances where CO$_2$ has been successfully retained for geologically long time periods offer opportunities to assess the conditions that will enable effective storage and CO$_2$–water–rock interactions (Allis *et al.* 2001; Gilfillan *et al.* 2009). The most important controls on the security of CO$_2$ retention can be established by comparing the characteristics of reservoirs that leak with reservoirs that seal (Miocic *et al.* 2016).

Resource exploration drilling in Italy has revealed the presence of CO$_2$ accumulations at a range of depths below surface (Casero 2004; Collettini *et al.* 2008; Chiodini *et al.* 2010; Trippetta *et al.* 2013). Italy is also a region of widespread surface CO$_2$ degassing; over 308 CO$_2$ seeps have been catalogued at 270 locations in mainland Italy and Sicily (Chiodini & Valenza 2008). Here, we explore the geological conditions that govern whether reservoirs leak or retain CO$_2$ and establish the

mechanisms of leakage. To do this, we identify CO$_2$-bearing reservoirs from borehole data and establish which boreholes are located geographically close to CO$_2$ seeps that may represent leakage from that reservoir to surface. We then examine and compare the structure and conditions of the CO$_2$ boreholes to investigate the controls on whether a reservoir leaks or retains CO$_2$. Finally, to inform the potential mechanisms of leakage, we assess the properties of possible pathways through the overburden that could enable CO$_2$ seepage at the rates and styles observed at the Earth surface. Understanding these natural processes over geological timescales is important for informing the long-term performance security of engineered CO$_2$ storage, since engineered storage sites will be selected and managed to minimize the risks of CO$_2$ migration. This work can therefore guide effective site assessment, injection strategy and remediation strategies in the case of leakage.

A summary of the geology and CO$_2$ fluids in Italy is presented in the next section. For completeness, the section that follows outlines CO$_2$ flow in rocks and the potential mechanisms of migration from a containing reservoir into the overburden (CO$_2$ leakage) and to the Earth surface (CO$_2$ seepage).

An overview of CO$_2$ geofluids in Italy

Hydrocarbon exploration drilling in Italy has encountered subsurface CO$_2$ accumulations, either as a component within hydrocarbon reservoirs (Casero 2005) or as the dominant gas (Collettini & Barchi 2002; Bicocchi *et al.* 2013). Such accumulations are mostly found in central Italy, which is also

where CO_2 degassing is most intense (Chiodini *et al.* 2004). In this region, there is a strong regional NW–SE structural trend (Fig. 1) resulting from the westwards subduction of the Adria Plate beneath the European margin. Crustal shortening stacked several tectonic–stratigraphic units originally located on the Apulian Palaeozoic crystalline carbonate basement, with flysch and synorogenic foredeep sediments (Scrocca *et al.* 2005) (Fig. 1a). To the west, coeval extension opened marine and continental basins and the Tyrrhenian Sea (Ghisetti & Vezzani 2002), leading to high heat flow and volcanism. Seismogenic normal faulting is currently active in the Apennines where exposed fault scarps date from 12 to 18 ka (Roberts 2008). Here, CO_2 fluids trapped at depths >5 km play a critical role in the nucleation and evolution of seismogenesis, and therefore in the deformation style and geodynamics of the region (Miller *et al.* 2004; Malagnini *et al.* 2012).

CO_2 degassing is most active towards the Tyrrhenian, west of the region of active extension (Chiodini *et al.* 2004). CO_2 seeps are mostly low-temperature emissions that are manifested as vents (pressurized CO_2 release, some are referred to as CO_2-driven mud volcanoes: e.g. Bonini 2009*b*), diffuse soil degassing, springs and pools of bubbling water (Minissale 2004; Chiodini *et al.* 2008; Roberts *et al.* 2011). Geochemical studies find that the CO_2 has a number of sources, including shallow biogenic processes, carbonate hydrolysis, mechanical breakdown and thermometamorphism of carbonates, and mantle degassing (Italiano *et al.* 2008; Frezzotti *et al.* 2009). There are few studies of the origins of CO_2 trapped in the subsurface in Italy.

Previous work at CO_2 seeps in Italy has explored the factors affecting the human health risk they pose, and the geological and geomorphological controls on their distribution and characteristics, to inform risk assessment and monitoring design above storage sites (Roberts *et al.* 2011, 2014). This article extends this work to examine the subsurface geological attributes that control CO_2 leakage to surface. This is the first study to summarize the properties of CO_2 traps in Italy and learn from these analogues to minimize risk of leakage at engineered CO_2 stores.

CO₂ flow in geological formations

CO_2 fluids are retained in geological formations either as a free phase or dissolved in formation water. Depending on the subsurface conditions, free-phase CO_2 may be present in a dense or light form, where we define 'dense' as CO_2 with densities greater than the critical density ($\rho_c = 464$ kg m^{-3}) and 'light' as CO_2 with densities below the critical density. CO_2 phase behaviour is primarily controlled by subsurface temperature and pressure conditions, but is also affected by the presence of other fluids. Free-phase CO_2 will dissolve when it is in contact with undersaturated formation waters, which results in an increase in the water density (Spycher *et al.* 2003).

How free-phase or dissolved CO_2 flows through a rock formation is dependent on the properties of the fluid itself and of the rock. A rock volume will commonly exhibit a distribution of fluid pathway geometries due to heterogeneity intrinsic to geological units and the presence (and orientation) of fractures (Krevor *et al.* 2015). The permeability of the rock will vary according to the properties of the fluid flowing through it. This 'effective permeability' (K_E) is determined by the bulk permeability of the rock (K_{rock}) and the fraction of the total permeability accessible to each fluid phase (the relative permeability, K_r):

$$K_E = K_{rock} K_{r_{CO_2}} \qquad (1)$$

In single-phase flow, all pores are saturated with a single fluid. For CO_2-saturated water flowing through a water-wet rock, K_E is equal to K_{rock}. However, for two-phase flow, such as free-phase CO_2 flowing through a water-wet rock, $K_{r_{CO_2}}$ is influenced by the saturation of formation water in the pores or fractures through which the CO_2 is flowing.
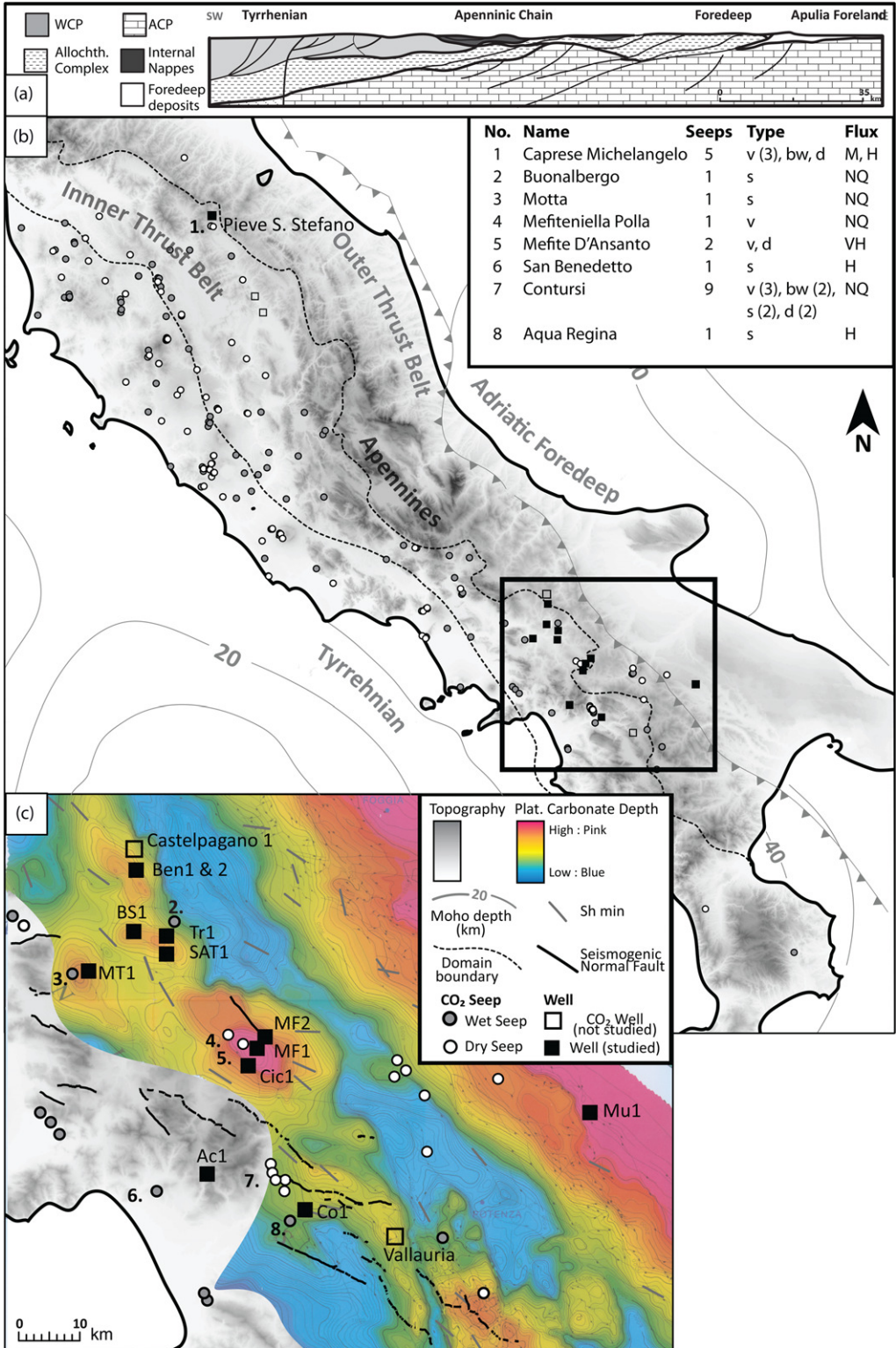
Rate of fluid flow per unit area, otherwise known as fluid flux, through a rock volume increases with effective permeability and fluid pressure gradients, and lower fluid viscosity. This is commonly approximated by capillary (or 'Darcy') flow:

$$\frac{Q}{A} = \frac{K_E}{\mu} \frac{\delta P}{\delta z} \qquad (2)$$

where Q (flux) is the CO_2 flow rate (m^3 s^{-1}) over the seepage area, A (m^2), K_E is the effective permeability of the fluid (m^2), $\delta P/\delta z$ is the pressure gradient, (Pa m^{-1}), where P is pressure and z is depth (m), and μ is CO_2 viscosity (Pa s^{-1}).

Light-phase CO_2 is less viscous and more buoyant than dense phase, and experiments find that the effective permeability for light-phase CO_2 is higher than dense phase (Bachu & Bennion 2008). According to equations (1) and (2), light-phase CO_2 will flow more readily than its dense phase. Once flow is established in a rock, the relative permeability to CO_2 may increase due to drying effects, whereby formation fluids dissolve into the flowing CO_2 phase, decreasing the water saturation (Pruess 2008*b*).

Darcy's law does not characterize fluid flow in fractures, where permeability pathways are spatially focused rather than distributed throughout the rock volume. If the fracture spacing, orientation and aperture are known, then fracture flow

No.	Name	Seeps	Type	Flux
1	Caprese Michelangelo	5	v (3), bw, d	M, H
2	Buonalbergo	1	s	NQ
3	Motta	1	s	NQ
4	Mefiteniella Polla	1	v	NQ
5	Mefite D'Ansanto	2	v, d	VH
6	San Benedetto	1	s	H
7	Contursi	9	v (3), bw (2), s (2), d (2)	NQ
8	Aqua Regina	1	s	H

can be modelled discretely. However, where this information is not available, then fractured rocks can be approximated as porous media, where fracture permeability is upscaled to bulk permeability values that represent the flow properties of the rock volume (see Kuhlman *et al.* 2015 and references therein).

Mechanisms of CO_2 migration from its containing reservoir to surface

Some naturally occurring CO_2 reservoirs have been found to successfully retain CO_2 for millennia (Gilfillan *et al.* 2008) and in a range of geological environments (Lewicki *et al.* 2007). Other sites leak CO_2 to surface (Miocic *et al.* 2016), which can occur through a range of mechanisms. Free-phase CO_2 is less dense than surrounding porewaters and will rise buoyantly, becoming structurally trapped beneath a sealing unit if both a low-permeability rock and a containing structure are present. Dissolved and free-phase CO_2 can leak from the reservoir formation by diffusion, but this is an extremely slow process (Lu *et al.* 2009). However, high leak rates (e.g. tonnes CO_2 per day) through the overburden of natural reservoirs will most likely arise from a buoyant free phase of CO_2 which may leak by capillary transport through pores or microfractures in the overburden, or along unsealed faults and associated damage zones (Zweigel *et al.* 2004; Bachu 2008). Otherwise, in natural CO_2 systems, a low-permeability seal may be bypassed if free-phase CO_2 'spills' from a trapping structure. In this case, the overburden directly above the CO_2 reservoir has not been compromised, but the space for CO_2 in the reservoir-trap structure has simply been exceeded, although CO_2 storage reservoirs will be engineered such that the capacity will not be exceeded. Advective flow of CO_2-bearing waters could transport CO_2 from the reservoir more rapidly than diffusion. Such flow could occur through high-permeability pathways through the overburden, or by hydrodynamic flow within the aquifer.

The capillary entry pressure of free-phase CO_2 within a given cap rock determines the maximum column height of the free-phase CO_2 in the reservoir before it invades the seal by capillary transport. The capillary entry pressure is a function of the fluid properties (e.g. interfacial tension, contact angle) and rock properties (e.g. rock pore and pore throat geometry), or fracture aperture and roughness (Bachu & Bennion 2008; Naylor *et al.* 2011). An extremely high gas pressure will be necessary to overcome the capillary threshold pressure of a shale cap rock; however, following capillary breakthrough, CO_2 can then flow through the seal and overlying overburden at capillary pressures below the initial entry pressure, facilitating further leakage. Subsidiary fluid components can affect the fluid properties of the CO_2 phase, and so can enhance or retard capillary breakthrough.

