PART III

NATURAL ANALOGUES OF CO_2 STORAGE

The Use of Natural Accumulations of Carbon Dioxide or other Greenhouse Gases to Predict the Eventual Evolution of Man-Made Storage Reservoirs

WHAT CAN WE LEARN FROM NATURAL ANALOGUES?

An overview of how analogues can benefit the geological storage of CO_2.

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Abstract: The timescales needed for the geological storage of carbon dioxide (CO_2) are potentially thousands of years. Therefore, before large-scale underground CO_2 storage can take place, it will be necessary to demonstrate that the processes are well understood, risks to the environment and human populations are low, and environmental disturbances can be minimised. One way of demonstrating that CO_2 can remain trapped underground for geologically significant times is to provide evidence from existing naturally occurring accumulations. These accumulations occur in a variety of geological environments and many can be demonstrated to have retained CO_2 for periods longer than those being considered for CO_2 storage. This fact will build confidence in the concept with non-specialist policy-makers, environmental NGOs and the public. Studies of natural analogues can be used to further validate predictive geochemical and geomechanical models, increasing confidence in these models to predict how CO_2 will behave during and after storage, helping to determine how much of the CO_2 will be permanently trapped through mineral reactions. The results have identified that kinetic reaction data need to be improved. It is unlikely that in reservoirs similar to those investigated here, significant mineral trapping can be expected, except over long geological timescales. Natural accumulations can be used to test methodologies for monitoring CO_2 leakage that may be appropriate for use above repositories, both onshore and offshore, to establish baseline conditions and to monitor sites at the surface during and after storage. Soil gas surveys and analyses of gas leakage rates can define how CO_2 migrates through the near surface environment. Techniques for determining the sealing capacity of caprocks have been tested on natural seals known to retain CO_2 and caprocks from future potential storage sites can be compared with these datasets.

Key words: geological storage, natural analogues, greenhouse gas emissions, risk assessment

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1. INTRODUCTION

In order to address the global warming threat posed by anthropogenic greenhouse gases, the European Union member states have committed themselves, through the Kyoto Protocol, to an 8% reduction in their greenhouse gas emissions from 1990 levels during the period 2008-2012.

In the medium to long term, however, it is becoming increasingly recognised that reductions of up to 60% will be needed in order to stabilise greenhouse gas levels in the atmosphere. Such a strategy requires several parallel approaches, including more efficient energy use, increased use of renewable energy sources, reduction of reliance on fossil fuels, removal of carbon dioxide (CO_2) from the atmosphere and geological storage of CO_2.

The capture and underground storage of industrial quantities of carbon dioxide is currently being demonstrated at the Sleipner West gas field in the Norwegian sector of the North Sea (see Chadwick et al., this volume). It has been suggested that such geological storage could offer potential long-term storage of significant quantities of CO_2 that would otherwise be emitted to the atmosphere.

Although the storage duration needed may be a few hundred years, so as to reduce atmospheric emissions during the fossil fuel era, it is likely that CO_2 will remain trapped for considerably longer, geological timescales. In order not to burden future societies with unacceptable environmental consequences, it is therefore necessary to have some understanding of site performance over the long term (10^4 to 10^5 years may be an appropriate timeframe).

This requires careful integration of several different approaches. Initial site characterisation will be necessary to provide a model of the geological system, as well as identifying past system behaviour. This site characterisation will include detailed baseline surveys that can be compared with future monitoring of site performance.

The prediction of site performance over long timescales also requires an understanding of, inter alia, CO_2 behaviour within the reservoir, the possibilities and mechanisms of migration out of the reservoir, and the potential impacts of a leak on the near surface environment. The assessments of such risks will rely on a combination of predictive models of CO_2 behaviour, that should in themselves include both a consideration of fluid migration and long-term CO_2-porewater-mineralogical interactions (see for example Stenhouse et al., this volume). Such predictive models must therefore be verified through comparison with laboratory-based experiments that provide carefully constrained thermodynamic equilibrium data on specific geochemical processes (see for example Czernichowski et al., this volume). However, such experiments are necessarily limited to relatively short timescales and so other lines of evidence are required from natural systems where processes have operated for geological timescales.

