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Natural Analogues for the Geological Storage of CO_2

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NATURAL ANALOGUES FOR THE GEOLOGICAL STORAGE OF CO_2

Overview

The capture of CO_2 from large point sources such as power plants and its subsequent storage in geological reservoirs could become one method, in a collection of measures that will help meet the target of deep reductions in anthropogenic greenhouse gas emissions. However, since it is a less well established technology, it is essential to develop the knowledge, expertise and confidence in geological storage. One way of helping to develop confidence in the technology is through practical research, development and demonstration (R, D & D) projects. The IEA Greenhouse Gas R&D Programme (IEA GHG) participates directly in a number of practical R&D Projects many of these activities. IEA GHG actively participates by providing expert advice to the project once it is underway and by helping to disseminate the project results. Currently, there are some 60 practical research, development and demonstration (R, D & D) on geological storage operating around the world[1]. These projects are helping to address some of the key technical issues that need to be addressed for this technology. One such key issue is the integrity of the formation containing the injected CO_2 and the related safety and environmental impact issues should leakage occur.

Storage projects such as Sleipner and Weyburn provide commercial scale examples that can help provide the knowledge to allow further storage projects to develop. However, none of these projects have been operating for longer than 10 years and will only be able to demonstrate long-term storage through predictive modelling. One way that long-term storage can be observed is to look at the examples of naturally occurring CO_2 accumulations. These natural accumulations can be seen as direct analogues for the storage of anthropogenic CO_2 over periods of time that can not be matched through any CO_2 injection project. Therefore, they give specific examples to study the behaviour of CO_2 underground, the long-term storage reactions and the nature of leakage if it occurs. There are several natural accumulations of CO_2 across Europe as well as in other parts of the world, notably in the USA where these accumulations are used as sources of CO_2 for CO_2-EOR operations.

A three year European Commission funded project titled NASCENT (Natural Analogues for the Geological Storage of CO_2) was developed to study these as analogues throughout Europe. The project has enabled an understanding of the long-term processes involved with underground storage of CO_2 to be developed. It also provided study sites that could not be recreated in a laboratory and provided experience that could not be gained through recent injection projects. In addition, it enabled comparisons with the predictive modelling results from other storage projects. Not only did NASCENT provide this unique opportunity to look at the long-term storage but the proximity of the natural accumulations near to areas of population throughout Europe provided an insight into storage in on-shore locations, the response to leakage and how it can be monitored and dealt with. The monitoring techniques developed during the project are appropriate for use in both onshore and offshore sites. By demonstrating that CO_2 has accumulated and been trapped for geological timescales in natural geological accumulations the project should help to build confidence in the concept with non-specialist policy-makers, environmental NGO's and the public.

The IEA Greenhouse Gas R&D Programme was an active participant in the NASCENT project and had been given permission by the project partners and the European Commission to disseminate the results of this project internationally through its membership.

[1] The IEA Greenhouse Gas R&D Programme maintains a database of approximately 100 practical research, development and demonstration projects from around the world on its website www.co2captureandstorage.info. The database contains a listing of projects with project summaries, links for further information and contact details.

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The final report of the Nascent project, co-sponsored by the Energy, Environment and Sustainable Development Programme of the EC Fifth Framework R&D programme

Organisations and authorship:

British Geological Survey

J.M. Pearce (project coordinator)

T.J. Shepherd C.A. Rochelle

S.J. Kemp J.E. Bouch

D. Wagner

MAFI

A. Nador I. Vető

J. Baker G. Toth

URS

S. Lombardi

A. Annuziatellis S.E. Beaubien

G. Ciotoli

BRGM

H. Pauwels

I. Czernichowski-Lauriol I.Gaus

Y-M Le Nindre J-P Girard

E. Petelet-Giraud H. Serra

C. le Guern-Marot

TNO

B.Schroot B. Orlic

A. Schuttenhelm

IGME

G. Hatziyannis Spyridonos, E

Metaxas, A.

IEA GHG

J. Gale A. Manancourt

Bundesanstalt für Geowissen-schaften und Rohstoffe

St. Brune E. Faber

J. Hagendorf J. Poggenburg

M. Teschner

BP

J. Iliffe

RWTHA

B. M. Kroos A. Hildenbrand

S. Alles

STATOIL

R. Heggland

Foreword

This is the final report of the Natural Analogues for the Storage of CO_2 in the Geological Environment (NASCENT) project. The Nascent project has studied natural accumulations of carbon dioxide (CO_2 – an important greenhouse gas, thought to be responsible for climate change) as analogues of the geological storage of anthropogenic CO_2 emissions.

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 timescales 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.

The following technical reports have been published by the Nascent project. A CD-Rom containing these reports together with this final report is available from J.M. Pearce, BGS, Keyworth, Nottingham, NG12 5GG, United Kingdom. Tel: +44 (0)115 9363 222, Fax: +44 (0)115 9363352 or email: jmpe@bgs.ac.uk.

Pearce, J.M. (Editor), 2003. *Natural Analogues for the Storage of CO_2 in the Geological Environment: Report on Field Characterisation* including Soil Gas Surveys, Characterisation of Offshore Shallow Gas Seeps, Hydrogeochemistry and Diagenetic Studies. British Geological Survey External Report CR/03/147, 333 pages.

Kemp, S.J. (Editor), 2003. *Natural Analogues for the Storage of CO_2 in the Geological Environment: CO_2 leakage mechanisms and migration in the near-surface.* British Geological Survey External Report CR/03/196, 55 pages.

Gaus, I. C. Le Guern, H. Serra. 2004. *Natural Analogues for the Storage of CO_2 in the Geological Environment: Modelling of CO_2/fluid/rock interactions*. BRGM External Technical Report BRGM/RP-52934-FR, 87 pages.

Orlic, B., Schroot, B.M. Hatziyannis, G. 2004. *Natural Analogues for the Storage of CO_2 in the Geological Environment: Geohazard Assessment.* TNO External Technical Report NITG 04-049-B0309, 44 pages.

There are two Nascent websites:

www.bgs.ac.uk/nascent

http://www.rwth-aachen.de/lek/Ww/nascent/nascent_password/1seite.html

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Summary

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. Current predictions (e.g. European Energy Outlook to 2020) indicate that although renewable sources of energy are expected to increase substantially, we will still be reliant on fossil fuels for much of our primary energy production. Approximately 43% of total world emissions are expected from power plants in 2030 (IEA, 2002).

In the short term more efficient energy use by the industrial, domestic and transport sectors, plus an increased use of renewable energy sources can lead to significant reductions in CO_2 emissions. 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, reduction of reliance on fossil fuels, removal of carbon dioxide (CO_2) from the atmosphere (e.g. through cultivating biomass with storage of the resulting CO_2 emissions), and geological storage of CO_2. Approximately one-third of anthropogenic emissions arise from transport, one-third from industrial and domestic sources and one-third from power generation. While achieving substantial reductions in emissions from either of the first two will be a long-term process, the technology to capture CO_2 from power plant is already available and could lead quickly to significant reductions in emissions – provided mechanisms are available to dispose of the CO_2 thus captured. 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. 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.

Geological storage of CO_2 involves pumping the CO_2 underground, in fluid form, such that it becomes trapped in the pore spaces between grains of sedimentary rock in exactly the same way that hydrocarbons are naturally trapped in oil and gas fields. The technique offers the opportunity to remove quantifiable, monitorable and ultimately secure amounts of CO_2 to a non-atmospheric sink, using technologies that are both currently available and constantly improving.

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 timescales 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 stored CO_2 for periods longer than those being considered for CO_2 storage.

The Nascent project has developed and demonstrated methodologies for monitoring CO_2 leakage above natural accumulations. 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. These methodologies could be further developed as standards for monitoring for CO_2 leaks above storage sites. Soil gas surveys and analyses of gas leakage rates have defined how CO_2 migrates through

the near surface environment. Design specifications for monitoring equipment can be used by field operators and engineers. National and European regulators, safety assessment advisers and license-issuers could use detection limit and sampling interval specifications to define environmental impact assessment criteria.

Data produced during the project has been used to further validate predictive geochemical models and geomechanical models. There can now be greater confidence in these models to predict how CO_2 will behave during and after storage and will help to determine how much of the CO_2 will be permanently sequestered through mineral reactions. Regulators and public health officials can use indicators that show the effects of CO_2 on aquifers to monitor storage operations and define protocols and standards.

A web-enabled GIS-based support system has enabled collation, interpretation, and presentation of data about these natural accumulations. It can be used to identify those processes and situations that increase the potential risks from CO_2 leakage. In this way, field operators, license-issuers and regulators can mitigate against such risks during design and location of storage facilities.

Providing examples of natural systems where CO_2 has accumulated and been trapped for geological timescales will build confidence in the concept with non-specialist policy-makers, environmental NGOs and the public.

The NASCENT project was a three-year research project (2001 to 2004) studying natural accumulations of CO_2 as analogues for geological storage of anthropogenic CO_2 emissions. It was funded by the EC Fifth Framework Research Programme (5.4.1 Energy, Environment and Sustainable Development) and coordinated by the British Geological Survey. There were 10 other partners involved in the project: BRGM, BGR, IGME, MAFI, TNO (these are the geological surveys of France, Germany, Greece, Hungary and the Netherlands respectively), University 'la Sapienza' Rome, University of Aachen, Germany, the IEA Greenhouse Gas R&D Programme, Statoil and BP.

The project had the following objectives:

- Proof of concept – does the existence of natural CO_2 accumulations offer confidence that long term geological storage is a viable and safe option?
- What hazards, such as seismicity, ground movement, groundwater contamination, leakage to the biosphere and atmosphere, might be associated with geological storage of CO_2?
- Can predictive models and laboratory experiments be verified by processes identified in natural systems?
- Demonstration of trapping mechanisms – what geological structures trap CO_2? What geological conditions have resulted in release of naturally generated CO_2 to the biosphere and atmosphere?
- Gas monitoring – where CO_2 is exploited, information can be obtained on field management techniques

Implications for geological storage of CO_2

This section briefly summarises the main implications of the Nascent project for future geological storage projects.

Monitoring techniques, both offshore and onshore, have been developed and tested on natural CO_2 systems. These techniques include

- 4D geophysical surveying of shallow gas in the subsea near-surface
- side-scan sonar in the shallow sea-bed and overlying water column
- soil gas surveying of CO_2 plus useful tracer gases
- automatic continuous monitoring of soil gas concentrations at fixed sites
- groundwater surveying

These methods could form the basis for monitoring protocols at future CO_2 storage sites. The monitoring equipment developed can be installed to monitor the performance of future storage sites. The techniques developed and tested at natural analogues can be used as follows:

- In initial site selection to determine its suitability for storage (for example, by identifying possible gas escape routes)
- In site characterisation, through determining background conditions prior to storage
- In site performance and safety assessment, during and post-injection, to monitor for early leaks both from the reservoir and infrastructure
- In predictions of long-term risks by identifying future potential gas migration pathways

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.

As part of the long-term risk assessments that are likely to be required to assess the appropriateness of a site, the models used to predict the long-term effects of CO_2 storage on the reservoir and caprock have been shown to reproduce the processes observed in natural systems, thereby providing greater confidence. The results have identified that kinetic reaction data need to be improved. The geochemical interactions of CO_2 in the reservoir and caprock are now better understood for specific lithologies but other types could be selected for storage and would therefore require investigation. It is unlikely that in reservoirs similar to those investigated here, significant mineral trapping can be expected, except over long geological timescales.

The potential for fracture reactivation and ground movement has been investigated at three sites. Results indicate that ground movement is not a significant risk, especially in previously depleted hydrocarbon fields, and large overpressures are required to activate faults. However, each storage site will be geologically unique and it should be stressed that, although providing confidence in the concept, each site should be assessed individually for their geomechanical integrity.

This project has identified, unsurprisingly, that fractures often control the migration of CO_2 through the geosphere, enabling CO_2 to by-pass seals that would otherwise successfully retain CO_2. This implies that future storage projects should make careful assessments of the nature and potential, including over geological timescales, for fractures to allow CO_2 to migrate out of the reservoir. A decision support tool designed within the project demonstrates one method of combining different datasets to identify those areas at the ground surface most at risk.

Evidence from some natural systems indicate that if CO_2 were to leak from a site it may, under certain geological conditions, carry other gases such as hydrogen sulphide and radon with it. These risks should also be included in site assessments.

This project has identified some of the risks in residential areas and potential solutions to very high CO_2 leaks. Risk assessments for future geological storage should consider these risks.

Groundwaters affected by high CO_2 fluxes have been chemically altered but the degree of alteration has not been sufficient to make waters unpotable. However, the potential for this above CO_2 storage sites should again be carefully assessed during risk assessments.

The near-surface attenuation of CO_2, leaking from depth and identified in this project, has not previously been studied in detail. These processes, however, could significantly reduce the amount of CO_2 that reaches the atmosphere. These processes should be further investigated.

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. 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.

To address these issues, several geological sites were studied. The sites chosen were the natural CO_2 fields in the Florina Basin, northern Greece and the Montmiral field in the Southeast Basin in France, plus the Sleipner natural gas field on the southern edge of the Viking Graben in the North Sea.

Montmiral is one of several small CO_2 gas accumulations in the Southeast Basin of France but 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. The brine composition indicates that the CO_2-water-rock system is not at equilibrium.