Confining pressure, defined by overburden thickness and density, improves seal quality by increasing the mean stress, and therefore rock strength, until the yield stress of the rock is approached. Hence, at higher confining pressures, greater fluid pressures are required for the seal to mechanically fail (Osborne & Swarbrick 1997). Confining pressure also reduces rock permeability by closing pores. Additionally, as rocks are buried, diagenesis may occlude pore throats and fracture apertures by cementation (Nara *et al.* 2011). Elevated fluid pressures can lead to the hydraulic opening of fractures or shear on existing fractures due to a reduction in effective stress resulting in enhanced permeability (Gudmundsson *et al.* 2001; Yang & Manga 2009). The effect of pore fluid pressure (P_f) on rock strength can be represented by the pore fluid factor, λv, which is the ratio of pore fluid pressure (i.e. reservoir pressure, P_{res}) to lithostatic stress (Streit & Cox 2001) after Hubbert & Rubey (1959):

$$\lambda v = \frac{P_{res}}{\rho_{rock}\, g\, z} \qquad (3)$$

where ρ_{rock} is rock density (typically assumed to be 2500 kg m^{-3}), g is acceleration due to gravity (m s^{-2}) and z is depth. For hydrostatic pressure, $\lambda v = 0.4$, and for lithostatic pressure, $\lambda v = 1$. The pore fluid factor indicates how close a coherent rock body is to failure, and will therefore be underestimated when applied to a fractured rock unit. Rock bulk permeability could therefore be increased by CO_2 buoyancy or fluid pressure, which in

Fig. 1. (**a**) Cross-section of Italy modified from (Improta *et al.* 2000). Most CO_2 reservoirs are hosted by the Apulian Carbonate Platform (ACP) in the Inner Thrust Belt, and the Allochthonous Complex forms the overburden. (**b**) Map of Italy modified from Patacca *et al.* (2008), detailing topography and the location of CO_2 seeps (dry and wet) and wells (including CO_2 wells not studied here), and geological terrane boundaries (Ghisetti & Vezzani 2002). (**c**) Map of the Southern Apennine region, showing the location of CO_2-bearing wells, stress field data (Barba *et al.* 2009; Sh min denotes minimum horizontal stress), mapped seismogenic normal faults (Roberts 2008) and deep platform carbonate structure (Nicolai & Gambini 2007). Table inset: detail of seeps shows in (c), including name, seep type (v, vent; bw, bubbling water; s, spring; d, diffuse) and flux information (M, medium; H, high; NQ, not quantified: see the text for definitions).

extreme cases can encourage rock failure (Collettini *et al.* 2008).

Should CO_2 leak from its primary reservoir, it may continue to migrate via available pathways through the overburden. During ascent, it is likely to encounter multiple reservoir and cap-rock units, and so CO_2 may accumulate in any overlying secondary reservoirs (Pruess 2008*a*) until these reservoirs, too, are breached or bypassed. Several mechanisms may attenuate the mass of migrating CO_2 during its ascent, including residual trapping or dissolution into unsaturated porewaters. Therefore the mass of CO_2 that reaches the near-surface it likely to be only a proportion of the mass that migrated from the deep rock formations, or none may reach the surface at all. Depending on the lithostatic pressure and geothermal gradient profile, CO_2 will typically become subcritical at depths shallower than 1 km. Subcritical CO_2 will pass through two hydrological zones: the phreatic (groundwater saturated) zone and the vadose (unsaturated) zone. In its light phase, CO_2 will be significantly more buoyant than groundwater in the phreatic zone. However, CO_2 at ambient temperatures will be denser than soil gas in the vadose zone, and so may disperse laterally in the shallow subsurface, perhaps above the water table (Annunziatellis *et al.* 2008; Kirk 2011). Depending on the soil properties, this could make the area of elevated soil CO_2 degassing substantially larger than the leak pathway from depth.

Observations at CO_2 and CH_4 seeps around the world find that gas release typically occurs over a discrete area (<0.01 km^2), although in some cases the region of CO_2 phenomena where seeps occur may be much larger (several km^2 or more) (Chiodini *et al.* 2004, 2010; Heinicke *et al.* 2006; McGinnis *et al.* 2011; Talukder 2012; Burnside *et al.* 2013; Elío *et al.* 2015; Nickschick *et al.* 2015).

Methods

CO_2 seep data was taken from Googas (Chiodini & Valenza 2008), a web-based catalogue of degassing sites in Italy and Sicily, which documents seep location and seep type, and, where available, rate of CO_2 degassing, gas composition and temperature. In the catalogue, the rate of CO_2 degassing is classified into low (<1 t CO_2/day), medium ($1–10$ t CO_2/day), high ($10–100$ t CO_2/day) and very high (>100 t CO_2/day).

Step 1: Selecting case studies

First, we identified CO_2 reservoirs, and established which are geographically close to CO_2 seeps, and therefore may be leaking.

Well logs and accompanying drilling notes for non-commercial boreholes in Italy are publicly available (www.videpi.com). By examining the VIDEPI dataset and in consultation with ENI and Independent Resources PLC, we selected non-commercial boreholes where test results document that the reservoir fluids are predominantly composed of CO_2. These boreholes, and boreholes nearby, were studied to constrain the subsurface structure and conditions.

A geographical information system (GIS) was populated with seep and well bore data. We included data on: 'active' faults, as defined by seismogenic fault scarps mapped (Roberts 2008); seismically capable faults (ISPRA 2007); the present-day stress field (Barba *et al.* 2009); elevation (SRTM 90 m: Jarvis *et al.* 2008); subsurface carbonate structure (Nicolai & Gambini 2007); and isotherms at 1 and 2 km depth (Geothopica 2010). The distance from the well bore to the nearest CO_2 seeps was calculated from this GIS.

Step 2: Case study geology

To explore the geological conditions that affect whether a CO_2 reservoir is sealed or is leaking, we determined the geology for each reservoir, the overburden thickness and properties, regional structure, and subsurface conditions, using the publicly available well logs and other published data.

Many of the selected boreholes were drilled in the 1960s and 1970s, and therefore lack downhole information available from more modern boreholes, including many well tests. Downhole rock formations and their properties were determined from the well log (from well cuttings and core) and accompanying lithological descriptions, and any data from formation tests. We define the CO_2 reservoir as the shallowest rock formation that has high CO_2 gas saturation, and 'seal thickness' was defined by the maximum and minimum thickness of impermeable rock units overlying the CO_2 reservoir. Deviated drilling was corrected to the true vertical depth (TVD) and assumed a standard depth error of approximately ± 10 m and normally distributed to 1 SD.

To reconstruct downhole conditions, a number of assumptions had to be made. Formation pressure information was estimated from formation tests, where available, or from the density of drilling fluids (mud weight). Pore fluid pressures from mud weights usually exceed the actual formation pressure. To account for this, we adjust the formation pressures by 10%, following the methodology of Wilkinson *et al.* (2013). Formation pressure measurements were not sufficiently regularly spaced, nor were mud weight data sufficiently detailed, to distinguish the CO_2 and water legs from the pressure profiles. However, where formation tests

documented a transition from CO$_2$ to the water leg, minimum CO$_2$ column heights were estimated.

A number of boreholes provided the information to calculate corrected geothermal gradient from downhole temperature measurements. Unusually low downhole temperatures are the expected result of circulation of cold drilling mud within the borehole. In these cases, and cases where downhole temperatures are unavailable, the geothermal gradient was interpolated from the geospatial dataset. Loss of drilling fluid circulation or significant mud absorption, which are sometimes recorded on the borehole logs, can be useful indicators of geological horizons with enhanced permeability, or where the rock fracture gradient has been exceeded. Overpressure was defined as measured pressure exceeding calculated hydrostatic pressure by 3 MPa, which allows for uncertainty in both measured depth and the mud weights.

Step 3: Modelling CO$_2$ properties

Downhole pressure (P) and temperature (T) conditions constructed from the well logs were used to model CO$_2$ properties, including density, viscosity, buoyancy and solubility at depth. The sensitivity of these fluid properties to the calculated P–T conditions were tested at 10 m intervals, for which we assumed a standard error of ± 0.1 MPa and $\pm 5°C$, to 2 SD. Surface temperature and pressure of 15°C and 1 atm, respectively, were assumed.

CO$_2$ density and viscosity was modelled using the Huang *et al.* (1985) and Span & Wagner (1996) equation of state. CO$_2$ solubility was calculated using the equation of Spycher *et al.* (2003) using values for freshwater rather than brines because formation tests in most of the wells show low salinities in the reservoir units. The viscosity of freshwater was calculated using the polynomial equation for variable temperature and pressure from Likhachev (2003). We neglect the effect of dissolved CO$_2$ on the viscosity of water, which is small at these temperatures (Islam & Carlson 2012), and also the effect of subsidiary gases such as CH$_4$ and H$_2$S which can affect CO$_2$ behaviour (Savary *et al.* 2012).

For column heights that could be estimated from the well log, the buoyancy pressure (B) of the CO$_2$ at the crest of the reservoir structure intersected by the well was calculated as:

$$B = (\rho_{H_2O} - \rho_{CO_2}) \, g \, h_{CO_2} \qquad (4)$$

where ρ_{H_2O} is the density of water (kg m^{-3}), ρ_{CO_2} is the density of the CO$_2$ (kg m^{-3}), h_{CO_2} is the CO$_2$ column height (m) and g is gravitational acceleration (m s^{-2}).

Step 4: Classifying the reservoirs

Each CO$_2$-bearing borehole was classified according to whether the corresponding reservoir is interpreted to be leaking CO$_2$ to surface or not, depending on its proximity to CO$_2$ seeps and the nature of the seep itself. Whether the distance between a borehole and a seep is considered to be 'near' or 'far' was determined by spatial analysis of the distance distribution between the boreholes, the CO$_2$ reservoir structure, CO$_2$ seeps and faults. If there are no CO$_2$ seeps located at the surface close to the CO$_2$-bearing borehole, the CO$_2$ reservoir is determined to be sealing. If there are high-flux or dry CO$_2$ seeps located at the surface near to the CO$_2$-bearing borehole, then the reservoir is inferred to be leaking. It is not uncommon for springs emerging from carbonate rocks to contain small quantities of CO$_2$ from the dissolution of carbonates, which is not related to CO$_2$ leakage from depth, and so if the seeps are CO$_2$ springs with small CO$_2$ content, or are located relatively far away from the borehole, then the leakage is classified as inconclusive.

Step 5: CO$_2$ leakage pathways

To evaluate the geological conditions that could enable the observed fluid leak rates from case studies inferred to be leaking CO$_2$ to surface, we examined the Darcy flow equation for CO$_2$ fluids at reservoir conditions. Reservoir fluid leakage into the overburden could occur by distributed migration through the overburden over a broad area (small K_E, large A) or focused migration via fault-related fracturing in the overburden (large K_E, small A). So, we calculate the combinations of overburden effective permeability (K_E) and area (A) necessary to sustain leakage from the reservoir at the observed rate of surface seepage.

Conservative mass transport is assumed: that is, no CO$_2$ attenuation/loss during ascent to surface. For leakage of free-phase CO$_2$, the minimum leak rate from the reservoir (m^3 s^{-1}) to deliver CO$_2$ to the surface at the measured rates (often reported in t/day) was calculated from CO$_2$ densities (ρ_{CO_2}) modelled at P–T conditions in the reservoir. The minimum leak rate of CO$_2$-saturated formation water needed to supply CO$_2$ to the near-surface at the measured CO$_2$ degassing rate was also calculated from the change in solubility of CO$_2$ in freshwater at reservoir conditions to surface conditions. These calculations assume water emergence temperatures of 15°C, and thus CO$_2$ solubility in freshwater is approximately 0.042 molal at 10 m depth.

The results could then be informed by any permeability measurements from rocks that comprise the overburden, and area of CO$_2$ seepage at the

surface. This area can be considered on two scales: the area of a single seep or the total area of a seep cluster (if relevant). It is important to note that the area of leakage in the subsurface could be much larger or smaller. The area of the CO_2 'cap' in the reservoir, and of high-permeability pathways offered by fault-related deformation, was also estimated to inform our results.

Results

Figure 1 shows the location of the 13 studied CO_2-bearing boreholes, neighbouring dry wells and all documented CO_2 seeps. Four additional boreholes in Figure 1 are known to contain CO_2 (Castelpagano 001, Vallauria, San Donato and Perugia 2), but their well logs are not publicly available and so are not studied here. Where two or more wells intercept what may be the same CO_2 reservoir, we refer to a CO_2 field. We classify the case studies into those with overburdens that successfully seal CO_2 (BS1, SAT1, Ben1/2 and Mu1), that leak CO_2 to surface (MF1 and PPS1), or are inconclusive – that is, it is not clear whether or not CO_2 is securely retained in the subsurface (Tr1 and MT1).

This section presents an overview of the broad structure and rock formations in the boreholes, and their relationships before detailing each case study

(including observations from the boreholes, subsurface structure, any nearby geological structures and seeps, and whether the case study is interpreted to be leaking or sealed). Figure 2 shows the lines of cross-sections that describe the subsurface structure in Figures 3–6, and Table 2 summarizes the reservoir and overburden geology, pressure conditions, and proximity to the nearest surface CO_2 seeps for each CO_2-bearing borehole studied.