This paper discusses some of the processes that have been studied at various analogue sites in western Europe during the EC-funded Nascent project (Pearce et al., 2004a) and serves as an introduction to other chapters in this book that provide much greater detail of specific studies (Lombardi et al., Chadwick et al., and Czernichowski et al., this volume; see also Schroot et al., 2005).

2. WHAT CAN ANALOGUE SITES TELL US?

The industrial demonstration projects that are now underway allow injection, reservoir evaluation and short term monitoring technologies to be refined and demonstrated. However, by their nature, such sites are very unlikely to leak. In contrast, some natural sites provide opportunities to study processes controlling how leaks may occur, their potential impacts on near-surface ecosystems and groundwaters and to develop and demonstrate methodologies for monitoring CO_2 leakage.

A key benefit of studying natural geological analogues is also their temporal and spatial scales. Many processes that must be assessed when predicting the performance of a storage site occur over long, often geological timescales and can only partially be simulated in the laboratory or observed in relatively short-term demonstrations. Studies of areas where these processes have been occurring naturally can therefore complement laboratory and demonstration studies (Pearce et al., 1996).

There have been several studies in recent years that have used natural CO_2 systems to understand long-term processes. As briefly reviewed here, and described elsewhere in this volume, Pearce et al. (2004a and references therein) have examined diagenetic processes, migration along fractures, caprock integrity and near-surface processes at several sites across Europe. Shipton et al. (2004) have studied CO_2 migration mechanisms along the Little Grand fault in the northern Paradox Basin. Stevens and Tye (2004) have studied CO_2 sources and trapping mechanisms in three CO_2 fields in the US: St John's Dome in Arizona and Texas, Jackson Dome in Mississippi and McElmo Dome in Colorado. Baines and Worden (2001) compared diagenesis in otherwise geologically similar CO_2-rich and CO_2-poor North Sea oilfields.

Techniques for monitoring CO_2 in the shallow subsurface can also be tested at naturally leaking sites. These methodologies are appropriate for use above repositories, both onshore and offshore, to establish baseline conditions and to monitor sites at the surface during and after storage. Soil gas surveys and analyses of gas leakage rates can define how CO_2 migrates through the near surface environment as well as identify migration pathways (using tracer gases like Rn and He) that may be potential routes for CO_2 escape in the near-surface (Lombardi et al., this volume). In addition, studies of the long-term geochemical interactions within the CO_2 reservoirs have been used to validate predictive geochemical models.

However, studies of analogue systems are not without their limitations. Establishing the timing of reservoir filling can often only be achieved indirectly and so precise 'dating', necessary to ascertain geochemical reaction kinetics, can be difficult. Natural systems are complex and particular care must be taken to identify those processes that are solely attributable to the presence of CO_2.

Although natural CO_2 accumulations provide greater confidence in the potential to store CO_2 for long periods, not all natural accumulations should be considered directly analogous to a storage scenario. For example, many near-surface CO_2-rich springs and seeps occur in volcanic terrains, which may not be tectonically comparable to storage in a sedimentary basin. These sites do provide many opportunities to study near-surface processes and to test monitoring methodologies. When studying natural systems to assess potential impacts on ecosystems, it is important to be aware that ecosystems may have evolved to cope, or exploit, the high CO_2 environment, which would be in contrast to an ecosystem being initially exposed to elevated CO_2 concentrations for the first time.

3. WESTERN EUROPEAN 'ANALOGUES'

Natural CO_2 occurrences are common across Europe (Pearce et al., 2004b and Figure 1) and, although they occur in a wide variety of geological settings, their distribution is principally controlled by the Cenozoic rift system and associated Tertiary volcanism. These occurrences can be classified into:

- *CO_2-rich waters both at depth and in springs.* These are often exploited for mineral waters and occur in a variety of geological settings, with the sources of CO_2 including mantle degassing, volcanic activity and thermal metamorphism of limestones.
- *Dry CO_2 gas vents ('moffettes').* These are associated with Cenozoic rifts such as the Eger and the Tyrrhenian rift systems. They are also associated with hydrothermal fields and Quaternary to Recent volcanic activity, such as in the Eiffel volcanic complex within the Rhenish Massif; the Larderello geothermal field, Italy and, of course, currently active volcanism.