Diagenetic studies suggest that 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. 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 at 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, at Sleipner the amount of dissolved CO_2 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 water of the pores 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.

At Florina, the quantitative impact of geochemical reactions is minor, due to the replacement of one mineral (siderite) with another (Fe oxide, probably goethite). Geochemical modelling indicates that the system is far from equilibrium and, as observed in petrographic examination of cores from the Florina CO_2 accumulation, CO_2 is not being precipitated as a carbonate mineral.

Injection of CO_2 into a subsurface reservoir may have an impact on the mechanical integrity of that reservoir and its surroundings through changes of reservoir pressure. Geomechanical modelling was performed to assess the impact of CO_2 injection on:

- the mechanical integrity of the reservoir rock and the caprock;
- the potential for fault re-activation, which could trigger induced seismicity in the area of CO_2 injection;
- ground deformation (subsidence and uplift).

The stress and deformation in the subsurface and at the ground surface, caused by CO_2 extraction and injection, were computed on a 2D numerical stress model of the Montmiral field. The maximum subsidence rate at full depletion was predicted to be of the order of 5 cm. During injection, when the reservoir pressure is equal to the virgin pressure, the state of stress on the fault is the same as it was in the initial state of stress. Hypothetical modelling of CO_2 injection, increasing the pressure to 1.5 times above the virgin reservoir pressure suggested a critical stress development until failure has been reached. At failure, a slip on the fault occurs with displacement of about 1 cm.

Geomechanical numerical modelling of the Sleipner West Field was carried out in order to predict changes in the *in situ* stress field and the associated deformation, induced by reservoir depletion and by subsequent CO_2 injection into the reservoir. In contrast to the current practice of the ongoing Statoil injection project, a scenario was assumed in which CO_2 would be injected into the same Hugin Formation, from which the gas and condensate had been previously produced. In the modelled scenarios, reservoir depletion was followed by a CO_2 injection phase, until the final pressure was reached, equal either to the initial reservoir pressure or to 50% higher. The model predicts the mechanical stability of the reservoir rock does not deteriorate as a consequence of reservoir depletion.

The effect of subsequent CO_2 injection is the opposite, becoming more important at injection pressures that exceed the original virgin pressure. The maximum reservoir pressure at the end of the hypothetical injection phase did not exceed the minimum horizontal stress. Consequently, the mechanical stability of the reservoir rock is not expected to deteriorate even if CO_2 injection pressures reached up to 50% higher than original reservoir pressure. However, at this pressure of 50% above initial virgin reservoir pressure, reactivation of bounding faults are predicted to occur.

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. The capillary displacement pressure for CO_2 is lower than 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 also show evidence of chemical interactions of the CO_2 with the sample materials. The interrelation of diffusive transport and chemical reaction of CO_2 in naturally occurring shale, marlstone and carbonate rocks requires further investigation.

To study the sequence of events resulting in potential caprock leakage, a simple dynamic leakage model has been developed. Based on the results of the laboratory experiments, this model can be used to estimate the time-scale and quantities of gas loss through the caprock.

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 up through the overlying rocks the CO_2 has migrated. In addition, the CO_2-rich fluid also contained hydrocarbons that could have been mobilised by the CO_2-rich fluid 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 of Thuringia, Germany, showed no evidence for a leak. 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 vegetation period are much larger.

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. The association of trace gases, which also present a health (H_2, H_2S) or greenhouse (CH_4) hazard, with the vent indicates that even if only CO_2 is stored at depth, a future leak may also result in the mobilisation of other gaseous species due to their transport within the higher volume CO_2 stream. Soil gas surveys, including the determination of the mobile noble gases helium (He) and radon (Rn) around known fault systems over a natural CO_2 accumulation in the Vorderrhön area, Thuringia, Germany, helped to identify the optimal position for the installation of continuously operated monitoring systems.

The results of the experimental injection of a helium (He)/ argon (Ar)/ CO_2 gas mixture at around 10 m depth and subsequent monitoring of soil gas concentrations clearly demonstrated how the chemical characteristics of each gas species can control its migration in the shallow subsurface. Data indicated that the non-reactive, low-solubility, highly-mobile He escaped to the surface immediately, at high concentrations and near the injection well. In contrast, the soluble, reactive and dense CO_2 arrived at the surface at much lower concentrations and at a much later time, due to its dissolution in groundwater as well as its lateral diffusion in the unsaturated zone. The laboratory column experiments conducted to examine the migration characteristics of ascending bubbles in the shallow environment supported these results.

These results indicate that gas migration and possible release to the atmosphere is controlled by the physical and chemical characteristics of the migrating gases and the geology and hydrogeology of the shallow subsurface. A major difference between the natural CO_2 vent and the gas injection test results, however, is the gas volume and time scale. For example, the natural gas vent has probably existed for tens (or perhaps hundreds) of years with an essentially unlimited source of CO_2. This, combined with the high flux rates, has resulted in a system at steady state. In contrast, the short-term injection of a finite amount of CO_2 into the shallow environment resulted in little transfer of this gas to the atmosphere due to natural attenuation. The scale of any eventual leak from a CO_2 storage reservoir would lie between these two extremes, as the amount of gas available at depth would be large but finite, and would be limited further by attenuation reactions during its upward migration. This smaller quantity of gas would then be further decreased within the near-surface environment through the processes of dissolution, dilution, chemical reactions and biological consumption observed in this work. If CO_2 volumes are small enough, advection rates low enough and the appropriate shallow environment exists, the near surface environment may even have the potential to prevent the transfer of deep CO_2 to the atmosphere, acting as the final barrier at the end of a long migration pathway.

Accumulations of shallow gas (mainly composed of methane) are known to occur in various parts of the North Sea. A study area in the northernmost part of the Netherlands North Sea sector was selected with the aim of carefully examining the nature, characteristics and the surface and subsurface expressions of the gas by different monitoring techniques. Reflection seismic and other marine acoustic data revealed the presence and distribution of the shallow gas in the subsurface and in the water column. Confirmation of the interpretation of the presence of gas was obtained through chemical analysis of the headspace gas from seabed sediment samples. Although the shallow gas is composed mainly of methane, and is therefore chemically different from CO_2, its physical behaviour in the subsurface, including the way it migrates through the near-surface environment and leaks to the surface, can be considered as similar to that of CO_2.

<u>Assessing the potential impacts of a leak</u>

Although the concept of geological CO_2 storage is sound, and any eventual project will be engineered to the highest level in order to prevent the leakage of the injected CO_2 to surface, a clear understanding of any possible risks is needed in order to best inform policy makers and the public at large.

The San Vittorino Plain to the north of Rome 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 inorganic species concentrations in the groundwater 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 always 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 here 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.

Contents

Chapter 1. Introduction and overview

1.1. GEOLOGICAL STORAGE OF CO_2

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 below 1990 levels in their greenhouse gas emissions over the period 2008-2012. Current predictions indicate that although renewable sources of energy are expected to increase substantially, we will still be reliant on fossil fuels for much of our primary energy supplies.

In the medium to long term, reductions of up to 60% may be needed, requiring several approaches, including the geological storage of CO_2. The most practical geological concept is underground storage of CO_2 which involves pumping the CO_2 underground, in fluid form, such that it becomes trapped in the pore spaces between grains of sedimentary rock. The technique offers the opportunity to remove quantifiable, monitorable and ultimately secure amounts of CO_2 to a non-atmospheric sink, using technologies that are both currently available and constantly improving. 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. 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.

Before large-scale underground CO_2 storage can take place, however, 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 timescales 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 stored CO_2 for periods longer than those being considered for CO_2 storage. The study of natural analogues is crucial to understanding the long-term impact of CO_2 storage as such long-term effects cannot be addressed by laboratory experiments. Long-term water-rock-gas interactions may affect the CO_2 storage capacity, the porosity and permeability of the host formation, the integrity of the caprock, ground stability, and quality of groundwaters in overlying aquifers.

If geological storage of CO_2 is to become acceptable, certain key issues must be addressed. These include the long-term safety and stability of storage underground and the potential effects of leakage from an underground storage reservoir. Natural CO_2 fields, and places where CO_2 is actively migrating from underground to the Earth's surface, are widespread in Europe and elsewhere in the world. These are direct natural analogues for the geological storage (and leakage) of anthropogenic CO_2. They therefore provide natural laboratories in which to address some of the key issues for geological storage highlighted above. The Nascent project specifically addressed these issues.

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1.2. THE NASCENT PROJECT

Natural geological accumulations of carbon dioxide occur widely throughout Europe, often close to population centres (Figure 1.1). Some of these CO_2 deposits leak, whereas others are sealed. The NASCENT project was a three-year research project (2001 to 2004) studying natural accumulations of CO_2 as analogues for geological storage and storage of anthropogenic CO_2 emissions. It was funded by the EC Fifth Framework Research Programme (5.4.1 Energy, Environment and Sustainable Development) and coordinated by the British Geological Survey. There were 10 other partners involved in the project: BRGM, BGR, IGME, MAFI, TNO, NITG (these are the geological surveys of France, Germany, Greece, Hungary and the Netherlands respectively), University 'la Sapienza' Rome, University of Aachen, Germany, the IEA Greenhouse Gas R&D Programme, Statoil and BP.

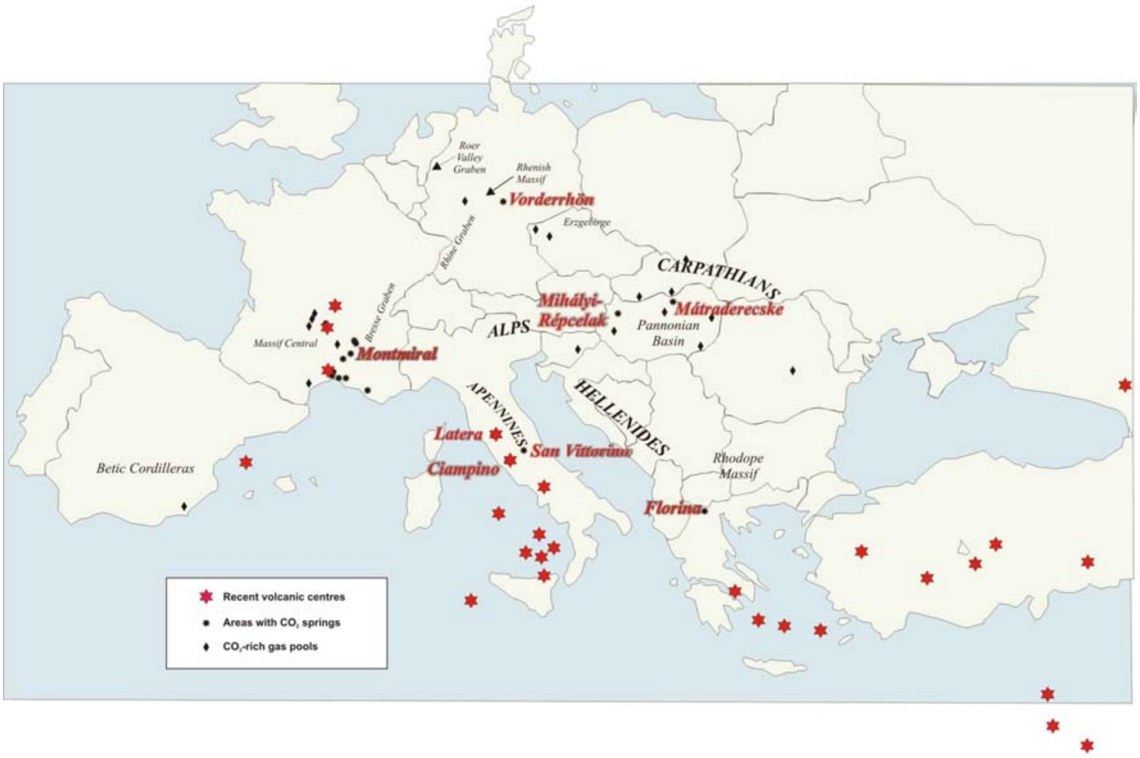

Figure 1.1: Location map of sites studied during the Nascent project, excluding the offshore sites in the North Sea.

1.3. OBJECTIVES

Natural CO_2 accumulations provide ideal analogues for CO_2 storage underground. NASCENT has provided an understanding of some of the potential risks of geological storage. The project had the following objectives:

- Proof of concept – does the existence of natural CO_2 accumulations offer confidence that long term geological storage is a viable and safe option?
- What hazards, such as seismicity, ground movement, groundwater contamination, or leakage to the biosphere and atmosphere, might be associated with geological storage of CO_2?
- Can predictive models and laboratory experiments be verified by processes identified in natural systems?
- Demonstration of trapping mechanisms – what geological structures trap CO_2? What geological conditions have resulted in release of naturally generated CO_2 to the biosphere and atmosphere?
- Gas monitoring – where CO_2 is exploited, information can be obtained on field management techniques

1.4. NASCENT OUTCOMES

The Nascent project has developed and demonstrated methodologies for monitoring CO_2 leakage above natural accumulations. These methodologies are appropriate for use above repositories to establish baseline conditions and to monitor sites at the surface during and after storage. These methodologies could be further developed as standards for monitoring CO_2 leaks above storage sites, both offshore and onshore. Soil gas surveys and analyses of gas leakage rates have defined how CO_2 migrates through the near surface environment. Design specifications for monitoring equipment can be used by field operators and engineers (see Pearce et al, 2003). National and European regulators, safety assessment advisers and license-issuers could use detection limit and sampling interval specifications to define environmental impact assessment criteria.