All but one of the CO_2-bearing boreholes are located in in the Central Apennines, and record CO_2 in anticline or horst structures in the Apulian Carbonate Platform units (Fig. 1c). Many of the well logs note that the Apulian Carbonate Platform units were associated with significant mud losses or loss of circulation, which can indicate a lower than anticipated pressure and/or increased rock permeability (e.g. the presence of a fracture system). A series of thrust-sheet deposits cap the CO_2 reservoirs. These nappes can be Middle Triassic–Miocene basinal flysch units of the Allochthonous Complex (including the basinal carbonates of the Lagonegro Formation or pelagic deposits of the Sannio Formation), or Miocene–Pleistocene-age sediments (turbidites, muds, sandstones and conglomerates). The thrusted contact between the reservoir and overburden is marked by a tectonic breccia or by a Messinian evaporite unit in some boreholes (indicated on the well logs in Figs 3–6). The thrust
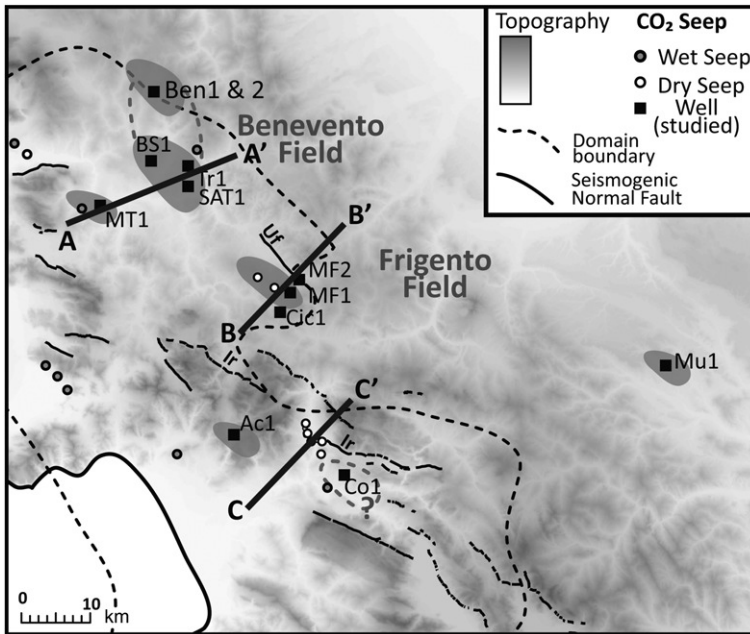

Fig. 2. Map of the Southern Apennine region, showing the location of studied CO_2-bearing wells, CO_2 seeps (shaded according to whether dry (vent, diffuse seeps) or wet (springs, bubbling water), mapped seismogenic normal faults (Roberts 2008) and lines of cross-sections in Figures 3–6.
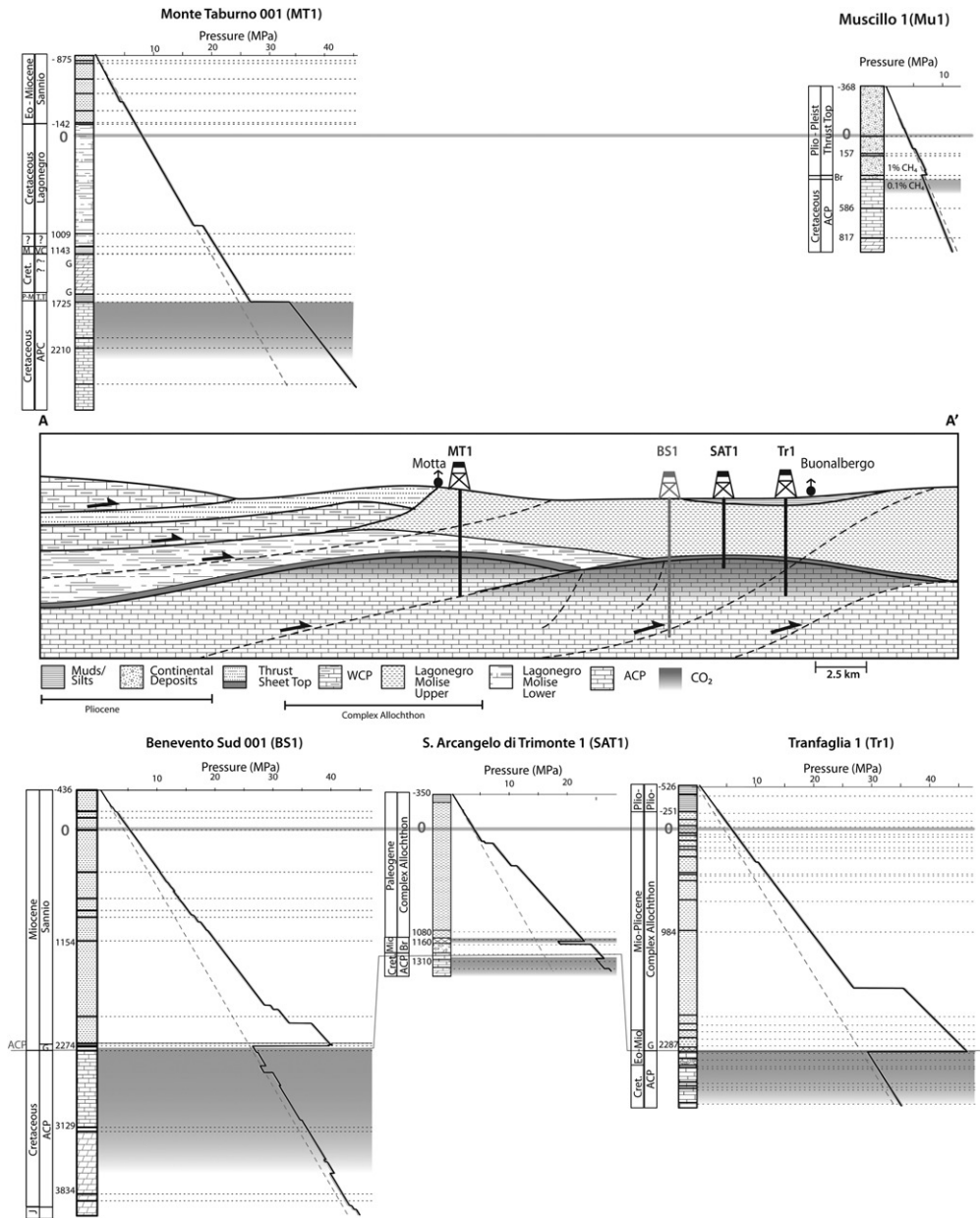
Fig. 3. Benevento and Monte Taburno structures (cross-section A–A′ in Fig. 2) and pressure–depth profiles for the Tranfaglia (Tr1), S. Arcangelo di Trimonte (SAT1), Benevento Sud (BS1), Monte Taburno (MT1) and Muscillo wells. CO$_2$-bearing formations are shaded in the depth profile of the well logs. It is unclear if the Motta and Buonalbergo CO$_2$ springs are related to the subsurface CO$_2$ fields, although they do exhibit significant deep CO$_2$ contributions. BS1, SAT1 and Tr1 show significant overpressure in the overburden. Data are from borehole logs, and from Improta *et al.* (2003*b*), Di Bucci *et al.* (2006), Nicolai & Gambini (2007) and Chiodini *et al.* (2010).

pile is now dissected by extensional structures relating to back-arc extension, including NW–SE- and east–west-trending high-angle faults, which tend to control seismogenesis in central Italy (Patacca *et al.* 2008). In Pieve Santo Stefano 1 (PSS1), CO$_2$ is hosted in the Burano Formation, a thick sequence
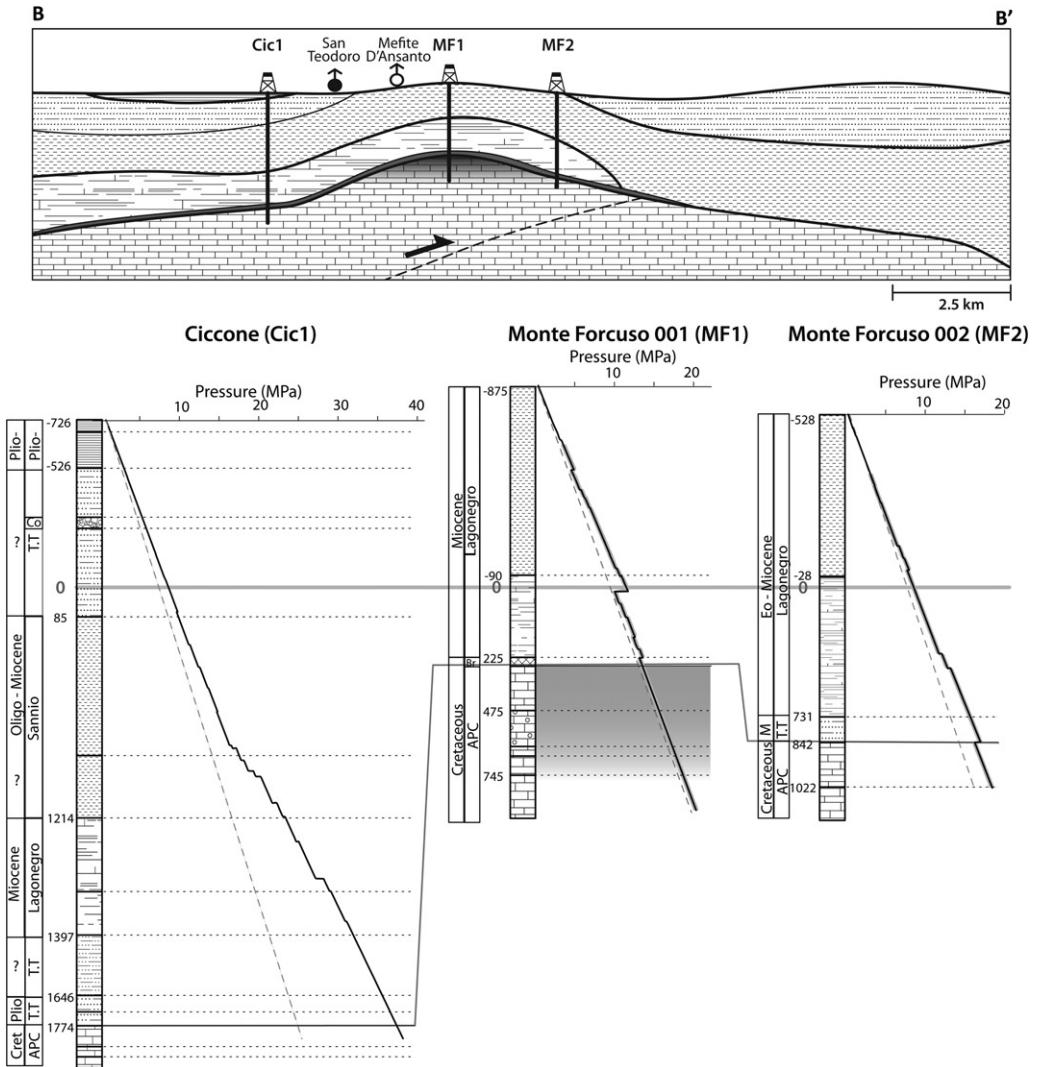
Fig. 4. Subsurface structure (cross-section B–B′ in Fig. 2) and boreholes that penetrate the Frigento Formation (Cic1, Ciccone; MF1, Monte Forcuso 1; MF2, Monte Forcuso 2). MF1 drills a CO_2 accumulation in the ACP at hydrostatic pressure (see the shaded horizon on the depth profile), but MF2 and Cic1 drill into the water leg. Mefite D'Ansanto (and Mefitiniella polla not shown here) are high-flux CO_2 vents. San Teodoro, located on the SW flank of the antiform, is a sulphurous thermal spring that does not degas CO_2. Data are from borehole logs, and from Improta *et al.* (2003*b*) and Di Bucci *et al.* (2006).

of Upper Triassic evaporitic carbonates which the Apulian Carbonate Platform overlies.

Benevento CO_2 field

Three boreholes, Benevento Sud 1 (BS1), San Arcangelo di Trimonte (SAT1) and Tranfaglia (Tr1), penetrate the large Benevento CO_2 field in the Campania region of Italy, as shown in Figure 3.

In BS1, CO_2 is continuously recorded in Apulian Carbonate Platform units from approximately 2707 to 4139 m (1432 m gross CO_2 column), and measurements show up to 98.5% CO_2 by volume, with small quantities of CH_4 (maximum 5.1%). Directly overlying the reservoir are 9 m of Cretaceous anhydrite and gypsum, overlain by 25 m of Messinian mudstone, and then 1 km of Miocene muds and marls. In SAT1, well tests record
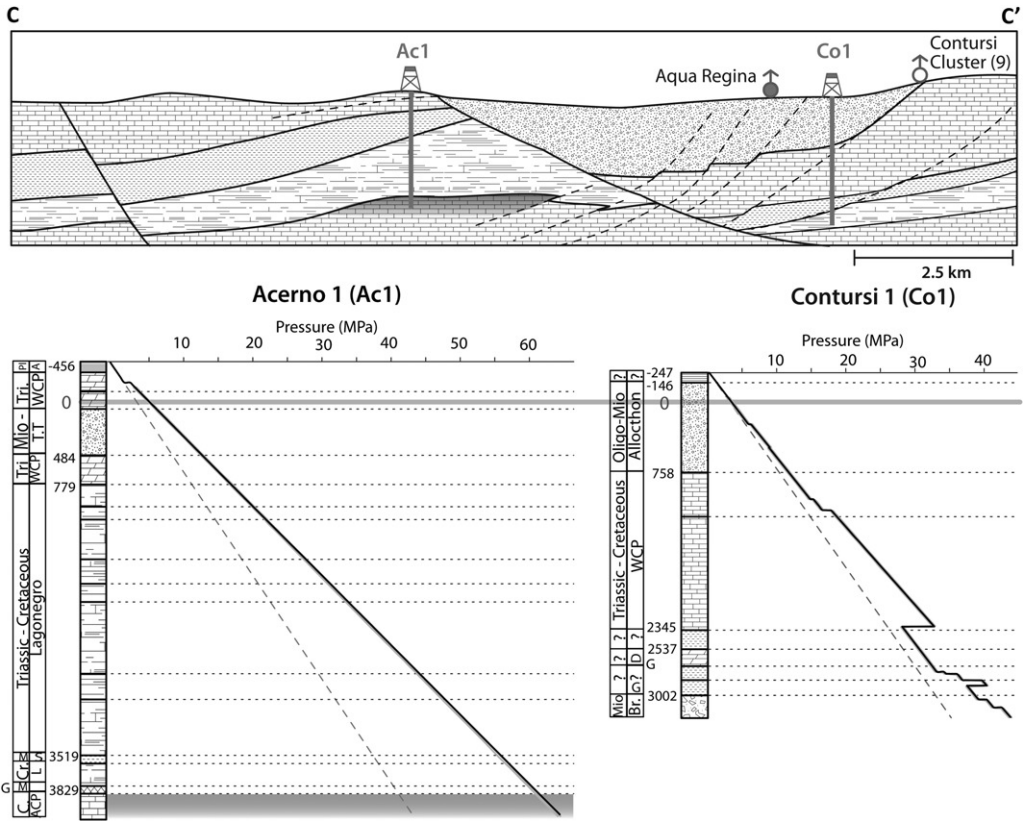
Fig. 5. Subsurface structure of the Acerno and Contursi reservoirs (cross-section C–C′ in Fig. 2) showing the location of the Acerno (Ac1) and Contursi (Co1) wells. Acerno (Ac1) contains CO_2 at 4263 m below surface (see the grey shaded horizon on the well log depth profile). The Contursi borehole (Co1) did not intercept any CO_2 accumulation at depth and so is not considered in our analysis. There are no known seeps above the Acerno horst structure. Data are from borehole logs, and from Improta *et al.* (2003*b*) and Scrocca *et al.* (2005).