- *CO_2 gas accumulations*. These occur in Cenozoic extensional basins such as within the sub-basins of the back-arc Pannonian Basin and the Florina-Ptolemais-Aminteo graben system. In addition, Mesozoic and Palaeozoic basins subject to Cenozoic tectonism such as the Triassic to Jurassic Southeast Basin of France (see below) and sub-basins within the Southern Permian Basin in Saxo-Thuringia, Germany (see below) can also host CO_2 accumulations.

The natural CO_2 accumulations in the Pannonian basin and the small gas pools in the Southeast Basin may be considered the closest analogues to a storage site in the Western Europe, since CO_2 has been trapped here for geological timescales. Many other known CO_2 accumulations are associated with volcanic regions and as such are not directly analogous to a storage site. However, they do provide opportunities to study near-surface leakage processes and the potential impacts on ecosystems on a scale not easily replicated experimentally.

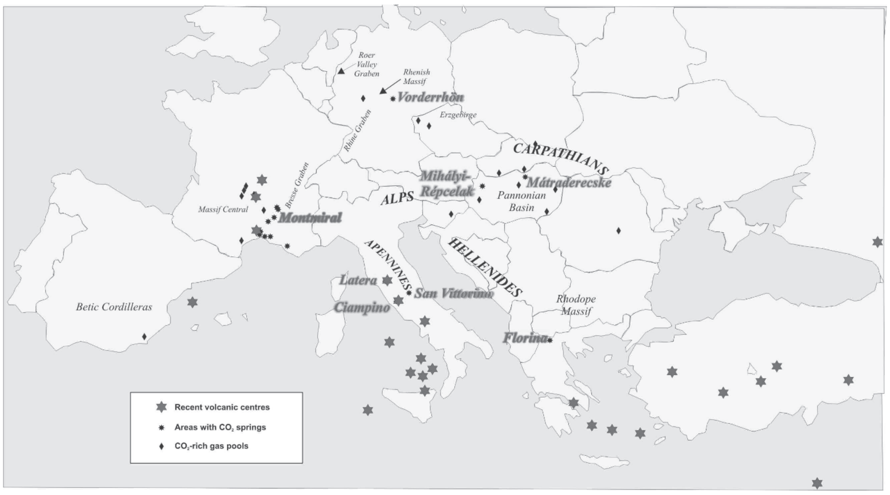

Figure 1. The locations of some natural CO_2 occurrences in Europe and sites studied during the Nascent project.

4. INTERACTIONS IN RESERVOIRS

Understanding the long-term effects of CO_2 on a reservoir is important for several reasons. In certain circumstances, CO_2 may dissolve in the reservoir pore water and react with minerals within the reservoir, which could ultimately lead to long-term trapping through precipitation of carbonate minerals. Our ability to model the geochemical and geomechanical processes that occur in the reservoir, that could ultimately influence its long-term storage performance, can be tested by modelling natural analogues of geological storage. Czernichowski et al. have discussed this in more detail (this volume). In addition, how CO_2 might migrate from the initial storage reservoir through fractures, and information about processes that could occur in fractures in limestones, has been obtained in this study.

Montmiral is one of several small CO_2 gas accumulations in the Southeast Basin of France but it is the only one currently being exploited. CO_2 is currently produced via a single production well as an industrial gas. In order to determine the CO_2-water-rock interactions within the reservoir, it was necessary to reconstitute the original brine composition, which has been evolving to increasing salinity during the lifetime of the CO_2 production. This temporal variability is due to changes in the respective volumes of discharged brine and CO_2-H_2O gas mixture (Pauwels et al., 2004). The brine composition indicates that the CO_2-water-rock system is not at equilibrium.