Data produced during the project has been used to further validate predictive geochemical models and geomechanical models. There can now be greater confidence in these models to predict how CO_2 will behave during and after storage and will help to determine how much of the CO_2 will be permanently sequestered through mineral reactions. Regulators and public health officials can use indicators that show the effects of CO_2 on aquifers to monitor storage operations and define protocols and standards.

A web-enabled GIS-based support system has enabled collation, interpretation, and presentation of data about these natural accumulations. It can be used to identify those processes and situations that increase the potential risks from CO_2 leakage. In this way, field operators, license-issuers and regulators can mitigate against such risks during design and location of storage facilities.

Providing examples of natural systems where CO_2 has accumulated and been trapped for geological timescales will build confidence in the concept with non-specialist policy-makers, environmental NGOs and the public.

Chapter 2. Interactions in reservoirs

2.1. SUMMARY AND CONCLUSIONS

This chapter summarises long-term geochemical and geomechanical processes that could occur in the reservoir. For geological storage, 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 influence its long-term storage performance, can be tested by modelling natural analogues of geological storage. In addition, information on how CO_2 might migrate from the initial storage reservoir through fractures, and about processes that could occur in fractures in limestones, has been obtained in this study.

To address these issues, several geological sites were studied. The sites were selected because relevant supporting background data were already available and, for the geochemical modelling, data could be obtained from rocks, waters and gases. The availability of these samples enabled detailed models of past behaviour to be created, which could then be compared with the geochemical and geomechanical modelling.

The sites chosen, therefore, were the natural CO_2 fields in the Florina Basin, northern Greece and the Montmiral field in the Southeast Basin in France, plus the Sleipner natural gas field on the southern edge of the Viking Graben in the North Sea. The geomechanical modelling work was led by TNO with collaboration and analytical support from Statoil and IGME. The geochemical work was led by BRGM with collaboration from BGS and IGME.

At Florina, the quantitative impact of geochemical reactions is minor, due to the replacement of one mineral (siderite) with another (Fe oxide, probably goethite). Geochemical modelling indicates that the system is far from equilibrium and, as observed in petrographic examination of cores from the Florina CO_2 accumulation, CO_2 is not being precipitated as a carbonate mineral.

Montmiral is one of several small CO_2 gas accumulations in the Southeast Basin of France. There are also numerous CO_2-rich springs and gas vents throughout the region, some of which are exploited as mineral waters. The CO_2 is considered to be of deep crustal or mantle origin. 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 not related to changes in water chemistry, but due to changes in the respective volumes of discharged brine and CO_2-H_2O gas mixture. The brine is derived from an evaporated Triassic seawater that underwent dilution by meteoric water before, or at the same time as, the CO_2 invasion. The brine composition indicates that the CO_2-water-rock system is not at equilibrium. Diagenetic studies suggest that introduction of CO_2 into this particular reservoir caused dissolution of feldspar, and a slight increase in reservoir porosity. Modelling suggests that dissolution of feldspar leads to some precipitation of kaolinite, carbonates and chalcedony (though the latter was not observed in the reservoir rock). For the model to achieve the porosity changes observed, it had to be assumed that the system was open, i.e. the reservoir has been flushed with fresh CO_2-charged waters. Even after contact times of at least hundreds of thousands of years, feldspars are still present in both cases. This illustrates that reaction kinetics, based on short term kinetic data derived from the literature, can be much slower than expected. 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.

Injection of CO_2 into a subsurface reservoir may have an impact on the mechanical integrity of that reservoir and its surroundings. The main cause would be the changes of reservoir pressure related to the injection of the CO_2. Geomechanical modelling was performed to assess the impact of CO_2 injection on:

- the mechanical integrity of the reservoir rock and the caprock;
- the potential for fault re-activation, which could trigger induced seismicity in the area of CO_2 injection;
- ground deformation (subsidence and uplift).

The stress and deformation in the subsurface and at the ground surface, caused by CO_2 extraction and injection, were computed on a 2D numerical stress model of the Montmiral field. The maximum subsidence rate at full depletion was predicted to be of the order of 5 cm. During injection, when the reservoir pressure is equal to the virgin pressure, the state of stress on the fault is the same as it was in the initial state of stress. CO_2 injection above the virgin reservoir pressure shows a critical stress development until the Mohr-Coulomb failure criterion has been reached. At failure, a slip on the fault occurs and the stress path further follows the failure line. The rate of plastic shear displacement along the fault is about 1 cm.

Geomechanical numerical modelling of the Sleipner West Field was carried out in order to predict changes in the *in situ* stress field and the associated deformation, induced by reservoir depletion and by subsequent CO_2 injection into the reservoir. In contrast to the current practice of the ongoing Statoil injection project, a scenario was assumed in which CO_2 would be injected into the Hugin Formation, the reservoir from which the natural gas and condensate had been previously produced. In the modelled scenarios, reservoir depletion was followed by a CO_2 injection phase, until the final pressure was reached, equal either to the initial reservoir pressure or to 50% higher. The model predicts the mechanical stability of the reservoir rock does not deteriorate as a consequence of reservoir depletion.

The effect of subsequent CO_2 injection is the opposite. The effects on the reservoir rock become more important at injection pressures that exceed the original virgin pressure. If injection pressures reach the minimum horizontal principal effective stress in the subsurface, a tensile failure will be initiated. However, the maximum reservoir pressure at the end of the injection phase did not exceed the minimum horizontal stress. Consequently, the mechanical stability of the reservoir rock is not expected to deteriorate, even if CO_2 injection pressures reached up to 50% higher than original reservoir pressure. However, at a pressure of 1.5 times higher than the original reservoir pressure, reactivation of bounding faults are predicted to occur.

Since the outcome of geomechanical modelling depends on a whole range of local and site specific parameters, it is difficult to draw general conclusions from two specific cases. A case specific geohazard assessment study will always be needed for any CO_2

injection site. Nevertheless, from the Montmiral and Sleipner fields a few conclusions can be drawn that are probably often generally applicable.

In both fields, modelling showed that:

- the mechanical stability of the reservoir rock does not deteriorate as a consequence of reservoir depletion.
- in the injection scenarios the effects on the reservoir rock are the opposite and the stress path development may become critical.
- As a long as the reservoir pressure is not raised above the level of the original virgin pressure in the reservoir, mechanical failure does not occur. Above that level the risk of failure increases. The extent of this risk again is strongly dependent on the specifics of the site under consideration.
- Similar considerations apply for the stability of bounding faults to the reservoir.

As far as subsidence and uplift of the ground surface or seafloor is concerned:

- assumed elastic behaviour of the rocks implies that CO_2 injection up to the virgin reservoir pressure will fully reverse any deformation (subsidence) caused by depletion.
- Further injection will cause the uplift.
- However, many rocks do not behave as ideal elastic materials over wide loading/unloading ranges such as those imposed by reservoir depletion, and therefore, deformation caused by loading is often not fully recoverable in unloading.
- It is reasonable to expect that injection of CO_2 will only result in very limited amounts of uplift.

2.2. INTRODUCTION

Two sites, at Montmiral, in the South-east Basin of France and at Messokampos in the Florina Basin of northern Greece, offered unique opportunities for detailed studies of the long-term interactions between CO_2-rich porewaters and reservoir rock. Knowledge of the chemical composition of the brine associated with the CO_2 within the reservoir contributes to formulating hypotheses on the origin and chemical composition of the water present before CO_2 invasion, and it also contributes to identifying chemical reactions induced by this invasion. With the knowledge of mineralogy, it constitutes a prerequisite to further detailed modelling subsequent to CO_2 injection.

BRGM conducted chemical and isotopic investigations of brine associated with the CO_2 in the Montmiral reservoir and of rock samples from the reservoir and caprock, as well as the subsequent geochemical modelling. BGS collaborated with BRGM and IGME, performing diagenetic and fluid inclusion studies of reservoir, caprock and mineralised fractures. Geochemical modelling of the Florina accumulation was conducted through collaboration between BRGM and IGME.

2.2.1. Montmiral Site

Several CO_2-rich gas pools and occurrences occur throughout the Ardèche palaeomargin of the Southeast Basin of France (Figure 2.1; more information can be found in Pearce, 2003). The Southeast Basin is located to the southeast of the Massif Central and is bounded to the east and south by the Tertiary thrust belts of the western Alps and the Pyrenees-Provence. The CO_2 occurrences are located along major fault systems, which, in the Massif Central, may be seen cropping out in the basement, related to the margins or to deep extensional structures of the Southeast Basin. Th Southeast Basin corresponds to the present Rhône river and tributary valleys and extends offshore in the Golfe du Lion. Montmiral is located in the northern part of this domain.

Oil exploration in the Southeast Basin has often been disappointed by the discovery of CO_2 rather than hydrocarbons, eight accumulations being discovered in total. This CO_2 is now extensively exploited by the sparkling mineral water industries centred around Vichy, Badoit and Perrier. As with other significant CO_2 occurrences throughout Europe, much (though not all) of this CO_2 appears to be of mantle or deep crustal origin. Reservoirs are in Lower Jurassic and Triassic limestones, dolomites and sandstones at depths of between 2000 and 5000 m depth. Among them, only the Montmiral site is currently exploited (Figure 2.1), with production starting in 1990.

CO_2 occurrences occur below 2400 m depth at Montmiral in both the Early Jurassic Hettangian marine and pelagic deposits, and Late Triassic Rhaetian and earlier, terrestrial or continental shelf evaporitic sediments. Layers of Late Triassic anhydrite, clays and dolomite separate the two CO_2 occurrences. The main CO_2 reservoir is within the lower Triassic sandstone. The caprocks are partly siliceous Sinemurian clayey limestone.

Although CO_2 is locally trapped below Triassic sequences of claystones, limestones and evaporites (mainly anhydrite but also halite), the many CO_2-rich springs and mineral waters provide evidence for CO_2 migration to the surface, through these caprock sequences. It is assumed that migration occurs along fractures and faults.

In order to assess the geochemical interactions between CO_2 and reservoir and caprocks at Montmiral, the research was focussed on the following activities:

- Assessing the origin of the CO_2-brine being produced today at the well-head through interpretation of detailed geochemical analyses, including isotopic analyses, of production waters and gases.
- Construction of a detailed geological model of the Southeast Basin with special focus on the Montmiral area.
- Detailed diagenetic studies of the Triassic reservoir rock, including comparisons with apparently equivalent lithologies from nearby boreholes that do not contain CO_2 to determine the effects of CO_2 on reservoir sandstones.
- Petrographic and fluid inclusion studies in mineralised fractures immediately above the reservoir to determine past history of CO_2 migration out of the reservoir.
- Geochemical modelling of the CO_2-water interactions in the reservoir and in the fractures.

More details of these investigations are available in Pearce (2003).

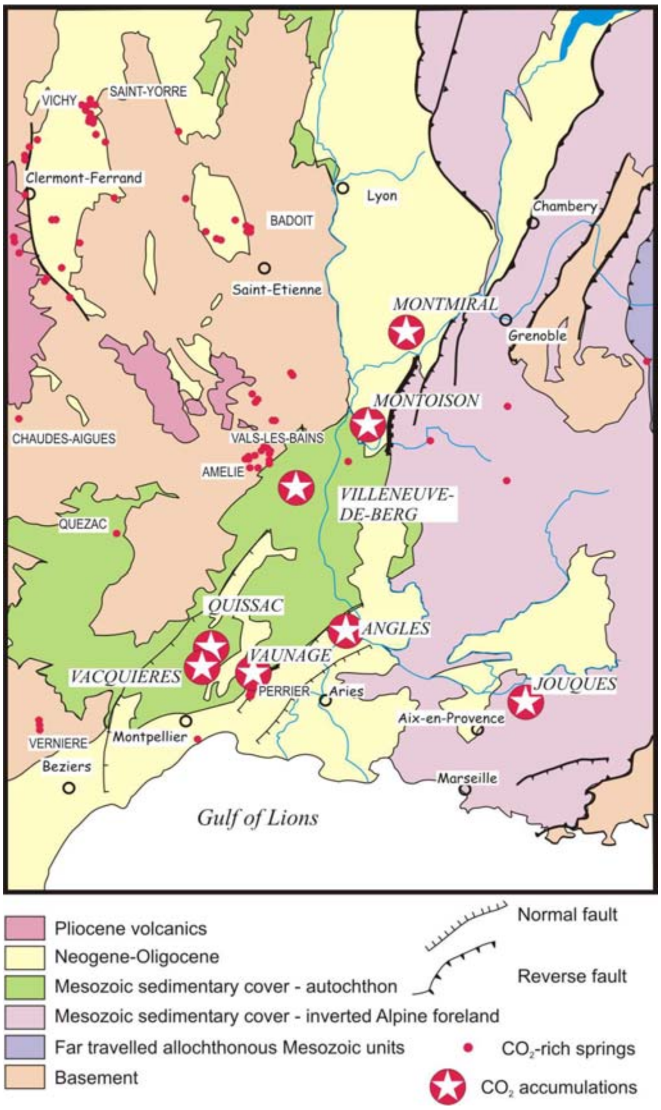

Figure 2.1: Simplified geological map showing locations of main CO_2-rich springs and accumulations across the Southeast Basin of France and part of the Massif Central.