CO_2 in the Apulian Carbonate Platform unit (at *c.* 1660 m depth) and also in a shallower, approximately 50 m-thick carbonate breccia, separated from the platform carbonate by approximately 80 m of muddy limestone breccia. It is not clear whether this represents continuous CO_2 from approximately 1520 m depth, or two distinct CO_2 shows.

The TR1 borehole intercepts a reservoir in the Apulian Carbonate Platform units at 2773 m depth containing 98% CO_2. Directly above lies 17 m of massive anhydrite, but there are shows of 2–17% CO_2 above the anhydrite for about a further 200 m and wet gas shows in the overburden all the way to surface. Without detailed geochemical data we cannot determine if the CO_2 documented above the reservoir in Tr1 represents CO_2 migration from the Apulian Carbonate Platform units through the anhydrite overburden, or *in situ* generation associated with the wet gas.

There are no formations in the TR1 borehole that qualify as a good seal; most of the overburden is comprised of siltstone–calcareous units of the Allochthonous Complex. This is in contrast to the SAT1 and BS1 boreholes, where the Allochthonous Complex overlying the CO_2 reservoir is comprised primarily of mudstones. The overburden is overpressured, exceeding 10 MPa in all three boreholes, however, which suggests that the units are low permeability.

The wells that intersect the Benevento field record different fluid pressure in the reservoir; BS1 and Tr1 show hydrostatic reservoir pressure, whereas in SAT1 the CO_2 is overpressured. As a result, the modelled CO_2 at reservoir conditions are different, finding that CO_2 is retained in the dense (BS1) and the light (Tr1) phase, and or close to the phase transition (SAT1). These differences in pressure and CO_2 properties may indicate compartmentalization of the reservoir.
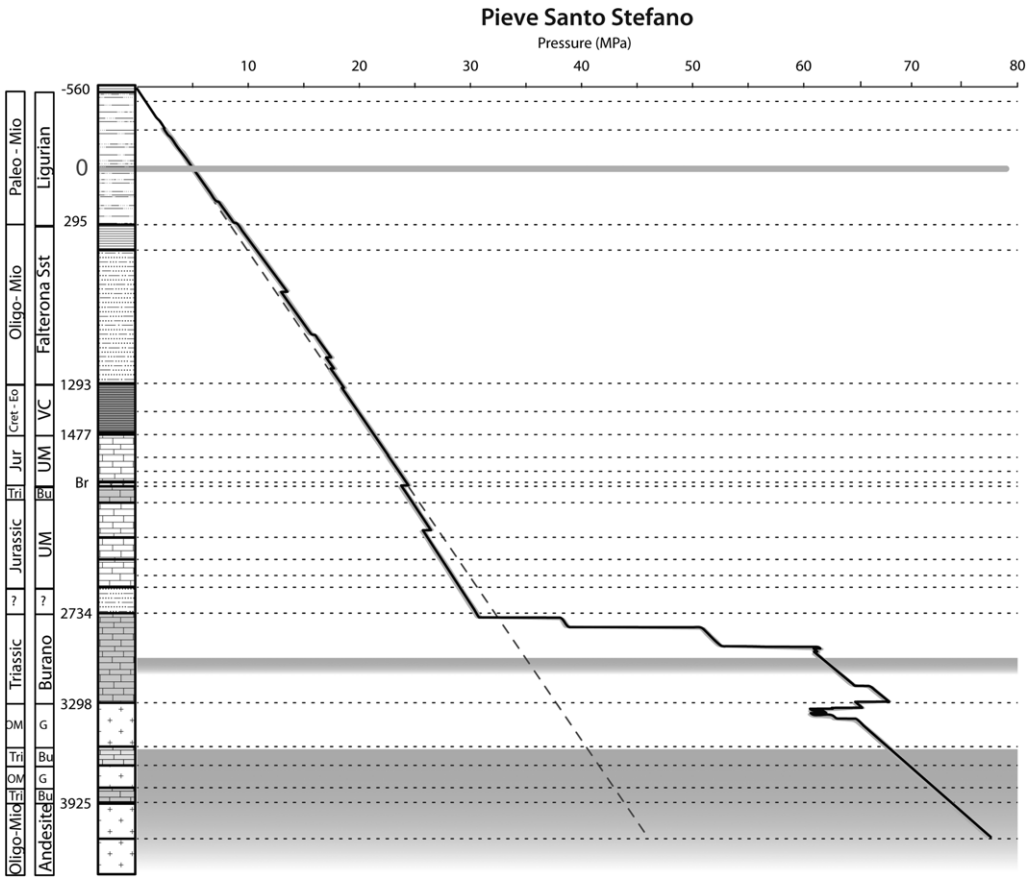
Fig. 6. Depth and pressure profile of the Pieve Santo Stefano borehole. This borehole is located in Tuscany, in the Northern Apennines (see Fig. 1). The multilayered CO_2 reservoir (shaded in grey in the well log) is hosted in thin dolomite layers (sandwiched between anhydrite layers) of the Burano Formation. The CO_2 is significantly above hydrostatic pressure conditions. The Caprese Michelangeo and Fungaia CO_2 vents are located near to the Pieve Santo Stefano well and are considered to represent surface seepage of the reservoir. Data are from borehole logs, and from Heinicke *et al.* (2006) and Bonini (2009*a*).

The Buonalbergo CO_2 seep is located 3.5 km from TR1, 5.3 km from SAT1 and 10.3 km from BS1. No further information, such as quantities of degassed CO_2, is available about this seep other that it is a CO_2 spring (Chiodini & Valenza 2008). Its visual appearance is unremarkable, suggesting that gas flux is not particularly high. The CO_2 dissolved in the spring could source from the Benevento CO_2 field or CO_2 in shallower formations (like those in Tr1 which show small quantities of CO_2 and hydrocarbons that could break down to CO_2). Otherwise it could source from carbonate rock dissolution (karstification), which is common where carbonate rocks form the shallow subsurface. Given the absence of a convincing seal in the Tr1 overburden and the presence of the Buonalbergo

spring nearby, it is inconclusive whether the CO_2 documented in the Tr1 borehole is leaking to surface. The CO_2 reservoirs intercepted by BS1 and SAT1 are considered sealed.

To the north of these wells, the Benevento boreholes (Ben1 and Ben2) also encountered CO_2 at approximately 3 km depth. These boreholes drilled a broad structural high (see Fig. 1c), and were also found to contain some short-chain hydrocarbons (maximum of 6.2% CH_4 by volume) at approximately 3300 m (Ben2). These wells show significant overpressure in the overburden, which is comprised of several muddy units, but the reservoirs are hydrostatically pressured. There are no CO_2 seeps in the vicinity of these boreholes, so the reservoir is considered to be sealing.

Table 2. *A summary of the reservoir and overburden characteristics for each CO_2-bearing borehole, including the properties of the CO_2, the presence of nearby seeps or faults and whether the reservoir is interpreted to be sealed or leaking CO_2 to surface*

Field/ Reservoir	Borehole name; abbreviation	Reservoir conditions				CO_2 properties		Overburden conditions			Distance from borehole to:		Interpretation
		Depth below surface (m)	CO_2 (%v.v)	Over-pressure	Porefluid factor	Density (kg m^{-3}) (phase)	Buoyancy (MPa)	Evaporite (thickness)	Seal thickness (m; min – max)	Overpressure (ratio compared to hydrostatic)	Seep name (no. in Fig. 1); distance (km)	Fault distance (km) (name, sense)	
	Benevento Sud 1; BS1	2710	98.5	N	0.4	624 ± 15 (dense – SC)	5	Y (9 m)	315–2710	Y (1.56)	None	5 (S. Matese, N); 15.7 (Telese Fault, N)	Sealing
Benevento Sud	S. Arcangelo di Trimonte; SAT1	1520	–	Y	0.6	503 ± 11 (dense – SC)	–	N	1520–1520	Y (1.62)	None	4.8 (S. Matese, N); 23.2 (Telese Fault, N)	Sealing
	Tranfaglia; Tr1	2773	98	N	0.4	279 ± 6 (light – SC)	–	Y (17 m)	None	Y (1.67)	Buonalbergo (1); 3.5	7 (S. Matese, N); 20 (Ufita Fault, N)	Inconclusive
	Benevento 002; Ben2	3300	94	N	0.6	797 ± 9 (dense – SC)	1.8	N	30–600	Y (1.68)	None	12.7 (Boiano, N); 22 (Telese Fault, N)	Sealing
Monte Taburno	Monte Taburno 1; MT1	2093	>90	Y	0.5	569 ± 10 (dense – SC)	1.1	Y (2 m)	543–890	N (1.08)	Motta (2); 1.6	8 (Montesarchio, N)	Inconclusive
Muscillo	Muscillo; Mu1	694	97 (low sat)	N	0.4	139 ± 19 (light – gas)	2.2	N	305–305	N (1.09)	None	>40 km	Sealing
Frigento	Monte Forcuso 1; MF1	1128	99.7	N	0.4	200 ± 5 (light – SC)	3.5	N	168–1128	N (1.21)	Mefiteniella polla (4); 5.4 Mefite D'Ansanto (5); 1.8	4.3 (Ufita, N)	Leaking
Acerno	Acerno 1; Ac1	4263	97	Y	0.6	919 ± 8 (dense – SC)	–	Y (80 m)	70–228	Y (1.48)	San Benedetto (6); 11 Contursi cluster (7); 15.5	2.6 (Sabato Valley; N); 11.5 (Volturata, N)	Sealing
Caprese	Pieve Santo Stefano 1; PSS1	3600	92.2	Y	0.7	830 ± 8 (dense – SC)	1.1	Y (70 m)	150–550	N (1.08)	C. Michelangelo (9); 2.5 Fungaia (10); 3.6	7.9 (Upper Tiber Valley, N)	Leaking

If reservoir or overburden formation fluid pressures are 3 MPa above hydrostatic, then it is considered to be overpressured. For CO_2 density, 'dense' refers to CO_2 with densities greater than the critical density ($\rho_c = 464$ kg m^{-1}) and 'light' refers to CO_2 with densities below the critical density, and SC refers to the supercritical phase. Where column heights are not known, the buoyancy pressure, B, cannot be calculated. Further detail about the seeps (number, type, flux, temperature) are tabulated in Figure 1b. Modelled conditions in SAT1 are unreliable (see the main text for details).

There are two recently active SW-dipping normal fault systems near to these boreholes (BS1, SAT1, TR1 and Ben1/2). The Southern Matese Fault (less than 10 km from the boreholes) is a NW–SE-trending complex of faults that has been historically seismogenic (Di Bucci *et al.* 2006; ISPRA 2007). The Telese fault scarp, a north-dipping topographical break in slope, is between 16 and 22 km away from the boreholes (Roberts 2008). Previous earthquake sequences to the east show that extension is largely NW–SE (Milano *et al.* 2006).

Monte Taburno CO_2 reservoir

To the east of the Benevento CO_2 field, the Monte Taburno 1 (MT1) borehole cuts a separate structure containing >90% CO_2 at 2 km depth (Fig. 4). CO_2 is mostly found in the Apulian Carbonate Platform but also in the overlying thin layer of muddy Mio-Pliocene thrust-top deposits. This is capped by 511 m of dolomitic limestone, the bottommost 2 m of which (i.e. capping the reservoir) is anhydrite-bearing, and then by over 1 km of low-permeability muds and sands of the Lagonegro and Sannio formations of the Allochthonous Complex. Overburden pressures are hydrostatic, but the CO_2 reservoir shows approximately 9 MPa over-pressure and under these conditions the CO_2 will be contained in its supercritical state. MT1 is 10 km from the Telese Fault, and 7 km from the SW-dipping Montesarchio and Ioannis seismogenic normal faults (Roberts 2008). The Motta thermal spring is 1.6 km away and has a small CO_2 emission (Chiodini & Valenza 2008), but no further information is available. Similar to the Buonalbergo spring near the Benevento field, there are several possible sources of CO_2 in a small spring that do not necessitate a subsurface CO_2 reservoir. Given the proximity of MT1 to the Motta thermal CO_2 spring, it is inconclusive whether the Monte Taburno reservoir is leaking to surface.

Muscillo $CO_2–CH_4$ reservoir

The Muscillo 1 (Mu1) borehole, located in the Basilicata region, penetrated a shallow accumulation of $CO_2–CH_4$ in the Apulian Platform Carbonate (Fig. 3). A CH_4 leg overlies a gas-phase CO_2 leg at 694 m below the surface, and both are low saturation. The reservoir top is marked by a thin breccia. The overburden is comprised of claystone and siltstone terrigenous deposits. In the outer thrust domain where the borehole is located, these sediments tend to represent rapid filling of structural depressions related to the development of extensional tectonics. Down-well pressures are hydrostatic and there are no CO_2 seeps in the vicinity of

this well. No other subsurface information is available and so its structure is poorly constrained. The nearest faults are over 40 km from the well. We classify the Muscillo reservoir as sealing, although we note that low CO_2 saturation could indicate residual trapping of leaked CO_2.

Frigento CO_2 reservoir

Three boreholes penetrate the Frigento Antiform, located in a region of Campania: Monte Forcuso 001 (MF1), Monte Forcuso 002 (MF2) and Ciccone (Cic1) (Fig. 4). This structure in the Apulian Carbonate Platform correlates with a gravity and thermal anomaly (Improta *et al.* 2003*a*) (Fig. 1c). The geothermal gradient here reaches over $90°C$ km^{-1} at the crest of the anticline (Chiodini *et al.* 2010). The MF1 borehole is the only one to encounter CO_2. It intercepts an approximately 472 m gross CO_2 column in the Apulian Carbonate Platform at just over 1 km depth, above a freshwater leg. The absence of CO_2 in neighbouring boreholes constrains the extent of the CO_2 cap (<2 km radius). The overburden is mostly comprised of muds and marls of the Allochthonous Complex's Lagonegro Formation, and also brecciated and cemented sandstone. The overburden and the reservoir are at, or close to, hydrostatic pressure. The MF2 and Cic1 boreholes, located on the flanks of the anticline, do not contain free-phase CO_2, only freshwater and saline water, respectively. The differences in formation salinity and pressure in these boreholes may indicate compartmentalization of the reservoir.