Diagenetic studies suggest that the introduction of CO_2 into this particular reservoir caused dissolution of feldspar, and a slight increase in reservoir porosity. The observed increase in porosity indicated an open system, i.e. the reservoir has been flushed with fresh CO_2-charged waters (Gaus et al., 2004). Even after contact times of at least hundreds of thousands of years, feldspars are still present. This illustrates that reaction kinetics can be much slower than expected, based on short term kinetic data derived from the literature. Reservoir temperature is an important parameter when assessing the storage capacity of a reservoir, with reaction rates potentially increasing by orders of magnitude where high temperatures prevail. However, to accurately constrain the kinetic rates of the geochemical reactions more detailed information on the reservoir evolution is required. No evidence was found of extensive mineral trapping of CO_2, through precipitation of carbonates. Reconstruction of the brine composition under reservoir conditions through geochemical modelling suggests that one kg of brine contained 0.86 mol CO_2 and 0.087 mol HCO_3. For comparison, the amount of dissolved CO_2 at Sleipner is 1.14 mol/kg H_2O (dependent on the fugacity, and thus temperature and pressure, plus salinity of the water). Therefore, a concentration of 0.86 mol/kg H_2O means, for an average porosity of 8%, that 3.44 g CO_2 will be dissolved in the pore waters of a volume per dm^3 rock. The total mass stored depends entirely on the volume of the reservoir. There is insufficient information on the Montmiral reservoir to estimate the volume saturated with CO_2.

5. LEAKAGE THROUGH CAPROCKS – PROCESSES AND IMPLICATIONS

The caprock or caprocks form the barriers that will prevent CO_2 from migrating out of the reservoir rock. Therefore understanding the sealing capacity of these low permeability rocks for CO_2 specifically will be necessary for site characterisation and estimating storage capacity. Capillary breakthrough measurements with CO_2 have been performed on initially water-saturated caprock samples from natural CO_2 sites (Hildenbrand, et al., 2004). The capillary displacement pressure for CO_2 is lower than that for the other gases on caprocks of equal effective permeability, i.e. for a given caprock permeability, the pressure at which CO_2 enters the caprock is lower than for nitrogen or methane. Considering the strong variability of permeability and capillary breakthrough values in natural caprocks, this effect, although discernible, is not expected to result in a substantially increased risk of capillary leakage when storing CO_2 in depleted methane- or nitrogen-dominated natural gas reservoirs.

Although diffusive loss of CO_2 through caprocks is considered negligible, the rate of potential geochemical "corrosion" of caprocks is determined by diffusion. Laboratory experiments have provided some basic information on the diffusion coefficients of CO_2 in seal rocks and have also shown evidence of chemical interactions of the CO_2 with the minerals (Hildenbrand et al., 2004). The interrelation of diffusive transport and chemical reaction of CO_2 in naturally occurring shale, marlstone and carbonate rocks requires further investigation.

Studies of fracture calcite mineralisation at Montmiral revealed that the latest millimetre-thick calcite generation formed in a CO_2-rich fluid, providing evidence of CO_2 migration above the reservoir. It is not clear how far through the overlying rocks the CO_2 has migrated. The CO_2-rich fluid also contained hydrocarbons that could have been mobilised in a similar manner to that employed during enhanced oil recovery. Geochemical modelling indicates that pressure decreases alone are insufficient to cause calcite precipitation and that a decrease in temperature is also required. The amounts of calcite precipitated however, are very small.

Continuous monitoring over deep-seated fault systems, basalt intrusions, gaps in the overlying cap rock (salt beds) and near former production wells of a natural CO_2 accumulation, in the Vorderrhön area, Germany, showed no evidence for a leak (Teschner et al., 2004). This may be because leaks, if they exist at all, release only small quantities of CO_2, which have to penetrate several aquifers where CO_2 will be naturally attenuated. The quantities of biogenic CO_2 recorded, which were produced in the shallow subsurface during the summer growing period, are much larger.

6. MIGRATION IN THE SHALLOW SUBSURFACE

The shallow subsurface may be the last barrier before CO_2 escape to the atmosphere. A detailed understanding of gas migration in this environment is therefore important to assess risk to human health and the environment.

Detailed soil gas and gas flux surveys, conducted in and around gas vents in several locations in central Italy, demonstrated how gas leaks occur over very small areas, on the order of a couple of metres, but that elevated CO_2 concentrations occur as a large halo around the actual vent, due to lateral migration in the unsaturated zone. This work is discussed in more detail by Lombardi et al. (this volume).