2.2.2. Florina Site

The Florina CO_2 field is located in northern Greece on the border with the Former Yugoslav Republic of Macedonia (FYROM) (Figure 2.2). From the geological evidence it is possible that it extends into this country, too. It has been a producing field for more than 10 years with an annual production, during the last 2-3 years, ranging between 20,000 and 30,000 tons of CO_2. The produced CO_2 is sold to domestic markets, mainly in the food and cryogenics industries.

The CO_2 accumulation occurs close to the surface (top of reservoir at a depth of 300 m) (Figure 2.2), at low pressure with some of the CO_2 dissolved in the groundwater. There are many mineral springs and wells in the wider area of the basin, resulting from a slow upward movement of CO_2 along rock discontinuities. The CO_2 composition is very pure, with CO_2 content > 99.5% with traces of methane and other gases. CO_2 occurs in Miocene sands alternating with silt and clays forming a layer-cake reservoir capped by several tens of meters of clay which form a good seal. More information can be found in Pearce (2003).

This NASCENT investigation is the first time that a detailed geological study of the CO_2 field has been carried out. Research at Florina included:

- Detailed diagenetic studies of newly acquired core samples from CO_2-rich zones in a fully-cored borehole drilled for this project.
- Detailed groundwater sampling from this new borehole
- Geochemical modeling of potential CO_2-water-rock interactions at Florina.

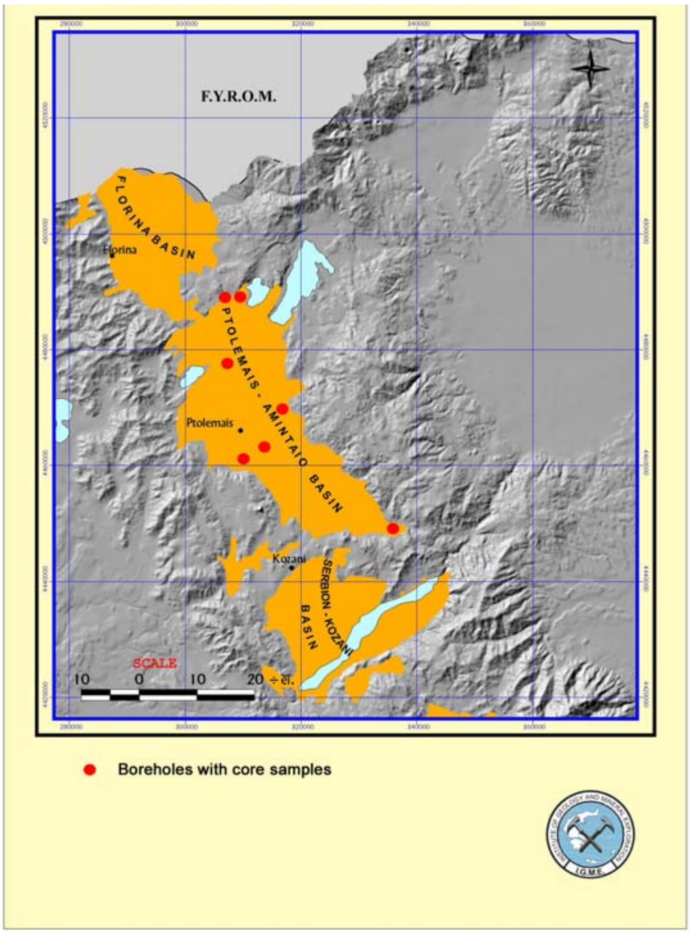

Figure 2.2: Graben of Florina-Ptolemais

2.3. HOW WILL CO_2 INTERACT WITH SILICICLASTIC RESERVOIRS?

2.3.1. Assessing evolution of the modern day CO_2-rich brine at Montmiral

A detailed assessment of the present chemical and isotope composition of the Montmiral CO_2-rich reservoir brine at reservoir conditions has been undertaken on the basis of surface fluid sampling at the well head of the CO_2 producing well. The gas-water ratio and detailed chemical and isotopic analyses of both the water phase and gas phase have been determined (Pearce et al., 2003). Comparison of the present-day chemical composition of the water collected at the well head with those determined from previous samples, which have been collected since production started, revealed that the produced water evolved with time to reach a salinity of more than 75 g/l. This temporal variability is not related to an evolution of the chemical composition of the water within the reservoir from a freshwater to a brine, but has been explained by an evolution of the respective volumes of discharged brine and CO_2-H_2O gas mixture. CO_2 gas and reservoir brine ascend together through the pipeline from the reservoir to the well-head (Figure 2.3). However, CO_2 is saturated with H_2O and due to the high CO_2/brine ratios, the condensation of H_2O within the phase separator induces a dilution of the brine (Figure 2.3). The temporal variability may therefore be explained as the result of variable proportions of H_2O and brine in the collected water; proportions that could be estimated in samples collected within the frame of this project thanks to the availability of gas and water flow rate data. Knowledge of the respective proportions of brine and H_2O enabled us to determine the chemical composition of the brine. The isotope (δ^2H, $\delta^{18}O$) composition of the brine was also calculated.

The procedure described above to determine the chemical composition of the deep brine has been possible thanks to the availability of two different CO_2 flow-rate / water flow-rate ratios. Such conditions will not be always available; in some cases, only a single reading of the gas and water flow-rates may have been made during production. However, the present study enabled us to propose a methodology based on isotope composition ($\delta^{18}O$ data for water and SO_4 or CO_2) for determining the $\delta^{18}O$ of the brine. This methodology is described in WP2 report and in Pauwels et al. (in press).

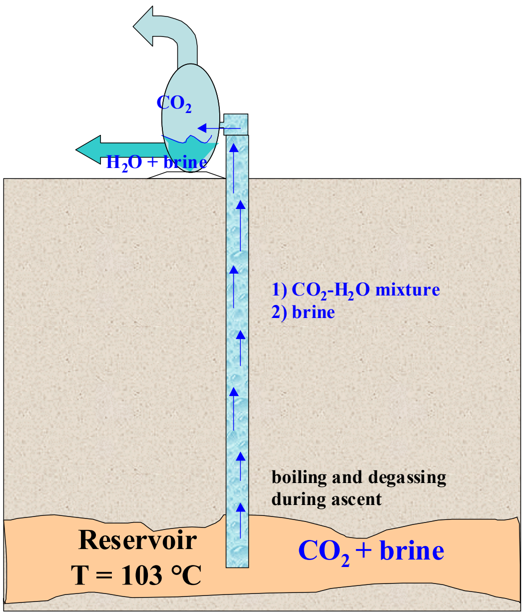

Figure 2.3: Schematic concept of processes occurring during CO_2 discharge from the reservoir to the wellhead, resulting in brine dilution by H_2O condensate in the gas separator.

The reconstituted brine has a salinity of more than 85 g/l and, according to its bromide content and isotope (δ^2H, $\delta^{18}O$, $\delta^{34}S$) composition, originates from an evaporated Triassic seawater that underwent dilution by meteoric water before, or at the same time as, the CO_2 invasion. Evaporation did not, however, exceed the halite precipitation point. Major-element (Na, K, Ca, Mg) concentrations are either higher or lower than would be expected from the degree of evaporation, which is taken as indicating the occurrence of dissolution and precipitation reactions (Figure 2.4), some of them being due to CO_2 invasion. The reconstitution of the brine's chemical composition thus enabled an evaluation of the water-rock CO_2 interactions based on comparison between mineral saturation indices and solid phase examinations. The chemical composition of the brine is close to equilibrium with respect to only a few minerals such as anhydrite, calcite and chalcedony, clearly indicating that the water-CO_2–rock system is currently not at equilibrium. The brine is undersaturated with respect to albite, which is consistent with the observed removal of albite.

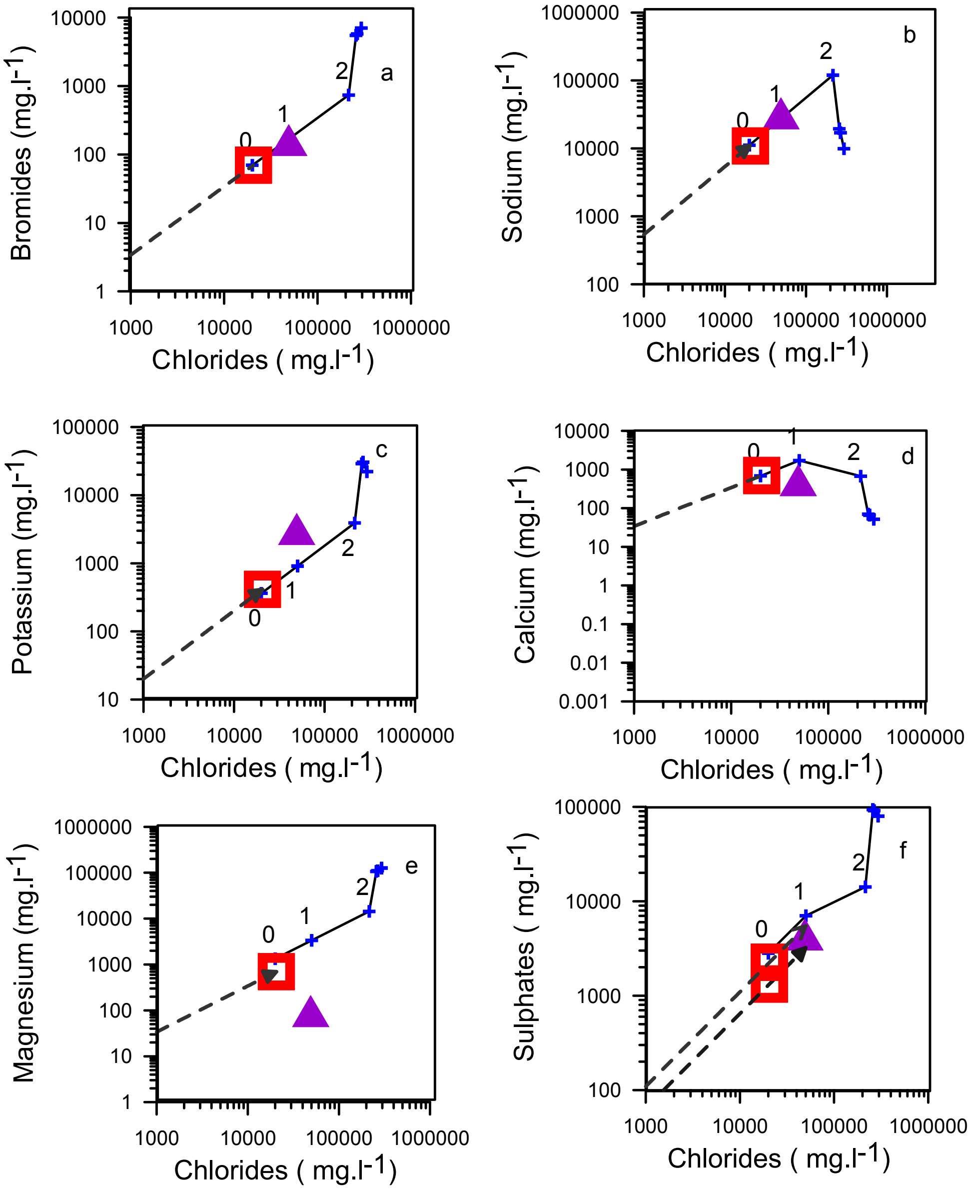

Figure 2.4: Chemical composition of the deep brine compared to the sea-water evaporation line; a) Br, b) Na, c) K, d) Ca, e) Mg, f) SO_4 versus Cl.
0: seawater; 1: gypsum precipitation point; 2: halite precipitation point
Purple triangles: Montmiral brine; Red open squares: Triassic seawater.

2.3.2. Assessing CO_2 interactions with siliciclastic reservoir rocks at Montmiral and Florina

Reservoir sandstones from the Montmiral CO_2-production borehole have experienced a similar diagenetic evolution to those of broadly equivalent lithology from St. Lattier that do not contain CO_2, although the relative significance of each event varies slightly between samples. Early diagenesis is marked in the St. Lattier sandstones by the presence of micritic calcite cement, which is either absent or only very poorly developed at Montmiral. These differences reflect differences in stratigraphic setting.

The most significant difference between reservoir and non-reservoir sandstone, however, is the greater degree of secondary porosity developed at Montmiral (3.8%

total secondary porosity from point counting) relative to St. Lattier (0.5% total secondary porosity from point counting) (Figure 2.5). This additional secondary porosity results from dissolution of K-feldspar, a rock-forming mineral and, although there was slightly more original feldspar at Montmiral prior to dissolution, the relative proportion of secondary porosity is higher at Montmiral i.e. there has been more K-feldspar dissolution at Montmiral. This is likely to be due to interactions with CO_2-charged waters at Montmiral. This hypothesis was subject to testing by geochemical modelling (Section 2.4).