The regional stress field (Barba *et al.* 2009) shows NW–SE extensional faulting which is currently active; the 1980 Irpinia earthquake (M 6.9) nucleated on the NE-dipping Irpinia Fault 32–35 km to the south of the reservoir. The SW-dipping Ufito normal fault scarp is located less than 1 km to the NE of the MF2 borehole, and 4.3 km from MF1 (Fig. 2) (Improta *et al.* 2003*b*; Roberts 2008). This is thought to be a splay from the Irpinia Fault (Brozzetti 2011), and thus the Frigento Antiform is located in the hanging wall of both faults.

Mefite D'Ansanto and Mefitiniella Polla CO_2 vents (seep nos 4 and 5 in Fig. 1c) are located above the structural high point of the NW–SE-trending Frigento Antiform (see Fig. 4). Mefite D'Ansanto emits more CO_2 than any other seep in Italy, releasing approximately 2000 t CO_2/day by venting and diffuse degassing over an area of 4000 m^2 (Chiodini *et al.* 2010). Mefitiniella Polla is a smaller CO_2 vent located 3.6 km NW from Mefite D'Ansanto and, although the seep rate has not been measured, field observations find that it vents CO_2 vigorously. On the flanks of the Frigento Antiform, less than 3 km ENE from Mefite, are the San Teodoro thermal springs. These springs do not

release CO_2, but their emergence temperatures (c. $15-27°C$, similar to the Mefite seeps) and geochemistry (Minissale 2004) indicate rapid fluid ascent of waters that have circulated in deep carbonate rocks, probably via fault-related flow paths (Duchi et al. 1995). Travertine deposits have been mapped within 5 km of the seeps (Roberts 2013) but these are no longer active, and there have been no geochemical investigations regarding their age or source.

Although there is currently insufficient geochemical information to irrefutably link the subsurface reservoir with the Mefite CO_2 seeps, or nearby thermal springs, it is reasonable to consider that the CO_2 released at the Mefite seeps could originate from the CO_2 reservoir located in the underlying anticline (Chiodini et al. 2010; Pischiutta et al. 2013). We therefore classify the Frigento CO_2 reservoir as leaking.

Acerno CO₂ reservoir

The Acerno 1 borehole (Ac1) penetrates the deepest studied CO_2 reservoir, located in a horst structure in the Apulian Carbonate Platform, 4363 m beneath Mount Picentini (Fig. 5), Campania region. The reservoir is overlain by a 305 m-thick evaporite and mud seal, then interlayered nappes of the Allochthonous Complex, basement carbonates and muds of the thrust-top deposits. Both the overburden and the reservoir are overpressured, with a pore fluid factor of 0.6 in the reservoir. Multiple mud losses were experienced when the well penetrated the Apulian Carbonate Platform, which suggests that the mud densities were too high for the reservoir properties (e.g. pressure or presence of pervasive fracture system); however, the mud densities were not adjusted. The borehole was plugged after drilling 300 m into the Apulian Carbonate Platform. The single drill stem test in this borehole yielded over 90% CO_2, which we model to be in the dense phase at reservoir conditions. The borehole is in the footwall of the east-dipping Sabato normal fault, which is considered to be seismogenic (ITHACA), and 11.5 km from the Volturara fault scarp (Roberts 2008). There are no CO_2 seeps located above the Acerno structure, but 11 km to the ENE is the San Benedetto CO_2 spring, which releases $10-100$ t CO_2/day (Chiodini & Valenza 2008), and 15 km to the NW is the Contursi seep cluster (Fig. 1c, No. 6). The Acerno reservoir is classified as inconclusive.

Caprese CO₂ reservoir

The Pieve Santo Stefano 1 (PSS1) borehole, located in Tuscany, commercially exploits a multilayered CO_2 reservoir at approximately 3.6 km depth in the Caprese Antiform (Bicocchi et al. 2013) (Fig. 6). The main CO_2 reservoir is hosted within dolomites and evaporites of the Triassic Burano Group (Bonini 2009b) where thin reservoirs of fractured dolostone (porosity $2-6\%$) with high pore fluid pressures are sandwiched between sealing anhydrite layers (Trippetta et al. 2013). The CO_2 cap in the Caprese Antiform is likely to be elliptical in shape, with a maximum radius as great as 5 km (Bicocchi et al. 2013).

The reservoir brines are highly saline due to the interaction of meteoric waters with the evaporites (Bicocchi et al. 2013). Logging notes record significant mud losses while drilling through the overburden, which is multilayered and approximately hydrostatically pressured. Beside the anhydrites of the Burano Group, there are few low-permeability units in the cap rock that would offer a convincing very-low-permeability seal, although, in general, the Ligurian units that comprise the overburden are considered to be low permeability (Bicocchi et al. 2013).

The region around the Caprese Antiform is associated with CO_2 reservoirs and seeps. For example, approximately 40 km to the SE of PSS1, the San Donato and Perugia 2 boreholes penetrate the Monte Malbe structure (an anticline bounded by two active normal faults) and find pressurized CO_2 fluids in the Burano Group (Trippetta et al. 2013). Indeed, NE-trending, steep-dipping faults in the region form part of a regional transverse lineament known as the Arbia–Val Marecchia Line (AVML) which has been associated with CO_2 seepage (Bicocchi et al. 2013). More locally, the seismogenic Alto-Tiberina Fault is approximately 8 km SE of the PSS1 borehole and bounds the west side of the Quaternary Upper Tiber Basin (Collettini & Barchi 2004; Heinicke et al. 2006; ISPRA 2007).

The Caprese Michelangelo seeps and the Fungaia seeps are within 4 km of the PSS1 well. Caprese Michelangelo is a cluster of at least four seeps in an area of $400 m^2$. The style of seeping is varied; there are CO_2 vents, bubbling water and diffuse degassing (seep No. 1 in Fig. 1c). The gas emission rate of two seeps has been measured: one seep in the Caprese cluster classifies as medium ($1-10$ t/day) and a seep in the Fungaia cluster classifies as high ($10-100$ t/day) (Chiodini & Valenza 2008). Here, we refer to the Caprese Michelangelo and Fungaia seeps collectively as the Caprese seeps. The rate and characteristics of these seeps (such as water content and area) are observed to vary with rainfall and following seismic events on the Alto-Tiberina Fault (Heinicke et al. 2006; Bonini 2009b).

CO_2 fluids from the PSS1 wellhead, the Caprese seeps and fluid inclusions from the PSS1 cores have a common origin (Bonini 2009b; Bicocchi et al.

2013; Trippetta *et al.* 2013). The seeps are aligned along NE−SW-trending faults that may connect to the deep CO_2 reservoir (Bonini 2009*b*; Bicocchi *et al.* 2013). On the basis of this information, we interpret that the Caprese CO_2 seeps source from the deep reservoir in the Caprese Antiform, and so this is classified as leaking.

Analysis: comparing the characteristics of leaking and sealing reservoirs

Four of the studied CO_2-bearing boreholes (PSS1, MF1 and Tr1, MT1) are located within 3 km laterally of documented surface CO_2 seeps. We interpret that two reservoirs are leaking: the Caprese (intercepted by the PSS1 borehole) and the Frigento (intercepted by MF1 borehole). Both reservoirs are hosted in antiform structures, and a number of CO_2 gas seeps with high rates of degassing are located within 3.5 km of the boreholes. In contrast, for Tr1 and MT1, very little is known about the small CO_2 springs located within 3.5 km of the boreholes, and so it is inconclusive whether the CO_2 in these reservoirs is leaking to surface. There are no seeps located within at least 10 km of the remaining boreholes (BS1, SAT1, Ben1/2 and Mu1) and so these are sealed.

Properties of the CO_2

Pressure, CO_2 density and, where possible, calculated CO_2 buoyancy pressure at the reservoir tops is shown in Figure 7. Most of the studied reservoirs contain CO_2 in the dense phase; MF1 and TR1 contain light-phase CO_2, and Mu1 is the only well to contain gaseous CO_2. No reservoirs contain liquid-phase CO_2. The physical properties of the CO_2 (phase or buoyancy) do not appear to be a first-order control on whether a CO_2 reservoir is leaking or sealed.

The sealed Benevento Sud reservoir has a higher estimated CO_2 buoyancy pressure at the reservoir− cap rock interface (5.0 MPa) than the seeping Monte Forcuso reservoir (3.5 MPa). The CO_2 column heights for SAT1 and Tr1 are unknown. If we assume the same CO_2−water contact in all three wells, the CO_2 buoyancy in SAT1 and Tr1 will be even higher than in BS1 because CO_2 is less dense. Despite this, unlike the Frigento Formation, the Benevento reservoirs are not obviously leaking. The Muscillo reservoir is the opposite; the net buoyancy pressure on the seal is effectively zero at the present day because gas saturation is so low. In this reservoir, CO_2 will also have extremely low relative permeability which will restrict its mobility.

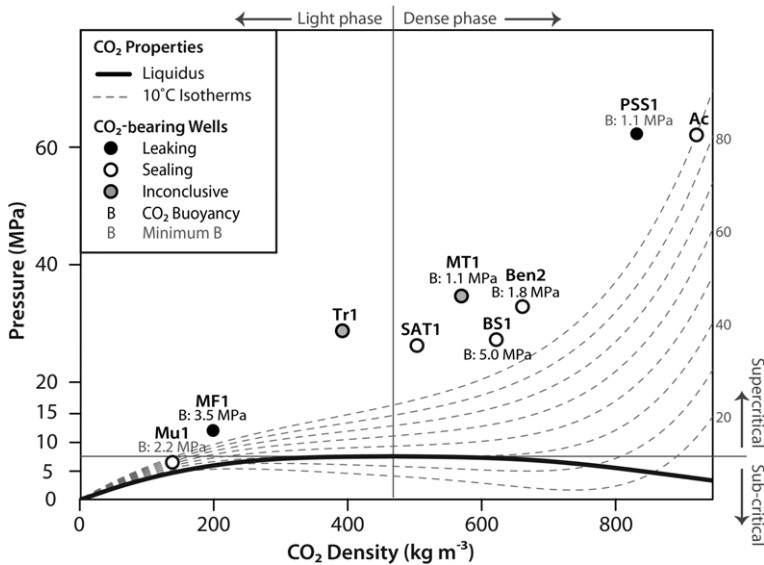CO_2 solubility in freshwater at reservoir conditions is typically between 1 and 1.5 molar

Fig. 7. CO_2 pressure−density phase diagram at the reservoir−seal boundary of CO_2-bearing reservoirs. Calculated CO_2 buoyancy is shown next to the data points where information is available. Critical density and critical pressure are shown as thin grey lines (and annotated). Only one reservoir, Mu1, contains CO_2 in the gas phase, all other case studies contain supercritical CO_2 in both the dense and light phase. Neither CO_2 density nor buoyancy determines whether a reservoir is sealing in these case studies.

($c.\ 40 - 60\,\mathrm{kg_{CO_2}\ m^{-3}_{(H_2O)}}$) for all case studies. The formation waters in these reservoirs therefore have potential to dissolve significant quantities of CO_2, and have a greater solubility capacity than surface waters.

In most of the case studies, a CO_2 leg overlies a water leg in the reservoir, and CO_2 saturation in the cap is high. The exceptions are PSS1, where the reservoir is complex and CO_2 (in high saturation) is trapped within more permeable layers between evaporite layers and Mu1, where CO_2 saturation in the reservoir is low. Further, a unit overlying the primary CO_2 reservoir in Tr1 also has low CO_2 saturation. Low CO_2 saturation could result from several mechanisms. If the reservoir's seal has been breached, low CO_2 saturation confirms that the reservoir is leaking or has leaked in the past. If the cap rock is acting as a good seal but CO_2 saturation is low, then this could indicate that there was insufficient CO_2 charge to fill the reservoir. *In situ* generation of CO_2 may result in low saturation if the quantities of CO_2 generated are small. Similarly, CO_2 coming out of solution from formation waters as they depressurize during ascent may result in low CO_2 saturation. In the absence of further geochemical information on the CO_2 and formation waters, it is not possible to distinguish these scenarios.

Other gases which may affect the properties of the CO_2 mixture are present in small quantities in many of the CO_2 reservoirs, including short-chain hydrocarbons, such as CH_4, and H_2S. Small proportions of H_2S decrease the interfacial tension of CO_2 (Bennion & Bachu 2008; Savary *et al.* 2012), whereas CH_4 increases interfacial tension and decreases the fluid density (Naylor *et al.* 2011). Since only trace amounts (0.1% C v/v) of H_2S are recorded in some boreholes, its effects on CO_2 properties are likely to be negligible. In contrast, sealing reservoirs Ben2, BS1 and Mu1 contain over 5% CH_4 (% C v/v), and so the buoyancy of the CO_2–CH_4 mixture in these reservoirs will be greater than for pure CO_2. However, the effect of CH_4 on the interfacial tension will be more significant than the effect on the buoyancy (Naylor *et al.* 2011). As a result, relatively small quantities of CH_4 may be enhancing reservoir sealing at the Benevento reservoirs.

Properties of the CO_2 reservoir

The geological structures of all the reservoirs are broadly similar: CO_2 has accumulated in platform carbonate units, and the overburden is comprised of thick, heterogenous nappes. This is similar to hydrocarbon discoveries in central-southern Italy, many of which are hosted in fractured Apulian Carbonate Platform (Casero 2005). Whether the reservoir is hosted in an anticline or horst does not affect whether it leaks or seals.

The leaking Caprese and Frigento reservoirs are both hosted in thrust-related anticlines located in Quaternary graben structures. However, the depth of the reservoirs is very different (see Table 2), and so confining pressure is not a primary control on the seal quality. The Caprese reservoir is deep and pressured beyond hydrostatic; in this reservoir, CO_2 is in its dense phase. The Frigento reservoir is much shallower, hydrostatically pressured, and so CO_2 is in its light phase. The two reservoirs have similar temperatures, since the shallower Frigento formation is located in a region with an anomalously high geothermal gradient.

In three boreholes (Ben1/2, BS1 and Tr1) the reservoir carbonate units are close to hydrostatically pressured, in contrast with the significantly overpressured overburden. These reservoirs must be hydrologically connected to the surface; either by permeable faults or through surface outcrop. Examples of hydrocarbon reservoirs at hydrostatic fluid pressures overlain with high-pressure cap rock are common in overpressured basins (O'Connor *et al.* 2008). Isolated reservoir units will be in pressure equilibrium with the encasing low-permeability units (such as shales). However, if reservoirs are connected to surface via lateral outcrop or fracture/fault networks, fluids can escape and drain the overpressure in the reservoir, bypassing any buoyant fluids trapped in the overlying formation. The overburden can remain overpressured even though fluids may slowly bleed into adjacent lower-pressure reservoirs. In contrast, the Caprese and Monte Taburno structures contain overpressured reservoir fluids with a close to hydrostatically pressured overburden. This is often indicative of reservoir compartmentalization, which Trippetta *et al.* (2013) interpreted for the complex and multilayered Caprese structure.