Accumulations of shallow gas (mainly composed of methane) are known to occur in various parts of the North Sea and their study can provide a better understanding of gas migration in the shallow subsurface (Schroot et al., 2005).

7. ASSESSING THE POTENTIAL IMPACTS OF A LEAK

To be able to evaluate site performance, some performance criteria will be needed, which will require a clear understanding of the potential impacts of a leak, in order to best inform policy makers and the public at large.

The San Vittorino Plain to the north of Rome, Italy, is a thinly populated area which has seen two major effects caused by the high-volume leakage of CO_2: modified groundwater chemistry and sinkhole formation. A clear correlation exists between high concentrations of CO_2, anomalous groundwater chemistry and the location of sinkholes. Modified groundwater chemistry resulted in a 5 to 10 times increase in most major and trace elements in surface springs, wells and water-filled sinkholes in the vicinity of a number of known fault structures. It is believed that acidic gases have risen along high-permeability pathways in the faults, causing the dissolution of carbonate and possibly silicate minerals. In spite of the increased ionic content of these altered ground waters a comparison with drinking water standards indicate that they are still considered safe for human consumption.

Closely linked to the formation of the anomalous waters at San Vittorino is the creation of various sub-circular collapse structures, many of which are now filled with water. These features, which pose a hazard for local infrastructure, were likely formed by acidic dissolution and the removal of fine-grained material by flowing ground water, followed by collapse due to low to moderate strength earthquakes. As such, the formation of such features will be highly dependent on the chemical composition of the local geology and the groundwater flow rates. A geochemical monitoring station was developed to monitor possible future collapse events. This monitoring station continually measures the concentration of CO_2 and H_2S dissolved in ground water, processes the data and then sends it via modem to a remote laboratory. The development and application of this technology has shown that such stations would be effective in monitoring dissolved gas concentrations and relatively inexpensive to construct and operate. The same system could be easily modified to monitor soil gas concentrations and installed above a CO_2 storage site (e.g. near an abandoned well) as an early warning system.

Ciampino is a rapidly growing city, close to Rome, which is constructed on the flanks of an extinct volcanic complex. Due to anomalously high heat flow and the occurrence of faults, significant quantities of CO_2 are released to the atmosphere at numerous points throughout the community. Concern has been expressed regarding the safety of the local population, as a sudden CO_2 release once killed 30 cows pastured in the city limits. Soil gas surveys and a limited number of gas flux measurements were conducted throughout the area in an effort to delineate areas of high risk. The soil gas surveys indicated areas with CO_2 concentrations in excess of 70%, along with associated high values of Rn. Despite the fact that a number of new housing developments had been built above these anomalous areas, a small pilot-scale study of indoor gas concentrations yielded CO_2 values that were typically less than 1%. These relatively low values are likely due to the Italian habit of leaving their windows open to allow for an exchange of air. Although risks exist in the Ciampino area, much is being done to minimise any danger to the local inhabitants, including the use of soil gas surveys to develop zoning bylaws and to identify pre-existing residential areas which may be at risk. Education programmes are also underway to explain to the local inhabitants what simple things they can do to greatly lower any risk.

The level of risk to human health related to CO_2 leaking from natural analogues is dependent on many factors that control the generation, migration and accumulation at dangerous levels of this gas. Work conducted partially within the Nascent project on the Latera site has attempted to examine some of the geological phenomena which influence gas emanation hazards, such as the occurrence of faults and the depth to source, using geostatistical analysis and GIS techniques. In addition, soil gas data should allow the generated risk model to be calibrated against the measured gas distribution. It is expected that the method developed during this study could be applied for site assessment of locations being considered for CO_2 storage.

A detailed hydrogeochemical survey of groundwaters was performed across the whole Florina Basin to determine if any changes in water chemistry could be observed in areas containing high CO_2 concentrations. The waters close to the CO_2 field have increased Ca, Mg, CO_3 contents and high total hardness. The remaining water samples show a good quality with some increased content of some elements in a few of those samples.

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