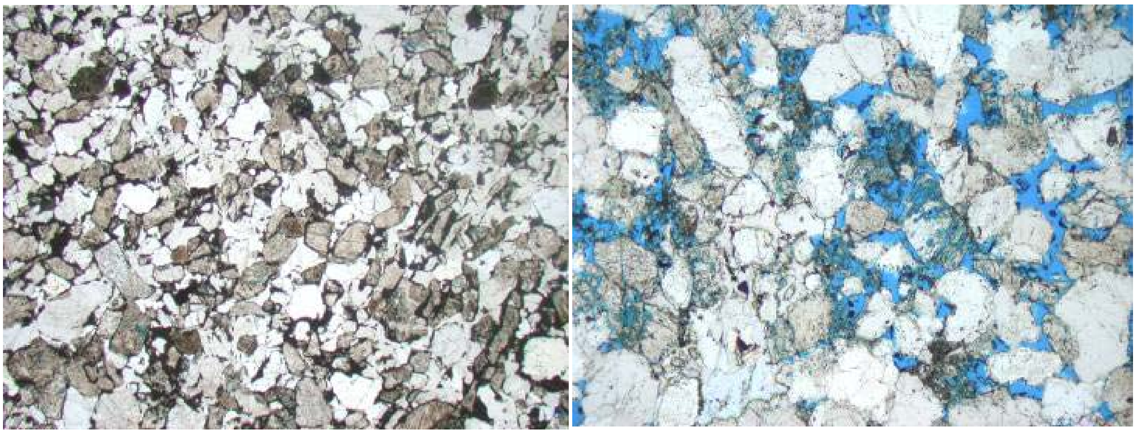

Figure 2.5: Comparison between broadly equivalent Triassic sandstones, showing differences in degree of porosity (indicated in both images by the blue colour): Left – From Saint Lattier, where no CO_2 is present; Right – from Montmiral – CO_2 production borehole. Field of view is 3.5 mm

At Florina, a detailed diagenetic study indicated that the latest diagenetic events - calcite corrosion, siderite breakdown and replacement by iron oxide, and precipitation of gibbsite are only recognised at depths below 390 m from the surface. These events may be attributable to the reaction of low pH CO_2-charged waters, since both calcite and siderite are expected to be unstable in low pH waters. Subsequent modelling (Section 2.4) tested this hypothesis.

2.4. HOW HAS OUR CONFIDENCE IN OUR PREDICTIVE MODELLING CAPABILITIES IMPROVED?

Geochemical modelling is applied to two sites studied within the NASCENT-project: Montmiral (Southeast Basin, France, 100 °C, 360 bar) and Messokampos (Florina Basin, Greece, 25 °C, 5 bar). The Montmiral and Florina natural analogues show many differences which have a large impact on the modelling itself as well as on the modelled results. While the Montmiral reservoir is a high-pressure and high-temperature reservoir at great depth, Florina is a shallow, low-pressure and low-temperature reservoir. From a mineralogical viewpoint however, differences are less marked since both are essentially sandstone reservoirs. Petrographic characterisation of the reservoirs enabled the effects of CO_2-induced geochemical interactions on reservoir lithologies to be identified. Geochemical modelling reproduced the observed effects, identified their driving parameters and assessed their impact in terms of potential mineral trapping and porosity changes.

In both cases, two types of modelling were applied. The first type was batch modelling while imposing a constant CO_2 fugacity on the formation water and the rock. This allowed the main reactions, which occur as a consequence of the imposed CO_2 fugacity, to be identified. The second type of modelling was flow-through modelling whereby the flow is incorporated in the geochemical reactions (still assuming thermodynamic equilibrium is established). Flow-through modelling allows the impact of geochemical reactions on the reservoir rock to be reproduced. Both types of modelling were executed assuming thermodynamic equilibrium is established instantaneously as well as taking into account full reaction kinetics.

The purpose of the modelling of the *Montmiral reservoir* was to:

- Confirm the observations of the petrographical analysis by reproducing the geochemical reactions caused by elevated CO_2 concentrations in the formation water;
- Explore the temperature and pressure conditions under which these reactions can take place;
- Investigate if the observed secondary porosity can result from the identified reactions.

In the case of the *Florina reservoir*, the modelling objectives were to reproduce potential reactions attributed to CO_2 interactions, including siderite dissolution, precipitation of iron oxides and gibbsite and to check their impact on the reservoir porosity.

The modelling of both the Florina and the Montmiral sites showed that geochemical reactions potentially leading to CO_2 storage can be identified and can reproduce the petrographical observations in both cases (Figure 2.6). Although the conditions are very different, in both cases the key interaction between dissolved CO_2, the formation water and the reservoir rock is feldspar alteration. In the case of Montmiral, K-feldspar dissolution induces the precipitation of kaolinite, some carbonates and chalcedony (although chalcedony precipitation was not confirmed in petrographical observations). In the case of Florina, albite and ankerite dissolution triggers the precipitation of gibbsite and iron oxides.

At Montmiral, this impact is significant in terms of increase in secondary porosity, while at Florina the quantitative impact of geochemical reactions is minor. Even after contact times of at least hundreds of thousands of years, feldspars are still present in both cases. This illustrates that reaction kinetics, based on short-term kinetic data derived from the literature, can be much slower than expected. It has been suggested that feldspar-rich sandstones would be beneficial target reservoirs for CO_2 storage because reacting CO_2 with feldspars and then precipitating the CO_2 as a carbonate results in permanent mineral storage. The results of this research indicate that, following geological storage, it would take hundreds of thousands of years for the feldspar in a reservoir to react with CO_2. This timescale should therefore be considered if mineral trapping is to be utilised. The reservoir temperature is identified as an important parameter when assessing the storage capacity of a reservoir, with reaction rates potentially increasing by orders of magnitude where high temperatures prevail.

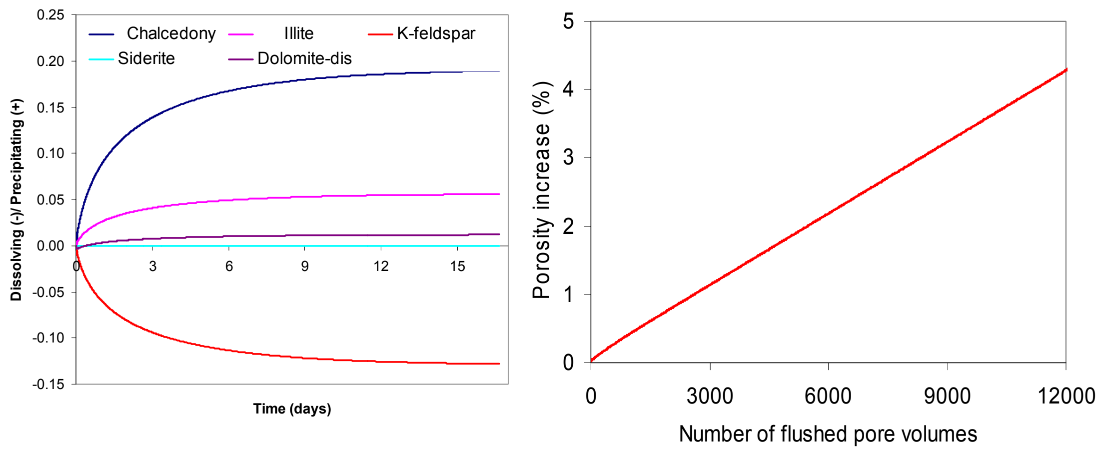

Figure 2.6: Geochemical modelling examples. Left: Mineral precipitation and dissolution in the Montmiral reservoir when taking into account reaction kinetics (closed system – kinetic batch modelling at 150°C, 50 MPa). Right: Porosity increase modelled in the Montmiral rock during flushing with CO_2-loaded formation water (open system - 150°C, 50 MPa).

The fact that reaction rates are much faster at Montmiral than at Florina required a different modelling approach. For the Montmiral case, the assumption that thermodynamic equilibrium is in place between the dissolved CO_2, the formation water and the reservoir rock, was demonstrated to be acceptable, allowing complex calculations to be executed within reasonable CPU calculation times. This assumption did not hold for the modelling of the Florina case. In order to gain insight into the reactivity of the system a full kinetic approach was necessary whereby reaction rates of all selected minerals were taken into account. Long CPU-calculation times necessary for these types of runs imply that the number of runs that can be executed is limited.

Both the Montmiral and Florina sites were studied in detail and a significant amount of accurate information was gained on their mineralogical and petrographical conditions, as well as on the nature of the CO_2 present and the geological history of the reservoir. However, the geological history of the site, with its tectonic activity, variations in pressure and temperature, the potentially phased CO_2 movement within the reservoir, as well as the existence of changing flow regimes of the formation water, prevent a sufficient level of detail to be obtained, which is necessary for the kinetic calibration of the geochemical models. Consequently, the kinetic rates of geochemical reactions attributed to CO_2 interaction cannot be reconstructed in the two cases studied.

Dawsonite is often referred to as an important CO_2-trapping mineral (e.g. Johnson and Nitao, 2002). However, dawsonite was not identified during the petrographical analysis at either Florina or at Montmiral. The modelling confirmed that under the observed conditions it was unlikely to precipitate. This does not exclude however that under different reservoir conditions (e.g. high pressure reservoirs containing evaporites) mineral trapping via dawsonite could have a significant impact.

The conclusions formulated are based on the findings derived from the modelling of two natural analogues only. It is clear that the potential geological and physical variability in current and future CO_2-storage projects is such that more natural analogues must be studied in order to confirm or refine our knowledge of long term CO_2-induced geochemical interactions. Though the directions, magnitude and rates of reactions will be site specific, increasing the number of examples studied will help to identify those processes that are more widely applicable. It is envisaged that before a site is selected for CO_2 storage, an assessment of the likely geochemical interactions within the reservoir could be made to determine long-term mineral trapping potential and CO_2 behaviour, with the increased confidence in the methodologies and results obtained through investigations such as those performed in this project.

2.5. HOW WILL CO_2 AFFECT THE MECHANICAL INTEGRITY OF THE RESERVOIR?

2.5.1 Introduction

Injection of CO_2 into a subsurface reservoir may have an impact on the mechanical integrity of that reservoir and its surroundings. The main cause for such a potential impact would be the changes of reservoir pressure related to the injection of the CO_2. In this respect injection of CO_2 is similar to injection of natural gas in underground gas storage (UGS) projects. Nowadays, UGS is common practice world-wide and technology exists to predict the possible geomechanical effects of increasing the reservoir pressure as a result of gas storage and subsequently decreasing the pressure again when retrieving the gas.

In the NASCENT project, such technology was applied in two case studies, thus making a geohazard assessment for two NASCENT sites. Geomechanical modelling was performed using TNO's finite element numerical modelling software package DIANA. Given sufficient input data this software package is capable of assessing the impact of CO_2 injection on:

- the mechanical integrity of the reservoir rock and the caprock;
- the potential for fault re-activation, which could trigger induced seismicity in the area of CO_2 injection;
- ground deformation (subsidence and uplift).

In principle it is possible that CO_2 would have an additional effect on the mechanical properties of the reservoir, because it can chemically interact with the reservoir rock (see Section 2.3) and thus change the rock strength parameters of the reservoir rock. Since these chemically induced changes in geomechanical properties are to some extent unknown, or at least cannot be quantified, this additional factor could not be taken into account in the geomechanical modelling. However, compared to the effects of the pressure changes, this unknown effect is expected to be small.

Extensive input is required for geomechanical modelling. In addition to the usual geological characterisation, the subsurface has to be characterised in terms of physical and mechanical rock properties. Existing in situ stresses and at least some reservoir engineering data, such as initial CO_2 pressures in the reservoir, are necessary. The initial data review performed in this project showed that hydrocarbon fields and CO_2 fields that are, or have been, in production generally provide more complete data sets for numerical geomechanical modelling than non-exploited natural analogues. Mainly for this reason we have selected for the geomechanical modelling the Sleipner field, which is a hydrocarbon reservoir and a CO_2 injection site, and the Montmiral field, which is a natural CO_2 accumulation that is currently being exploited.

2.5.2 Geomechanical modelling of the Montmiral CO_2 accumulation

The Montmiral site is the only natural CO_2 accumulation in the French Carbogaseous Province to be exploited. Available data about this site comprise regional geological data, well completion data and, in contrast to the other natural CO_2 accumulations in the area, some reservoir engineering data (Pearce, 2001). The Montmiral field was therefore selected to study potential anthropogenic geological hazards related to CO_2 extraction and injection. The human-induced geological hazards considered here are subsidence, uplift and induced seismicity, caused by fault reactivation. The results obtained provide fundamental insight into, and understanding of, causes of geohazards, related to gas extraction and injection. The preliminary results of this modelling study were presented in Orlic (2003). The main objective of the geomechanical numerical modelling was to predict changes in the stress field and associated deformation induced by past and future CO_2 extraction from the reservoir, followed by future CO_2 injection. It has been assumed that the reservoir will be first fully depleted, and then used for CO_2 storage. The final pressure in the reservoir, after CO_2 injection, was assumed to be at or above the initial (virgin) reservoir pressure.

The stress and deformation in the subsurface and at the ground surface, caused by CO_2 extraction and injection, were computed on a 2D numerical stress model of the Montmiral field. A plane strain finite element model was developed, based on a lithostratigraphic/structural cross-section supplied by BRGM (Figure 2.7). The numerical model generally preserves the lithostratigraphic division from the geological cross-section and includes a major fault (Figure 2.8). Differentiated geomechanical model units were characterised by the physical and mechanical properties, which were determined from literature and rock mechanics tests. The tests were conducted on samples taken from the core of the V.Mo.2 well. Initial loading conditions for the model were determined taking into account the weight of overburden, the initial reservoir pressure and the existing state of stress in the study area.