The CO_2 contained in PSS1, MT1, Ac1 and SAT1 is overpressured. High fluid pressures can enhance or retard seal integrity, depending on the mechanism of seal failure. CO_2 density increases with reservoir pressure, which in turn decreases CO_2 buoyancy. CO_2 overpressure therefore reduces the likelihood of capillary seal failure. Indeed, reservoir overpressure in the leaking Caprese structure decreases CO_2 buoyancy by approximately 0.3 MPa compared to hydrostatic conditions. However, significant fluid overpressure can lead to seal failure by fluid-driven fracture propagation. For example, in the case of PSS1, Ac1 and SAT1, the reservoir pore fluid pressures are over 60% of lithostatic. These fluid pressures could jeopardize the integrity of the seal, particularly if the seal contains pre-existing fractures that are critically stressed. However, since only the Caprese reservoir leaks

CO_2, reservoir fluid pressure alone cannot control reservoir leakage. Regardless of the degree of overpressure in the reservoir, overpressure in the seal and in the overburden above the seal can act as a significant barrier as it increases the pressure required to drive CO_2 upwards and through the seal and overburden.

Properties of the overburden

Although the geological structure of all the cases studied is broadly similar, the overburden is variable in both rock type and thickness. Figure 8 shows the seal thickness, defined as the total thickness of units documented from drill cuttings that would be likely to be impermeable to CO_2.

There is no correlation between reservoir depth (overburden thickness) or seal quality/thickness and the presence of surface CO_2 seeps. Some well logs record thick low-permeability sequences in the overburden: for example, in SAT1, there are 1520 m of muds overlying the reservoir all the way to surface, and overlying the BS1 reservoir there are muds that, although becoming a little siltier towards the surface, remain low permeability. In contrast, TR1 records 17 m of massive anhydrite directly overlying the reservoir but no definable seal above this; the overlying (calcareous) siltstone records low-saturation CO_2 (for *c.* 200 m above the anhydrite) and wet natural gas all the way to surface. Similarly, PSS1 records 70 m of gypsum above the CO_2 reservoir overlain by sandy-marls

(*c.* 160 m), but no other low-permeability formations above this.

The thrusted contact between reservoir and overburden is marked by a tectonic breccia in three boreholes (SAT1, MF1, Mu1), whereas Messinian anhydrite-bearing units (massive, or associated with muds) directly overlie the CO_2 reservoir in other boreholes (BS1, Tr1, Ac and MT1; see Table 2). Such low-permeability units may contribute to the sealing capability of the overburden at the sites. However, the Burano Triassic Evaporite Formation forms the reservoir–seal complex of the leaking Caprese reservoir. Thus, while evaporites often make a very effective seal, their presence or absence is not the only factor in determining overburden integrity.

The relationship between CO_2 seepage and overburden overpressure is summarized in Figure 9. CO_2 reservoirs that lack strong overpressure in overburden units (maximum pressure/hydrostatic pressure <1.3) are associated with surface seeps (boreholes MF1 and PSS1). In contrast, where the overburden shows significant overpressure (maximum pressure/hydrostatic pressure >1.3) there are no surface seeps within 10 km of the borehole (Ben2, BS1 and SAT1). The remaining boreholes are inconclusive (Ac1, Mu, Tr1 and MT1). The pressure conditions in the overburden seem to be a primary control on successful CO_2 retention.

Figure 10 shows the relationship between the fluid pressures in the overburden and the lateral distance from the wellbore to active normal faults
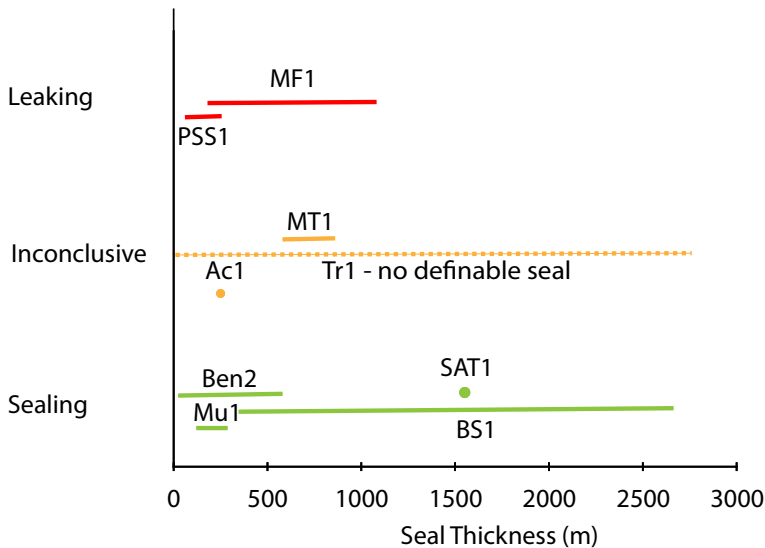

Fig. 8. Thickness of impermeable rock formations in the overburden, as interpreted from the well logs of CO_2 reservoirs, and the leaking–sealing classification of the reservoir. The thickness of low-permeability formations does not control whether or not the reservoir leaks CO_2 to surface.
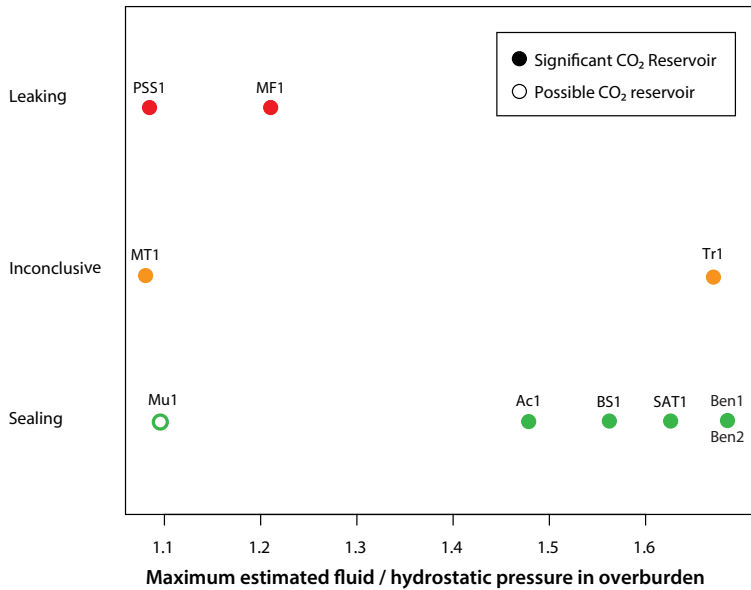
Fig. 9. Fluid overpressure in the overburden of studied CO$_2$ reservoirs and the interpretation of whether or not the reservoir is leaking CO$_2$ to surface. The degree of overpressure is indicated by the ratio of fluid pressure (P_f) to hydrostatic pressure as interpreted from the density of the drilling mud in the well log. The data points are coloured according to whether the reservoir is interpreted to be leaking (red), sealing (green) or is inconclusive (orange). CO$_2$ reservoirs with fluid overpressure (>3 MPa) in the overburden do not have CO$_2$ seeps located within at least 10 km of the borehole and so are considered to be sealing reservoirs (green). In contrast, deep CO$_2$ reservoirs that have little or no overpressure in the overburden are located close to CO$_2$ seeps (red). The shallow Mu1 reservoir shows low CO$_2$ saturation; hence, this is why it is not considered to be a significant CO$_2$ reservoir.

(faults with exposed scarps that are considered to pose a seismic hazard). The boreholes that penetrate the two leaking CO$_2$ reservoirs are located within 5–7 km of the surface trace of seismogenic normal faults. These boreholes record no overpressure in the overburden. Reservoirs located further from these faults show overpressure in the overburden rock units.

The exception to this trend is borehole Mu1, which is over 40 km from any known recent faults, and yet shows only minor deviations from hydrostatic pressure. However, this reservoir is at a relatively shallow burial depth compared to the other study sites (c. 700 m), and the overburden consists of sands, silts, clays and conglomerates which may be permeable even if not breached by faulting.

Analysis: characteristics of leakage and implications for risk management

As described in the sections above, the Frigento and Caprese antiforms are considered to be leaking. Both structures have a cluster of CO$_2$ seeps at the surface above the reservoir, and both have hydrostatically pressured overburden. However, in many respects,

they are end-member case studies; the Frigento Antiform is one of the shallowest CO$_2$ reservoirs and has an anomalously high geothermal gradient, whereas the Caprese formation is the deepest CO$_2$-bearing structure in a region with relatively low geothermal gradient. The downhole conditions in the wells that penetrate these structures are therefore very different (as can be seen in Table 2). This has implications for the area-permeability criteria to leak a given mass of free-phase CO$_2$ from the reservoir. For example, for the same mass of CO$_2$ to leak from the reservoir, the volume of free-phase CO$_2$ that must leave the Caprese reservoir ($\rho_{CO_2} = 830$ kg m^{-3}) is a quarter of the volume that must leave from the Frigento reservoir ($\rho_{CO_2} = 200$ kg m^{-3}). As such, small volumes of free-phase CO$_2$ escaping from the Caprese structure would mean relatively high rates of CO$_2$ leakage. For both structures, much greater volumes of CO$_2$-saturated water must leak from the reservoir than free-phase CO$_2$; six times the volume of free-phase CO$_2$ for the Frigento Formation and up to 10 times for the Caprese Formation. Thus, larger permeabilities are needed for CO$_2$-saturated waters to transport the same rate of CO$_2$, unless the relative permeability to water is at least an order of magnitude higher for free-phase CO$_2$.
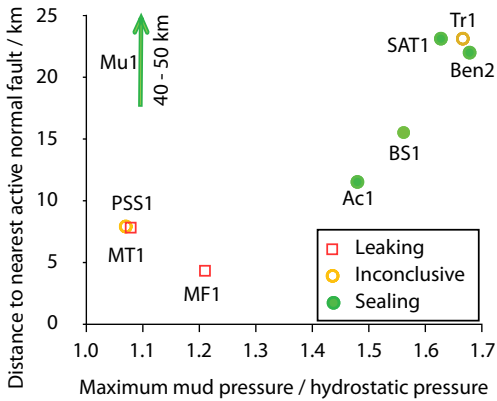
Fig. 10. Fluid overpressure in the overburden of studied CO_2 reservoirs and the lateral distance of the well to the nearest modern extensional fault structure. CO_2 structures that are located within 8 km of a fault leak CO_2 to surface. The degree of overpressure is indicated by the ratio of fluid pressure (P_f) to hydrostatic pressure as interpreted from the density of the drilling mud in the well log. Wells are coloured according to whether the reservoir is leaking CO_2 to surface (red) or not (green) or indeterminately so (orange). Overburden overpressure correlates with distance to the modern extensional faults mapped by Roberts (2008). CO_2 reservoirs that are classified as leaking (i.e. are located within 5 km of CO_2 seeps) show hydrostatic pressures in overburden formations, and are located within 8 km of a modern extensional fault. Mu1 does not fit this trend, possibly because it is so shallow; it is located over 40 km away from any mapped structures and so cannot fit on these axes.

Pathways of CO_2 leakage

CO_2 leakage from a reservoir could, in theory, occur over a large area (distributed flow through a large rock volume) or over a smaller area (focused by enhanced-permeability pathways such as those offered by faults, whether the fracture network is localized or more distributed). We use the Darcy flow (equation 1) to approximate flow through the rock volume and fracture networks in order to examine the area and permeability requirements to permit CO_2 leakage from the Caprese and Frigento reservoirs into the overburden (not through the overburden to surface). Figure 11 shows the combinations of overburden effective permeability (K_E) and area (A) for leaking free-phase or dissolved CO_2 at 100 and 2000 t CO_2/day from the Caprese and Frigento antiforms, respectively. These leak rates correspond to the maximum estimated CO_2 release rate at the Fungaia and Mefite D'Ansanto seeps, since there are no published estimates for CO_2 release from all the seeps in the Caprese and Mefite seep clusters. The permeability of formations
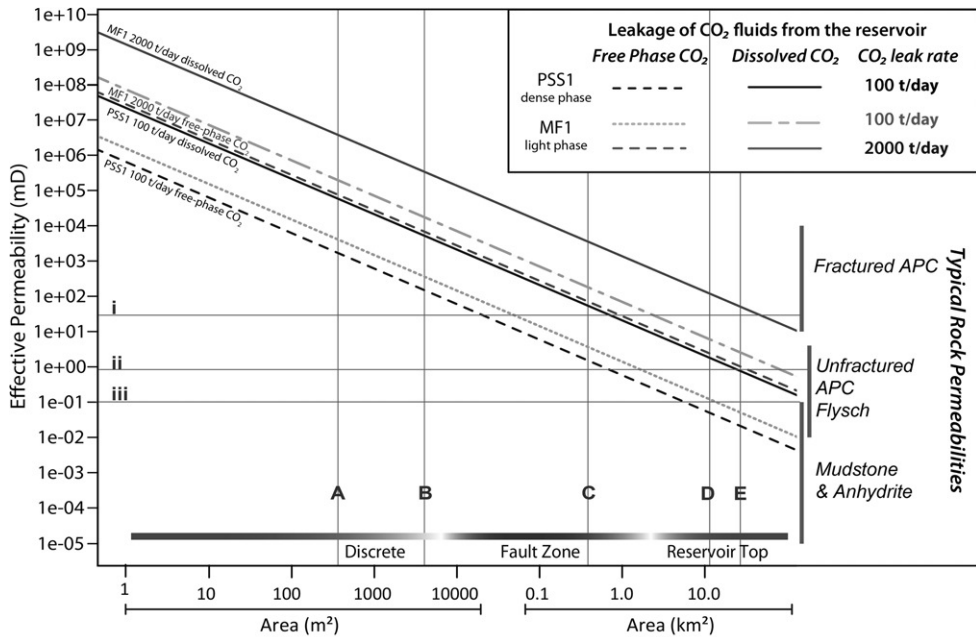
measured from the PSS1 and MF1 well logs, and elsewhere, guides the possible cap-rock permeability. Further, reasonable possible leakage areas are indicated in Figure 11 for discrete and clustered seepage, the possible extent of a free-phase CO_2 caps in the antiforms, and the geometry of rock deformation related to faulting. Similar calculations are not performed for the case studies that are inconclusive (Tr1 and MT1) because we do not have information about seep rates, or seep area.