The initial stresses in the model were initialised by applying the gravity load and the fluid pressures present in the subsurface. Withdrawal of gas from the reservoir was then modelled by decreasing the fluid pressure in a step-wise manner. Subsequent CO_2 injection in the depleted reservoir was modelled by increasing the pressure until the end pressure, which was set to be either equal to the initial (virgin) reservoir pressure (37 MPa) or 50% greater than the initial pressure. A 20-year long depletion period, from 1990 to 2010, was assumed to be followed by a 20-year long injection period, until 2030.

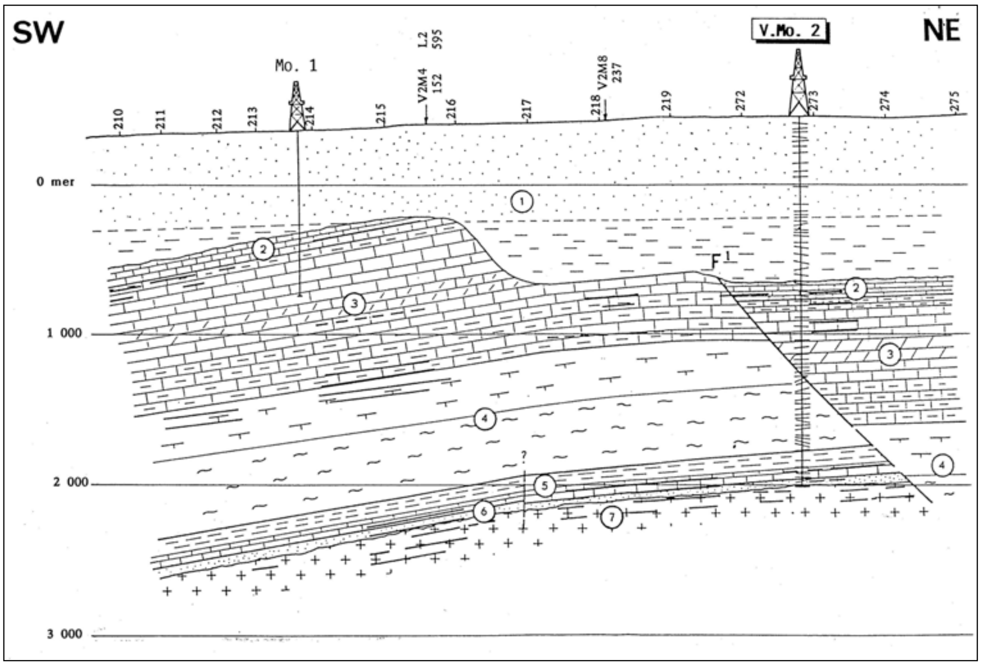

Figure 2.7: Lithostratigraphic/ structural cross-section interpreted from the seismic profile V2M6. Unit 6 includes the Triassic sandstones containing CO_2.

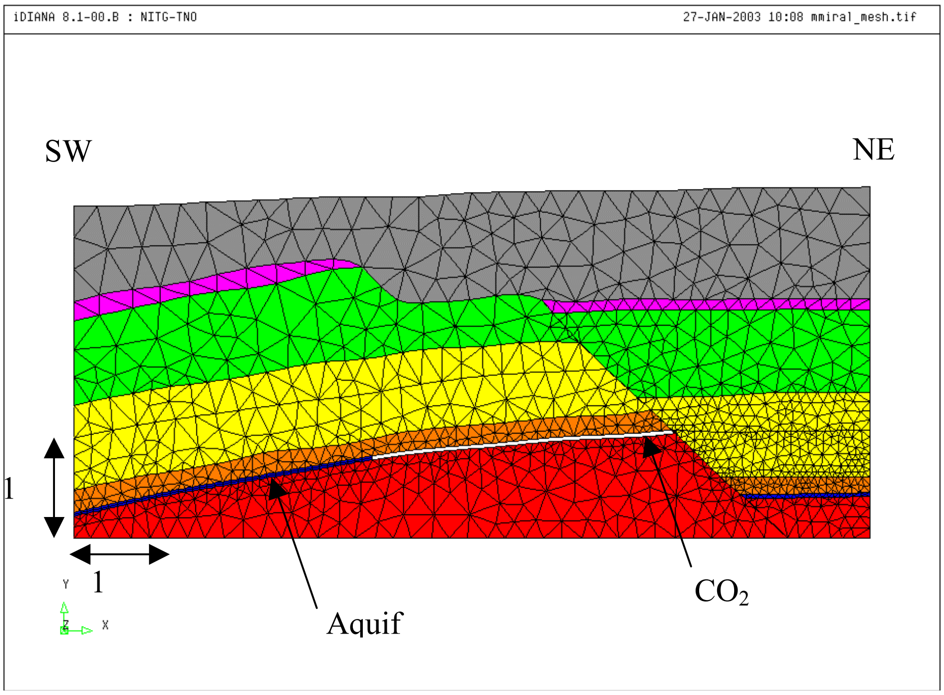

Figure 2.8: Finite element model of the Montmiral field.

For the characterisation of the cap rock and the reservoir rock, samples were collected from available cores from the V.Mo.2 well and additional rock mechanics tests were conducted by IGME. In total eight uniaxial compressive strength tests with determination of elasticity modulus and Poisson's ratio were carried out, and three point load tests. An overview of geomechanical parameters, used to characterise the geomechanical units and faults, is presented in Orlic and Schroot (2004). An elasto-plastic constitutive model, according to the Mohr-Coulomb plasticity, is assumed for both the reservoir and other units.

The pore pressure histories over the full CO_2 extraction and injection cycle determined the input pressure loads for DIANA stress modelling. The pore pressure changes in the reservoir and in those parts of the fault, which are bounded by the reservoir, while the other parts of rock are unaffected. The changes are spatially uniform throughout the gas reservoir and linear in time.

The full CO_2 extraction and injection cycle comprises reservoir depletion from 1990 until 2010, followed by projected CO_2 injection, from 2010 to 2030 (Figure 2.9). Reservoir depletion was modelled by decreasing the pore pressure in the reservoir and in the part of fault that is located in the initially overpressured part of the reservoir. During depletion, the pressure in the reservoir drops from the initial value of 37 MPa to 0 MPa.

Subsequent CO_2 injection was modelled by increasing the pore pressure. Two injection scenarios were considered. In the first scenario, the reservoir pressure at the end of injection period is equal to the original, virgin reservoir pressure. In the second scenario, the end pressure is 1.5 times greater than the initial reservoir pressure.

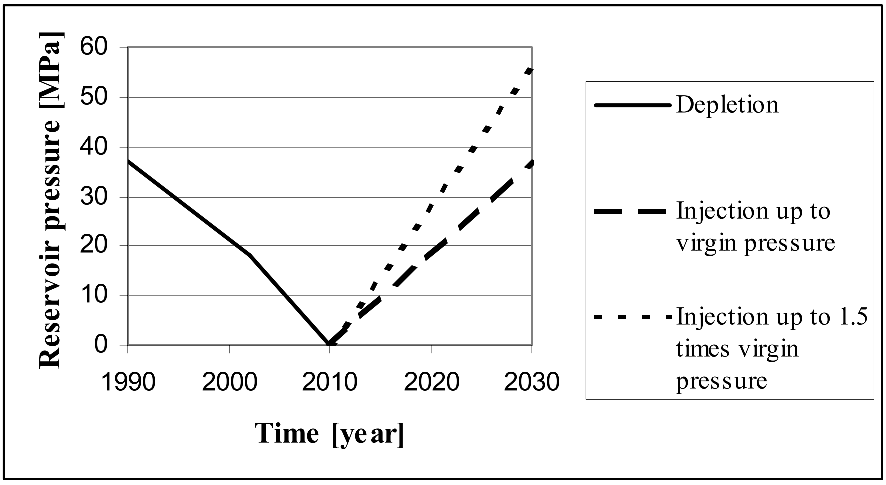

Figure 2.9: Pressure histories for two simulated scenarios of CO_2 extraction and injection.

Stress and deformation due to CO_2 extraction and injection:

The maximum subsidence rate of 5 cm at full depletion is based on the numerical model with a non-calibrated elastic material model. Predicted subsidence therefore does not have absolute meaning, but it indicates a realistic order of magnitude of subsidence that could occur due to CO_2 extraction.

Due to the elastic behaviour of the rock, CO_2 injection up to the virgin reservoir pressure will fully reverse deformation caused by depletion. Further CO_2 injection above the virgin reservoir pressure will cause an uplift. The maximum uplift will reach 50% of the maximum subsidence rate, at reservoir pressure equal to 1.5 times the virgin pressure. The potential for fault reactivation during CO_2 extraction/injection is analysed using a graphical means of presentation.

The stress path presented in Figure 2.10a shows that the fault is initially stable, but that over 90% of its shear resistance (i.e. strength) to slip has been mobilised. During depletion, the stress path diverges from the failure line, meaning that the stress development is not critical and the stability of fault improves. The rate of elastic shear displacement along the fault is very small, up to 1 mm.

Contrary to depletion, the stress path during CO_2 injection converges towards the critical line, meaning that the stress development is critical (Figure 2.10b). At the reservoir pressure equal to the virgin pressure, the state of stress on the fault is the same as it was in the initial state of stress, before CO_2 extraction. Due to the elastic response of the fault to injection up to the virgin reservoir pressure, the stress path for depletion and the stress path for injection overlap.

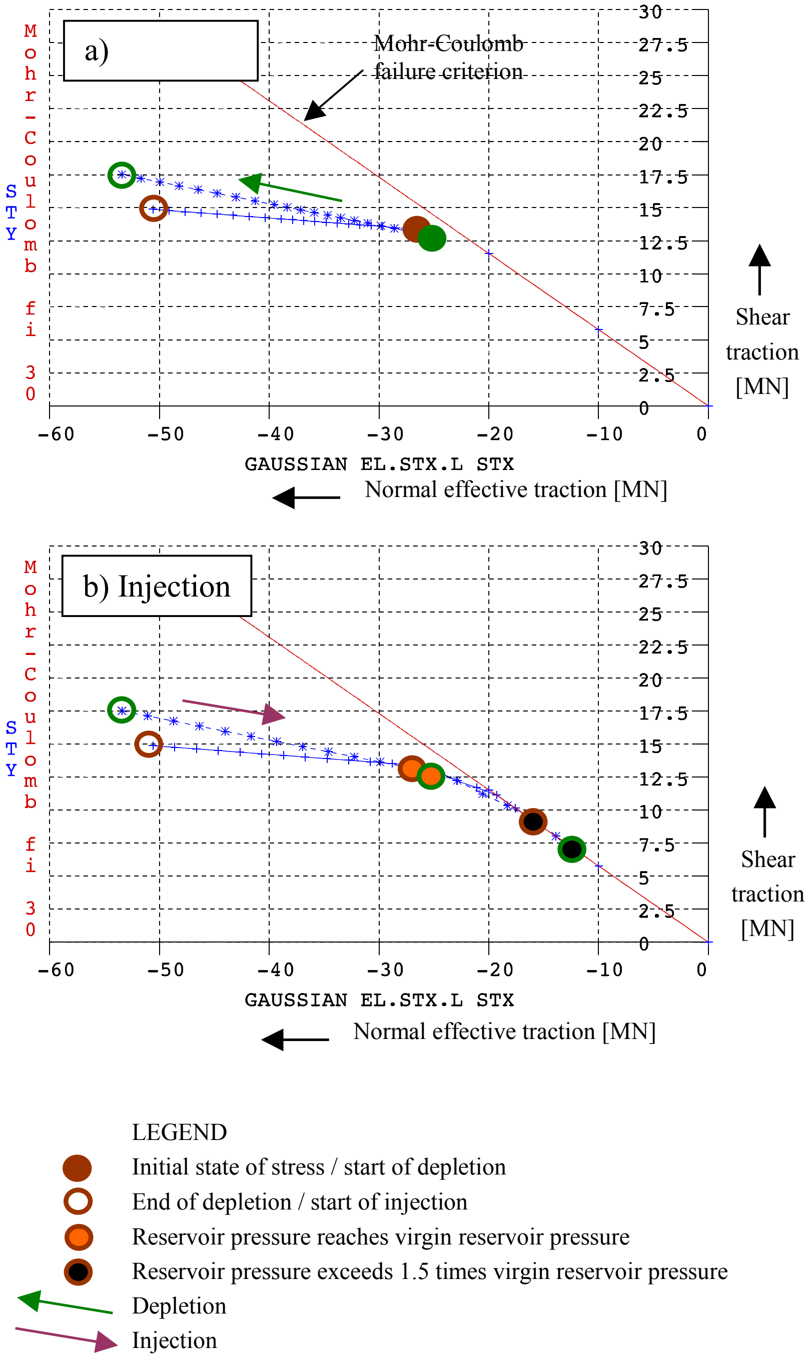

Figure 2.10: Stress paths in the fault during a) CO_2 extraction and b) CO_2 injection.

CO_2 injection above the virgin reservoir pressure shows a critical stress development until the Mohr-Coulomb failure criterion has been reached (Figure 2.10b). At failure, a slip on the fault occurs and the stress path further follows the failure line. The rate of plastic shear displacement along the fault is about 1 cm.

2.5.3 Sleipner gas-condensate fields (block 15/9, offshore Norway)

The Sleipner gas and condensate fields comprise two fields: the Sleipner West (Vest) field, located at the southern edge of the Viking Graben in Norwegian Blocks 15/9 and 15/6, and the Sleipner East (Øst) field, located in Block 15/9, on the eastern margin of the South Viking Graben. The Sleipner West field was discovered in 1974 and has been producing since 1996. Its reservoir consists of a 100-170 m thick sandstone, of the Jurassic Hugin Formation (Ranaweera, 1987).