Figure 11 and its table inset shows that high leak rates of free-phase CO_2 can occur over smaller areas and lower permeability than for CO_2-saturated water. Enhanced-permeability pathways (i.e. faults) may not be necessary for free-phase CO_2 fluids to leak from the Caprese reservoir at 100 t/day. CO_2 could leak at this rate over an area smaller than that of the Caprese Michelangelo seep cluster if the permeabilities of the overlying rock formations are similar to measurements of the overburden recorded in the PSS1 well log. For the same CO_2 leak rate and permeability, CO_2 dissolved in water would need areas similar to the Caprese seep cluster, or faults. In contrast, to leak 2000 t/day from the Frigento reservoir, Darcy flow of free-phase CO_2 through mudstones (maximum permeability *c.* 0.8 mD) would require leakage over an area much larger than that estimated for the CO_2 reservoir top. For CO_2 leakage over smaller areas, such as those of faults, overburden permeabilities approaching 10^2 mD are necessary. At approximately 1.1 km depth, such permeability could only be provided by a network of open fractures, which could localized or distributed, and could be related to faulting. Fluid flow rates of $480 \, l \, s^{-1}$ of CO_2-saturated waters would transport 2000 t/day of CO_2 from the Frigento reservoir. Such flow rates are not impossible, since spring flow rates in Italy can exceed $800 \, l^{-1}$ (Minissale 2004). However, rock permeabilities greater than 10^7 mD would be needed to enable these flow rates over a discrete area, which is difficult to achieve unless the rocks are karstified. Although karst environments are common in central and southern Italy (Santo *et al.* 2011), it is unlikely that karst in the overburden is responsible for CO_2 leakage from the reservoir, since karst environments are typically found in the region of the water table (current or historical). However, it is possible that karst could aid the rapid seepage of CO_2 from the near-surface.

Driving mechanism for CO_2 leakage

The results discussed above consider possible rock properties and geometries required to permit a given rate of fluid flow into the cap rock, not the mechanism driving the fluid flow. For free-phase or dissolved CO_2 to migrate from the reservoir and

Fig. 11. The area and effective permeability at the reservoir top necessary for reservoir fluids (free-phase or dissolved CO_2) to seep at 100 t of CO_2 per day from PSS1 reservoir conditions, and 100 and 2000 t CO_2/day from MF1 conditions. For light- or dissolved-phase CO_2 to leak from the reservoir at these rates, high-permeability pathways in the overburden such as those offered by open fractures or faults are needed. In contrast, it is possible for dense-phase CO_2 to leak from PSS1 into low-permeability overburden formations at 100 t CO_2/day without the need for fracture permeability. Typical rock permeabilities and seepage area are annotated to the right of the plot. Permeabilities from well logs are annotated: i, Jurassic Umbria–Marche overburden in PSS1; ii, Allochthonous Complex overburden in MF1 well; and iii, Apulian Carbonate Platform units in MF2. Vertical lines A–D show estimates of minimum area of seepage at Caprese and Frigento case studies: (**a**) main area of degassing at the Caprese Michelangelo; (**b**) area of degassing at Mefite; (**c**) cluster area at the Caprese Michelangelo (0.2 × 1.52 km) and the Mefite and Mefitiniellapolla vents (3.5 × 0.1 km); and minimum area of seepage from (**d**) the Frigento CO_2 reservoir top (2 km radius circle) and (**e**) the Caprese CO_2 reservoir top (5 × 10 km ellipse). The table inset show calculated seep areas using relevant permeabilities, and permeability calculations using areas A–E. These illustrate that for dense-phase CO_2, high seep rates require only very small volumes of CO_2 to leak from the reservoir compared to light-phase CO_2. Similarly, for the same leak rates, much larger volumes of CO_2 must leak from the reservoir compared to free-phase CO_2.

into the overburden, there must be a driving force. This could be buoyancy pressure of free-phase CO_2, which is less dense than formation waters.

Modelling of CO_2 properties at downhole conditions finds that CO_2 in the Frigento Formation is much more buoyant than CO_2 in the Caprese

reservoir. Indeed, in PSS1, it finds that CO_2 will be in its dense phase (with low buoyancy) for several kilometres above the reservoir. Instead, fluid pressure in the Caprese reservoir could be driving CO_2 leakage, since the reservoir pore fluid pressure is much greater than hydrostatic.

Whether fluid pressure or buoyancy is driving fluid leakage, these forces will change during fluid ascent. For example, as shown in Figure 12a, CO_2 leaking from the Caprese reservoir will remain in its dense phase for a few kilometres and pass very close to the liquidus, where buoyancy will be lowest, during its ascent from 1 km depth, if the fluids are in thermal equilibrium with the geotherm. This means that CO_2 experiences a rapid increase in buoyancy as its density decreases approaching 800 m depth, and CO_2 solubility will concurrently decrease rapidly. These are depicted in Figure 12b, c, which also shows that, although CO_2 buoyancy is high in the Frigento reservoir, the buoyancy increases gradually and to a lesser degree during ascent to surface. For example, during the 500 m ascent between 1250 and 750 m, ρ_{CO_2} decreases by approximately 325 kg m^{-3} in PSS1 and approximately 75 kg m^{-3} in MF1. This could have a pronounced effect on the way that CO_2 leaks to surface. For PSS1, the area permeability of flow paths would need to rapidly increase to sustain the mass flux of leaking CO_2 since there will be a corresponding volume increase of the leaking fluids over this depth interval.

Effective permeability

Our calculations do not account for the effective permeability of CO_2 compared to water. The relative permeability of CO_2 can be very low when flow first establishes in water-wet rocks. However, the Caprese and Mefite seeps are long-established degassing sites. Due to drying-out effects, single-phase flow could now be established along the leak paths, and so effective permeability may approximate to rock permeability.

For CO_2-saturated waters migrating through water-wet rocks, the waters will initially behave as a single phase. However, two-phase flow may initiate towards the phase-transition depth, where solubility rapidly decreases (see Fig. 12c) causing CO_2 to exsolve. The resulting decrease in the effective
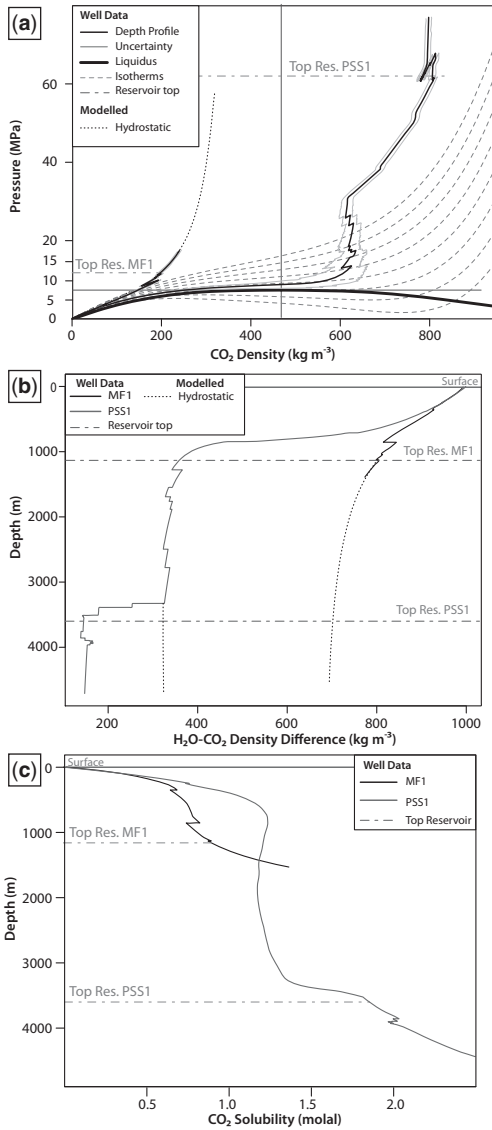
Fig. 12. Down-well pressure$-\rho_{CO_2}$ profiles for MF1 and PSS1 plotted on a vapour pressure curve (**a**) and down-well depth and density difference ($\rho_{H_2O} - \rho_{CO_2}$) profiles (**b**), and change in solubility in freshwater (**c**). The depth of the reservoir top is shown on each graph. These graphs illustrate how changes in CO_2 properties, which will affect how CO_2 flows in geological formations, differ depending on the reservoir properties, and how changes are greatest towards the CO_2 phase transition. Increased reservoir pressure decreases the density difference between CO_2 and CO_2-saturated waters, thereby decreasing the buoyancy drive of the fluids. This effect is particularly enhanced in the MF1 reservoir. The vapour pressure curve (a) shows how the cooler PSS1 passes closer to the liquidus, which leads to more rapid changes in density

Fig. 12. (*Continued*) (b) as the fluids ascend to approach 1 km depth, and a pronounced change in solubility in freshwater (c). Note the rapid change in CO_2 solubility in both cases towards the phase transition. For leakage of dissolved CO_2, two-phase flow will become established towards the phase transition, decreasing the relative permeability of both the water and the CO_2 phase.

permeability will impede flow of both phases, although the buoyancy of the water may increase as a result of 'gas lift' (the buoyant CO_2 bubbles). The exsolved CO_2 will redissolve if it comes into contact with unsaturated water, and so will only remain as a separate phase if its flow path is isolated from the ascending fluids (e.g. channelized flow in faults) or if the rocks through which it is flowing are not water-saturated. This is more common at shallower depths (vadose zone). If CO_2 remains as a separate phase, then its buoyancy and high interfacial tension could allow free-phase CO_2 to follow a different flow path to its parent waters.

It is also important to note that fracture flow is not accurately represented by Darcy's law. However, in the absence of further information about the fracture properties of the overburden, the simplified approach allows us to explore the constraints on the geological conditions that could enable leakage at the observed rates.

CO₂ mass transport

Our calculations assume conservative mass transport of leaked CO_2 (i.e. that there is minimal CO_2 loss during ascent), and so CO_2 leaks from the reservoir at the same rate that it reaches the Earth's surface regardless of its subsurface interactions. When CO_2 leaks first establish, or if leakage occurs through a large rock volume rather than a focused flow path, it is more reasonable to assume that CO_2 will disperse and attenuate as CO_2 becomes residually trapped or accumulates in secondary formations. Similarly, for many geological situations, the migrating CO_2 will encounter multiple barriers and cap rocks that will inhibit escape to surface. However, for long-established degassing sites, such as those studied here, the rocks and fluids that the CO_2 comes into contact with during ascent are probably saturated with CO_2. The quantity of CO_2 loss during ascent from the Caprese and Frigento reservoirs may therefore be limited. However, it is unlikely that the mass transport is truly conservative, and, in fact, geochemical studies at the Caprese reservoir and seeps find evidence of CO_2 mixing with shallow waters during ascent (Bicocchi *et al.* 2013).

Synthesis and discussion

Our study of CO_2 reservoirs in Italy identifies that reservoirs that are successfully sealed have low-permeability units and overpressured units in the overburden, and are located over 10 km from seismogenic normal faults.

The thrusted sediments that comprise the overburden of the studied reservoirs have experienced compressional tectonics, which is one mechanism

of elevating pore fluid pressures beyond hydrostatic (Osborne & Swarbrick 1997). Overpressure is only preserved in low-permeability rocks, since the pressure will dissipate where there is sufficient permeability (whether due to the presence of slightly more permeable rock types in the overburden or a connected fracture and/or fault network, whether it is localized or distributed). While we find that there is no simple relationship between overpressure and the type of rock comprising the overburden, we do note that for many of the sealing reservoirs an evaporite-bearing formation caps the CO_2 reservoir. The presence of evaporites will contribute to the sealing capability of the overburden due to their low inherent permeability and the possibility that when mobilized they can cement pores or fractures (Trippetta *et al.* 2013). This may be the case for the Caprese reservoir where the CO_2-bearing horizons are overpressured and are confined by evaporites (Bicocchi *et al.* 2013), but there are no other evaporite layers in the overburden, and the Caprese reservoir is leaking. However, observing the borehole pressure profiles for leaking and sealing reservoirs finds that the most overpressured formations in a cap rock are rarely those that are evaporite-bearing (see Figs 3–6), and the boreholes that show greatest overpressure are not necessarily those that contain evaporite. Thus, the presence of evaporites does not systematically affect the overburden integrity or overpressure.

Several factors affect fracture connectivity in rocks, including confining pressure (corresponding to depth) and the regional stress regime. We find that confining pressure does not affect the maximum overpressure, but that proximity to active normal faults (as defined by Roberts 2008) does. Away from these faults, overpressure from the contractional tectonic regime could be preserved in the heterogeneous and compartmentalized thrust-top deposits. The primary control on overburden overpressure may, hence, be the hydraulic conductivity of localized or distributed fractures within the overburden; high connectivity resulting from either the presence of recent 'open' extensional faults or from high overpressures resulting in a reduction of overburden stress. For example, CO_2 leakage from the Frigento reservoir may be facilitated by the low confining pressures (from being relatively shallow) opening fractures in the overburden, and by permeability offered by extension and fault damage zones related to the nearby Ufito normal fault. In contrast, the leaking Caprese reservoir is overpressured, although its overburden is not. Faults in the region could have relieved any overpressure that once existed in the overburden units; however, the reservoir horizons are not in pressure communication with their overburden because they are interlayered with the low-permeability evaporites of the

Burano Formation. This reservoir is deeply buried and the resultant high confining pressure will have closed mesoscale fractures in the reservoir and much of the overburden, unless the high fluid pressures in the reservoir opens them locally or faults are critically stressed. Both scenarios are feasible. PSS1 is located <8 km from a seismically active fault, and also the pore fluid pressure in the Caprese reservoir could be sufficient to open fractures in the cap rock, locally enhancing rock fracture permeability and enabling CO_2 escape from the reservoir. Indeed, pressure pulses associated with seismicity have increased CO_2 degassing at the Caprese Michelangelo seeps (Heinicke *et al.* 2006; Bonini 2009*a*). These observations stress the need to understand the crustal stresses around potential storage sites.

Although we do not consider this here, the burial history might have affected the geomechanical properties and, as such, the fluid flow properties of the overburden, and therefore whether a reservoir leaks or seals. Further work could aim to resolve how the geomechanical context influences reservoir leakage.