CO_2 extracted from produced gas (from the Hugin Formation) of Statoil's Sleipner West field has been injected into a large deep saline reservoir, the Utsira Formation, about 800 metres below the seabed. This world's first commercial-scale storage of CO_2 has been monitored and researched by a special project, the SACS project (http://www.ieagreen.org.uk/sacshome.htm).

Within the Nascent project, geomechanical numerical modelling of the Sleipner West Field, was carried out in order to predict changes in the *in situ* stress field and the associated deformation, induced by reservoir depletion and by subsequent CO_2 injection into the reservoir. In contrast to the current practice of the ongoing Statoil injection project, a scenario was assumed in which CO_2 would be injected into the same Hugin Formation, from which the gas and condensate had been previously produced. Available data about the Sleipner fields comprise detailed field and lab data made available by Statoil to the NASCENT project, and publicly available data. In the calculation scenarios first reservoir depletion of a part of the Hugin Formation of the Sleipner West Field was simulated, starting from the initial (virgin) reservoir pressure, down to a reservoir pressure of 5 MPa. Subsequently, a CO_2 injection phase was simulated until the final pressure in the previously depleted part of the reservoir was reached, which was either equal to the initial reservoir pressure or 50% higher. Thus two different injection scenarios were modelled. A plane strain finite element model was developed, based on a lithostratigraphic/structural cross-section supplied by Statoil (Figure 2.11).

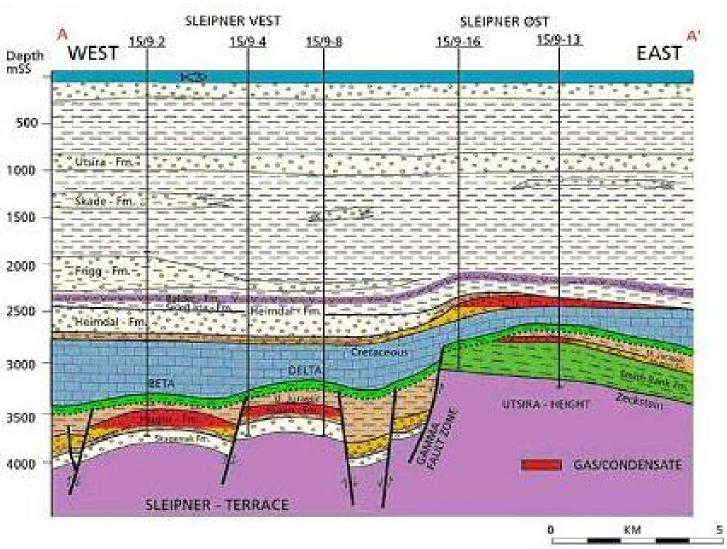

Figure 2.11: Geological cross-section through the Sleipner West and Sleipner East gas-condensate fields (courtesy Statoil).

The numerical model generally preserves the lithostratigraphic division from the geological cross-section and includes major faults (Figure 2.12). Differentiated geomechanical model units were characterised by the physical and mechanical properties, which were determined from data supplied by Statoil and from the literature. Initial loading conditions for the model were determined, taking into account the weight of the overburden, the initial reservoir pressure (43 MPa, which amounts to 7 MPa of over-pressure) and the existing state of stress in the study area. The initial stresses in the model were initialised by applying the gravity load and the pressure of fluids present in the subsurface. Withdrawal of gas-condensate from the reservoir was modelled by decreasing the fluid pressure in a step-wise manner in one part of the Hugin reservoir down to 5 MPa. Subsequent CO_2 injection in the previously depleted part of the reservoir was modelled by increasing the pressure until the final pressure, which was set to be either equal to the initial (virgin) reservoir pressure (about 43 MPa) or 50% greater than the pressure drop in depletion (62 MPa). A 14-year long depletion period, from 1996 to 2010, is assumed to be followed by a 15-year long injection period, from 2012-2027.

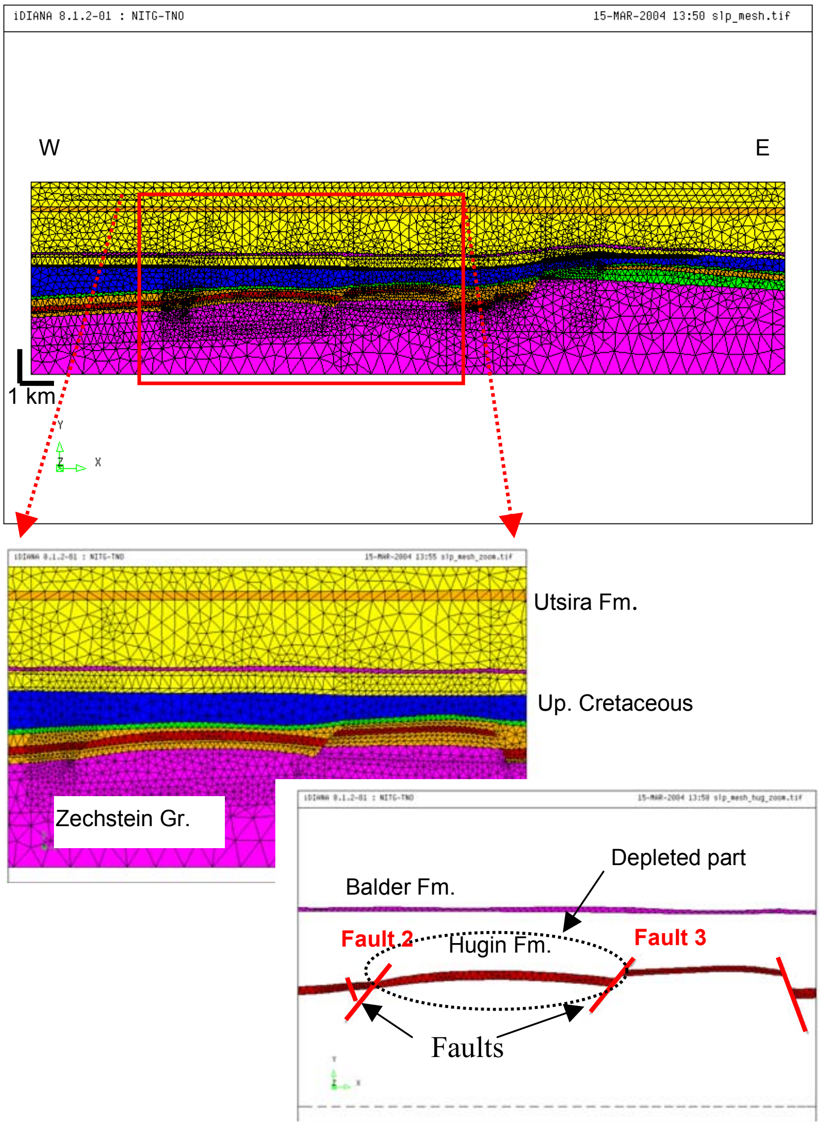

Figure 2.12: Finite element model of the Sleipner field (top) and an enlarged part of the model (bottom), showing the faulted Jurassic reservoir layer (Hugin Formation). Fault 2 and Fault 3 laterally bound the depleted part of the Hugin reservoir.

Simulation results show the evolution of the stress and deformation in the subsurface during a full cycle of gas-condensate extraction and CO_2 injection into the Hugin reservoir. An overview of geomechanical parameters, used to characterise the geomechanical units and faults, is presented in Orlic and Schroot (2004). An elasto-plastic constitutive model, according to the Mohr-Coulomb plasticity, is assumed for both the reservoir and other units. From the geomechanical modelling the following effects of CO_2 extraction and injection were observed.

Effects on the reservoir rocks:

Although both the normal effective stress and the shear stress in the reservoir rock increase, the stress path for the reservoir rock does not converge towards the Mohr-Coulomb failure line (Figure 2.13). Consequently, the mechanical stability of the reservoir rock does not deteriorate as a consequence of reservoir depletion.

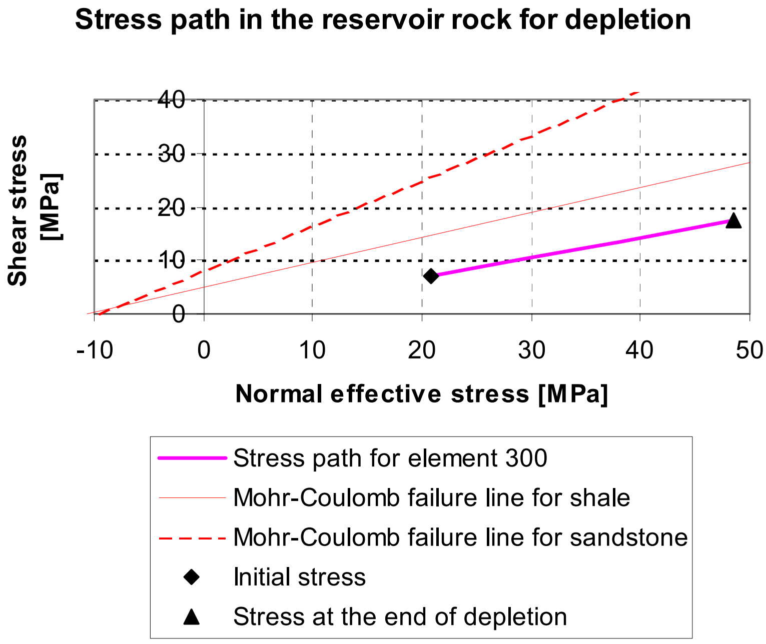

Figure 2.13: Stress path in the reservoir rock (Hugin) for depletion, showing a non-critical stress development.

The effect of subsequent CO_2 injection is the opposite (Figure 2.14). The effective stresses in the Hugin reservoir will decrease and reach the initial state of stress in the reservoir, according to injection scenario 1. The effects on the reservoir rock become more important at injection pressures that exceed the original virgin pressure. When injection pressures approach and reach the minimum horizontal principal effective stress in the subsurface, a tensile failure will be initiated. Such a trend in stress development is characteristic for the injection scenario 2. However, the maximum reservoir pressure at the end of the injection phase will not exceed the minimum horizontal stress. Consequently, the mechanical stability of the reservoir rock is not even expected to deteriorate due to CO_2 injection according to the injection scenario 2. Although these results are site specific and depend very much on the local site conditions, the modelling showed that during injection the stress path development may become critical. As a long as the reservoir pressure is not raised above the level of the original virgin pressure in the reservoir, mechanical failure does not occur. Above that level the risk of failure increases. The extent of this risk again is strongly dependent on the specifics of the site under consideration.

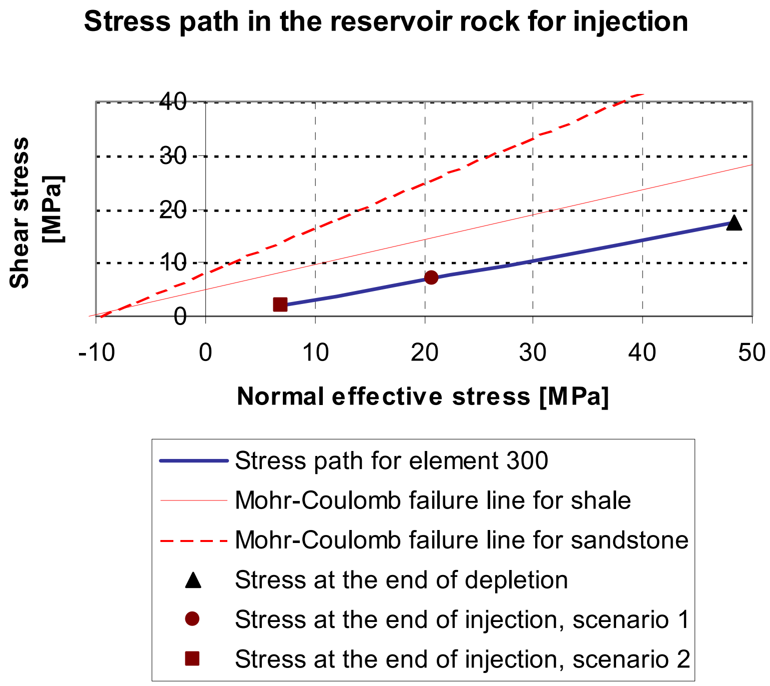

Figure 2.14: Stress path in the reservoir rock for CO2 injection, showing a possible critical stress development towards a tensile failure.

Effects on the bounding faults:

The effects of gas-condensate extraction on the stability of the two faults bounding laterally the depleted part of the Hugin reservoir are comparable to those observed above in the reservoir rock. During reservoir depletion, the stress path on the fault is diverging from the Mohr-Coulomb critical line, which means that the fault stability is not jeopardised.

The effects of CO_2 injection on the stability of the two bounding faults are the opposite compared to the depletion phase. The stress path is now converging towards the shear failure. The results of the injection scenario 1 show that the state of stress at the end of injection is the same as the initial state. Further increase in the injection pressure, exceeding the initial reservoir pressure, leads to a critical stress development towards a shear failure and initiation of the fault slippage. This may be accompanied by the opening of the fault zone and formation of a gap between the fault blocks in a tensile failure. The results of the injection scenario 2 show that the critical state of the stress on fault 2 will be reached at the end of the injection period when a plastic slip on the fault will occur.