The recorded overpressure in low-permeability units could be an artefact of deriving formation pressure from drilling mud weights. When drilling through low-permeability rocks, the borehole will not be in pressure communication with the rock and so high mud weights will be tolerated without affecting the well integrity. However, we assume that this is not so for two reasons: first, significant health and safety risk is associated with drilling with the incorrect mud weight, and it is considered poor practice to drill using mud weights that are not carefully calibrated to the subsurface conditions. Secondly, for many of the well logs, it is clear that the mud weights have been adjusted many times during drilling to reflect the complexity of the overburden formations.

Implications for storage site selection

Pressure seals are commonly observed in the overburden of hydrocarbon provinces. They are a highly effective seal for two reasons: first, they indicate the presence of very-low-permeability formations, like those proposed for cap rocks in sequestration operations. Secondly, where the overburden fluid pressure exceeds that of the reservoir, the net fluid pressure gradient over the interval between the reservoir and overpressured formation is directed downwards. Fluids would therefore flow into the reservoir rather than up from the reservoir into the overburden. Despite this, to date, little attention has been paid to the role of pressure seals in ensuring secure CO_2 storage. For the case studies in Italy that are presented here, it is not possible to determine which of these two retention mechanisms

offered by the pressure seal is important for CO_2 security – if any.

Current industrial screening practices and the regulatory framework for site selection typically focus on possible mechanisms of CO_2 leakage from the reservoir into the overlying cap rock (capillary breakthrough, tensile fracturing of the cap rock or fault slip, and brine displacement) or necessary reservoir conditions, rather than the barriers to fluid flow offered in the overburden overlying the reservoir (Hannon & Esposito 2015). Multilayered reservoir–cap rock systems are identified as an effective barrier for leakage for storage site selection criteria (IEA-GHG 2009), but the only site selection guidance document to mention cap-rock fluid pressure gradients are those prepared by the World Resources Institute (2008), which note that the presence of a pressure differential between the reservoir and cap rock is one characteristic that may demonstrate the ability of the cap rock to prevent vertical migration of injected CO_2.

Table 3 summarizes the published criteria for storage site selection that will minimize the risks associated with the geological storage of CO_2, and how our case studies would perform against these criteria. All the reservoirs studied here, whether leaking or sealing, would not be deemed suitable for CO_2 storage. This suggests that site selection criteria are robust, and perhaps err on the side of caution. Table 3 shows how many of the reservoirs fulfill the most prescriptive criteria such as cap-rock thickness, and reservoir pressure and temperature conditions. Only one reservoir, Muscillo, would be deemed too shallow for storage, since it is less than 800 m deep. Most of the other case studies would be deemed too deep according to Chadwick *et al.* (2008) and Smith *et al.* (2011), but not according to IEA-GHG (2009), who provided no depth cut-off. Avoiding deep reservoirs does not minimize the risks of leakage, but, rather, the cost and ease of injection and monitoring, which at depths below 2500 m may become too difficult or expensive. In any case, the Aquistore CCS project in Canada is injecting at 3400 m (Rostron *et al.* 2014) and so clearly only the minimum depth criterion is prescriptive.

There is some uncertainty regarding the selection criteria for reservoir structures and cap-rock continuity. The leaking Frigento reservoir would fail several selection criteria (it is shallow, CO_2 in the reservoir is in is the light phase, see Table 3); however, the only criterion that the Caprese reservoir might fail regards proximity to faults. Site selection guidelines for CCS recommend that reservoirs selected for CO_2 storage should have no faults, or should at least have only small or a low density of faults. However, these are descriptive criteria; the constraints that define 'low fault frequency' or

Table 3. *A summary of how the natural CO$_2$ reservoirs in Italy studied in this paper would perform against published criteria for CO$_2$ storage site selection, for (A) Chadwick* et al. *(2008) (B) IEA-GHG (2009) and (C) Smith et al. (2011)*

Guidelines	Property	CO$_2$ properties	Reservoir properties						Cap-rock property	
	Feature	CO$_2$ State	Structure		Depth (m)		Temp	Pressure	Thickness	Continuity:
	Criteria	Dense phase	(i) Small or no faults; (ii) Low fault frequency	Multilayered system	800–2500	>800	>35°C	>7.5 MPa	10–100 m	(i) Uniform; (ii) Extensive
	Source	A	A, B, C	B	A, C	B	B	B	A, B, C	(i) A (ii) B
Leaks Case studies										
	MF1	N	N	N	Y	Y	Y	Y	Y	?
	PSS1	Y	N	Y	N	Y	Y	Y	Y	?
Inconclusive	TR1	N	N	N	N	Y	Y	Y	N	?
	MT1	Y	N	N	N	Y	Y	Y	Y	?
Seals	BS1	Y	N	N	N	Y	Y	Y	Y	?
	SAT1	N	N	Y	Y	Y	Y	Y	Y	?
	BEN 2	Y	?	N	N	Y	Y	Y	?	?
	Ac	Y	N	N	N	Y	Y	Y	?	?
	Mu	N	Y	N	N	N	Y	N	Y	?

All the case studies, whether leaking or sealing, would not be deemed suitable for CO$_2$ storage. Two of the features, reservoir structure and cap-rock continuity, are descriptive and therefore it is difficult to determine whether the case studies would fulfil these criteria or not.

'small faults', and whether this refers to fault length or fault throw, or only open faults, are not clear. Nor is it clear how their potential for storage integrity should be characterized; there are many examples from the hydrocarbon sector of sealing normal faults, and so the regional crustal stresses should also be considered. Further, the criteria refer mostly refer to faults in the reservoir (which our results indicate are not necessary for rapid CO_2 leakage from PSS1), rather than buried or surface faults in the overburden or nearby. Our results suggest that for dense-phase CO_2 to leak from a reservoir at a considerable rate (>100 t/day), faults do not need to connect from reservoir to surface; however, to seep CO_2 to surface, permeable faults are needed to provide flow paths for less dense CO_2. We would therefore argue that any faults in the overburden, as well as those that intersect the reservoir, should be characterized during site screening. Although the site selection criteria in Table 1 do not make it explicit, it is unlikely that sites located close to seismogenic faults would be considered for CO_2 storage.

The cap rocks of most case studies are suitably thick; however, it is difficult to determine if they would be considered 'uniform' or 'extensive' as required by Chadwick *et al.* (2008) and IEA-GHG (2009). This is because the well logs provide the only information about the case study overburden. Since most are comprised of thin interlayered nappes, the cap rocks may not be considered uniform on that basis. It is clear, though, that several case studies have interlayered cap rock–reservoir units comprising the overburden. This structure could be desirable above prospective CO_2 stores because interlayered reservoir units could, in the case of leakage, act as secondary or tertiary reservoirs and inhibit surface seepage. Our study suggests that CO_2 is securely retained in reservoirs with cap rocks that would be deemed unsuitable for storage according to current criteria. It might be reassuring to policy-makers and the public to learn that imperfect geosystems are capable of trapping large quantities of CO_2 in the reservoirs.

This work has identified two key controls on CO_2 retention: fluid pressure in the overburden and lateral distance of the reservoir from an active fault. The criteria for desirable properties of the cap rock and overburden above prospect CO_2 stores should therefore be improved. The regional stress regime and the overburden should be characterized during site assessment in order to identify the geological structure, pressure conditions, and possible fracture and fault properties (orientation, connectivity, stress state) in the overburden units. We recommend that the pressure seal becomes one of the first-order screening criteria for storage site selection. Furthermore, we support previous work proposing the artificial pressurization of overburden units as an effective remediation option should leakage from an engineered CO_2 storage reservoir occur, since this would decrease or reverse the normal fluid pressure gradient (Benson *et al.* 2003; Reveillere & Rohmer 2011).

The ascent of leaked CO_2

The Caprese Michelangelo and Mefite seeps are low-temperature CO_2 emissions, mostly characterized by CO_2 venting, where CO_2 is released above ambient pressure (Chiodini & Valenza 2008; Roberts *et al.* 2011). CO_2 is denser than air at surface temperature and pressure, and therefore subsurface pressure must be driving the escape of these fluids rather than buoyancy alone, otherwise gas would spread below surface in permeable soils. Pressurized CO_2 escape implies that flow is restricted below the surface. Previous work by Roberts *et al.* (2014) found that CO_2 vents in Italy tend to occur along faults in low-permeability rocks, and suggest that these rocks could be restricting CO_2 release from a more permeable (and CO_2-saturated) lithology beneath. Thus, CO_2 release through low-permeability rocks is limited to permeable pathways offered by open faults, and with minimal lateral CO_2 spread. As such, CO_2 flow could be restricted in the shallow subsurface.

Changes to fluid and rock properties encountered during ascent may also restrict CO_2 flow at depth. Our calculations find that as CO_2 density decreases during ascent, the seepage area or rock permeability must increase for mass transport to be conserved, unless fluids are not in pressure equilibrium with the rocks that they flow through. Baffles to flow are intrinsic to matrix and fracture complexities in geological units, and may encourage the channelling of ascending fluids. Fracture connectivity and rock permeability will not be continuous during fluid ascent from the reservoir. For example, there are several rock units in the Caprese overburden that have much lower permeability than that of the carbonate units directly overlying the reservoir, and so fracture permeabilities would be necessary for CO_2 transport through these units. What this amounts to is that, while free-phase CO_2 may not initially need fault-related rock permeability to leak from the Caprese reservoir, such pathways will become necessary for CO_2 transport to the surface. The location of CO_2 seeps in Italy is largely fault controlled (Ascione *et al.* 2014; Roberts *et al.* 2014) and, indeed, the Caprese Michelangelo seeps emerge along fault traces (Bonini 2009*b*). As such, natural CO_2 seeps illustrate the importance of considering the implications of fracture permeability for carbon capture and storage integrity (Bond *et al.* 2017).

Similarly, if CO_2 is migrating in its dissolved form, baffles to flow will arise from changes in the effective permeability when two-phase flow establishes towards the phase-transition depth, where CO_2 will start to exsolve from saturated waters. Flow rates will be inhibited as the effective permeability decreases, although gas lift may oppose this effect and, as discussed in our analysis, as the CO_2 and water phases have different properties they may follow different flow paths. If both phases subsequently reach the surface, several seep types will emerge in the seep cluster. Otherwise, if the hydraulic head driving the ascending waters is not great enough to enable the fluids to reach the surface, only dry CO_2 seeps will manifest. In this way, CO_2 can be transported from the reservoir in its dissolved phase and seep as a free phase at the surface. Conversely, CO_2 can leak from the reservoir as a free phase and dissolve into overlying aquifer units during ascent, and seep as a dissolved constituent in springs. Detailed geochemical studies could elucidate possible transport paths.

This is important for site selection. The likely style of CO_2 seep that might establish at the surface near a leaking store has implications for the design of subsurface and surface monitoring systems for both verification and for early warning systems. Additionally, if a leak or seep is detected, then the remediation strategies adopted would be dependent on the style of seep (Hepple & Benson 2003). Our work suggests that the characteristics of the overburden would allow some degree of forecasting of the risk and the potential risk-mitigation strategies.

Conclusions

We have studied nine boreholes in Italy that penetrate CO_2 reservoirs. Two reservoirs have high-flux surface CO_2 gas seeps within 2.5 km of the wellbore and are inferred to be leaking, whereas five have no surface seep expression and are inferred to be effectively sealed. The remaining two have small CO_2 springs located within 5 km of the borehole. These reservoirs are deemed to be inconclusively sealing, since the springs could originate from water circulation through carbonate rocks rather than from reservoir leakage.

The CO_2 reservoirs exhibit a range of subsurface structures and conditions. Reservoirs successfully retain CO_2 in the light or dense phase, and in some cases this CO_2 can be close to the critical point or exert high buoyancy pressures on the cap rock. The presence of surface CO_2 seeps is also unaffected by the structure or burial depth of the CO_2 reservoir, although the presence of evaporites may enhance its sealing capabilities. There are no seeps above reservoirs with fluid overpressure in the overburden; high fluid pressures may indicate the presence of an effective seal. The pressure seal could indicate the presence of a very-low-permeability formation, or where the net fluid pressure gradient between the reservoir and overpressured formation is directed downwards. Where there is a pressure seal, CO_2 buoyancy must be extraordinarily high to penetrate – or hydrofracture – the overpressured formation. CO_2 seeps are located at the surface above reservoirs with hydrostatically pressured overburden. These case studies are located near seismogenic extensional faults, which may be responsible for subsurface pressure connectivity at these sites, which, together with the higher permeability potentially offered by fault-related damage zones, may enable CO_2 to leak to surface.

We assess the geological conditions that could enable CO_2 leakage from the reservoir at the rates observed at the surface seeps. This finds that CO_2 is most likely to leak from the reservoir in a free phase. While formation waters have the potential to dissolve large quantities of CO_2, high leak rates of free-phase CO_2 can occur over smaller areas and lower permeability than those needed for the transport of CO_2-saturated water at the same rate. Significant (>100 t/day) leakage of dense-phase CO_2 from the reservoir can occur by flow through the overburden without the need for faults or enhanced-permeability pathways. In contrast, for the same mass flux of CO_2 leaking in its light phase, fault permeabilities are necessary since seepage through the overburden would otherwise have to occur over areas too large to be geological feasible. Changes in CO_2 properties during ascent from the leaking reservoir may therefore lead to the fluid channelling along high-permeability pathways such as faults. This leads to CO_2 venting and seep clustering observed at these sites in Italy.

This work informs the site selection of potential CO_2 stores, and the monitoring and leakage remediation strategies at selected sites. We find that all cases studied, leaking or sealing, would fail current storage site selection criteria. Although cap-rock thickness and reservoir conditions would be deemed suitable for most case studies, the proximity to faults would probably be considered detrimental to storage security. However, there is little guidance on the acceptable properties (density, scale, aperture) of fractures or faults, which is significant because our work suggests that, where the primary seal is breached, permeable fractures could permit significant leak rates from reservoirs containing dense-phase CO_2. We recommend that the overburden should be well characterized to inform the site selection process and monitoring design, and that more work is needed to detail the selection criteria for suitable overburden properties. The presence of a pressure seal could be used as a first-order screening

criteria for potential stores, where this information is available. Monitoring should focus on high-permeability pathways, such faults. It must be borne in mind that faults do not need to connect the reservoir to the surface; even if they do not connect to the reservoir at depth, they could provide efficient fluid pathways to surface; or they could provide pathways through a cap rock into the overburden. Artificial pressurization of overburden units overlying a breached engineered CO_2 store could be an effective remediation option.

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