If only one part of the reservoir is depleted, as is the case here, differential compaction on either side of the fault will occur. When the foot-wall part of the reservoir is depleted, the additional shear stresses on the laterally bounding reservoir fault (Fault 2 in our case) are directed downwards, at the top of the reservoir, and upwards, at the bottom. Reverse fault slip will be favoured. When the hanging-wall reservoir is depleted (Fault 3 in our case) normal fault slip occurs. Injection into only the foot-wall part of the reservoir generally favours normal faulting, while injection into only the hanging-wall part of the reservoir favours reverse faulting.

Ground deformation:

Reservoir depletion will cause compaction of the reservoir and subsidence of the seabed, while injection will cause expansion of the reservoir and at least some rebound, i.e. the recovery of subsidence. The calculated maximum compaction rate at the reservoir level of 22 cm and subsidence of the seabed of 12 cm at the end of depletion period can be regarded as realistic order-of-magnitude values.

The DIANA geomechanical modelling assumed elastic behaviour of the rocks. As a result, CO_2 injection up to the virgin reservoir pressure will fully reverse earlier deformation caused by reservoir depletion. Further CO_2 injection above the virgin pressure will cause uplift. For the injection scenario 2 (final reservoir pressure is 50% higher than the pressure drop in depletion), the uplift will be equal to 50% of subsidence (that is, 10 cm at the reservoir level and 6 cm at the seabed). It should be noted, however, that many rocks do not behave as ideally elastic media over a given loading/unloading range. Deformation caused by loading is often not fully recoverable by unloading. Consequently, elastic material models for the rock will likely overestimate the amount of rebound during unloading.

2.5.1. Geomechanical Modelling of the Florina site

The Florina natural CO_2 field represents a shallow (between 300 and 600 m below the surface) reservoir in Tertiary sands interbedded with silt and clay (further details can be found in Pearce, 2003). The evaluation of the geohazards from CO_2 extraction and subsequent injection in this shallow reservoir (Hatziyannis, 2004) simulates the case of slow leakage (through fractures) of the gas from a geological storage site and accumulation at shallow depth below surface. CO_2 is dissolved in the groundwater of an existing aquifer and this is what will happen in the case of a leak from geological storage.

In the wider area of the Florina sedimentary basin, CO_2 leakage creates mineral springs in some places and/or gas bubbles in shallow wells where the geological structure (fractures, permeable cap rock, etc.) allowed this slow migration. In other places, geological structure creates impermeable non-leaking reservoirs where commercial CO_2 fields were formed, for example the commercial CO_2 deposit. Before discovery drilling took place, there was no indication of leakage at the surface and the pressure of the CO_2-charged groundwater exceeded 50 bars (at a depth of 300 to 600 m below surface). Therefore the geomechanical modeling of the behavior of the reservoir and cap rocks and of the existing faults bounding the reservoir to the east and west at Florina contributes to the understanding of the prediction of the effects of CO_2 leakage from storage sites.

Existing data available to this study comprised regional geological data, and detailed field and well data from producing wells made available by Air Liquide to the NASCENT project. Data were also acquired from fresh samples, which retained their *in situ* physical properties, from one borehole drilled in the NASCENT project. Finally data from old lignite boreholes and data on the initial reservoir pressure and production data were used. Many of the input parameters required for geomechanical modelling, such as the rock mechanics parameters and principal horizontal stress magnitudes, were not known and had to be estimated. For characterisation of the reservoir and cap rock, additional samples were collected from available cores from the new borehole in the study area and rock mechanics tests were conducted by the Department of Engineering Geology of IGME.

The results of geomechanical numerical modelling of the Florina field provide fundamental insight into the causes of human-induced geohazards, related to CO_2 extraction and injection. Numerical modelling predicted changes in the stress field and associated deformation assuming that the natural CO_2 accumulation will be first exploited until full depletion of the reservoir, and then used for CO_2 injection. The model assured the observations made during production history, i.e. there was no geohazard induced by the CO_2 production. Up to now, no increase in the seismicity of the area has been observed and surface subsidence is not noticeable.

The human-induced geohazards considered in the numerical modelling comprise subsidence and uplift of the ground surface, and induced seismicity, caused by fault reactivation. These phenomena were studied on a plane strain finite element model constructed from a synthetic geological cross section, running in a NE-SE direction and compiled from old and recent sub-surface information, as described above.

Prediction of subsidence during reservoir depletion and uplift due to CO_2 injection was based on the assumption of the elastic behavior of rock mass and on non-calibrated elastic rock properties. Maximum predicted subsidence amounts to about 7 cm, while injection up to the initial reservoir pressure leads to a full recovery of the subsidence profile. Further CO_2 injection above the initial reservoir pressure will cause minimum uplift of the surface.

Very important for this shallow reservoir is the prediction of the potential for fault reactivation and differential movement during depletion and reinjection. For the assumed fault shear strength parameters, the stress path is diverging from the failure line and the stress development is not critical. CO_2 injection into the depleted reservoir results in a stress path which is anti-parallel (i.e. has the opposite gradient) with the stress path for depletion. Due to elastic response of the fault when injecting up to the virgin reservoir pressure, the stress path for depletion and the stress path for injection overlap.

Injection above the virgin reservoir pressure shows a critical stress development. The stress path is converging towards, and reaches, the Mohr-Coulomb failure line, when a plastic slip on the fault surface occurs. CO_2 injection above the original reservoir pressure generally deteriorates the fault stability leading to its reactivation and an upwards movement of some centimeters on the downthrown sides.

2.6. FURTHER READING

NASCENT REPORTS:

CZERNICHOWSKI-LAURIOL I., PAUWELS H., VIGOUROUX. P., LE.NINDRE.Y.M. 2002. The French carbogaseous province: an illustration of natural processes of CO_2 generation, migration, accumulation and leakage., in GHGT-6 - Kyoto - Japan - 01-04/10/2002, Vol. I, pp. 411-416

CZERNICHOWSKI-LAURIOL.I., AUDIBERT.N., FOUILLAC C., BONIJOLY D. 2003. Combining hydrogen production and geological sequestration of CO_2, a way toward a low GHG emission society, in 1st European Hydrogen Energy Conference, 2-5 September 2003 - Grenoble, France, 7 p.

HATZIYANNIS, G., SPYRIDONOS, E & METAXAS, A. 2004. Work Package 5: Geohazard Assessment, NASCENT project.

ORLIC, B. & SCHROOT, B.M. 2004. NASCENT Work Package 5: Geohazard Assessment. TNO report NITG 04-049-B0309.

ORLIC, B. 2003. Modelling of man-induced geological hazards caused by gas extraction and injection. *Annual Conference of the Int. Assoc. of Mathematical Geology (IAMG). Session 4/9.* CD-ROM. Portsmouth.

PAUWELS, H., GAUS , I. , LE NINDRE, Y M, PEARCE, J. M. CZERNICHOWSKI-LAURIOL, I. In press. Chemical and isotope composition of fluids from a natural CO_2 accumulation (Montmiral, France): estimation of reservoir water composition and evidence for water origin and water-CO_2-rock interactions. *Submitted to Chemical Geology* (special issue on CO_2 sequestration).

PEARCE, J.M. (ed.) 2001. NASCENT, Natural Analogues for the Storage of CO_2 in the Geological Environment, Work Package 1: Data collation, review and site selection. First Interim Report of Energy, Environment and Sustainable Development Programme, project No. ENK5-CT-2000-00303, 188 pages.

PEARCE, J. (ed), 2003. Natural Analogues for the Storage of CO_2 in the Geological Environment. Report on Field Characterisation including Soil Gas Surveys, Characterisation of Offshore Shallow Gas Seeps, Hydrochemistry and Diagenetic Studies. British Geological Survey, External Report CR/03/147.

OTHER REFERENCES

JOHNSON, J.W. AND NITAO, J.J., 2002. Reactive Transport Modeling Of Geologic CO_2 Sequestration At Sleipner. In: J. Gale and Kaya, Y., 6th International Conference on Greenhouse Gas Control technologies, 1-4 October 2002, Kyoto, Japan. 327-332.

RANAWEERA, H.K.A., 1987. Sleipner Vest. In Spencer, A.M. et al. (Eds.), *Geology of the Norwegian Oil and Gas Fields.* Norwegian Petroleum Society. Graham & Trotman, 253-264.

Chapter 3. Leakage through caprocks – processes and implications

3.1. SUMMARY AND CONCLUSIONS

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 during geological storage. This chapter also describes evidence of past CO_2 migration along fractures.

Capillary breakthrough measurements with CO_2 have been performed on initially water-saturated caprock samples from natural CO_2 sites in Florina, Montmiral and the Vorderrhön. The results were compared with those for capillary breakthrough of methane and nitrogen.

Statistical analysis of the data indicates that the capillary displacement pressure for CO_2 is lower than for the other gases on samples of equal effective permeability (maximum gas permeability after breakthrough). This behaviour implies a reduced gas/water interfacial tension and/or a reduced wetting angle in the CO_2/water/rock system. 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.

Diffusive loss of CO_2 through caprocks is considered negligible; but diffusion is rate-determining for potential geochemical "corrosion" of caprocks. Laboratory experiments have provided some basic information on the diffusion coefficients of CO_2 in seal lithotypes and evidence of chemical interactions of the CO_2 with the sample materials. The interrelation of diffusive transport and chemical reaction of CO_2 in naturally occurring shale, marlstone and carbonate lithotypes remains a challenge and requires further investigation.

To study the sequence of events resulting in potential caprock leakage, a simple dynamic leakage model has been developed. Based on the results of the laboratory experiments (capillary breakthrough pressure, effective gas permeability as a function of capillary pressure difference) this model can be used to estimate the time-scale and quantities of gas loss through the caprock.

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 up through the overlying rocks the CO_2 has migrated. In addition, the CO_2-rich fluid also contained hydrocarbons that could have been mobilised by the CO_2-rich fluid in a similar manner to that employed during enhanced oil recovery. Geochemical modelling of this process indicates that pressure decreases alone (such as during fracture reactivation and migration of CO_2 from the reservoir) are insufficient to cause calcite precipitation and that a decrease in temperature is also required. The amounts of calcite precipitated however, are very small.

3.2. INTRODUCTION

The term “caprock” refers to layers of sedimentary rocks overlying accumulations of petroleum or natural gas and providing, ideally, a natural barrier to the escape of the reservoir fluids to overlying strata and the atmosphere. Caprocks are a precondition for the formation of petroleum and natural gas fields and their preservation over extended periods of geologic time. The existence of hydrocarbon fields of geologic age is, on its own, compelling evidence for the potential sealing efficiency of caprocks. On the other hand, the occurrence, areal extension and continuity, sealing capacity and integrity of caprocks represent risk factors in petroleum and natural gas exploration that have prompted the development of tools and procedures for caprock characterisation, classification and appraisal.

Experience shows that the sealing efficiency of sedimentary layers ranges from essentially perfect to practically zero.

This scope of caprock sealing efficiency is reflected in the case studies investigated in the NASCENT project:

- due to highly efficient seal layers (“caprocks”, massive CO_2 accumulations go essentially unnoticed in terms of surface manifestations and are only discovered by coincidence (Montmiral/St. Lattier, Vorderrhön, Mihályi-Répcelak)
- poor quality or absence of sealing layers characterises locations with high-flux CO_2 emanations (Mátraderecske, Florina) occurring partly in densely populated areas (Ciampino)

While even considerable natural emanations of CO_2 by caprock leakage are tolerated by the population in regions prone to this phenomenon, the predominant goal of anthropogenic CO_2 storage activities must be to avoid any risk of spontaneous and catastrophic outbreaks and to ensure long-term storage reliability. The assessment of long-term gas sealing efficiency of sedimentary strata is an important issue in natural gas and petroleum exploration. Research in this field over the past decades has resulted in substantial expertise, which has provided a starting point for the experimental and conceptual work conducted in the NASCENT project.

The basic concepts of hydrocarbon entrapment are well established and have been discussed by a number of workers. Berg (1975) presents the concepts of capillary sealing and its role in hydrocarbon migration and trapping. A comprehensive overview of this mechanism has been given by Schowalter (1979) while the work of Hubbert (1953) emphasises the hydrodynamic aspects of hydrocarbon entrapment. Downey (1984) stresses the importance of seal characterisation in risk evaluation and points out that hydrocarbon seals need to be evaluated on a "micro" and a "mega" scale. The establishment of a link between the macro scale and petrophysical and transport parameters, which can only be measured experimentally on the laboratory (micro) scale, is one of the fundamental problems in the analysis of basin-wide fluid flow.

3.3. HOW COULD CO_2 LEAK FROM A RESERVOIR?

3.3.1. Identifying past CO_2 migration along fractures

Evidence was obtained of CO_2 migration along fractures in overlying Rhaetian limestones at Montmiral. These limestones have been subjected to a prolonged and episodic history of fracturing and mineralisation of these fractures, which can be related to basin development and subsequent uplift. The latest generation of fractures are partially mineralised by coarse (millimetre-scale) calcite crystals. Detailed studies of fluid inclusions, which are tiny bubbles of gases, liquid hydrocarbons and water that are trapped in this calcite, provide information on the temperature and pressure conditions during mineral precipitation and in this study revealed that some of these fractures have enabled CO_2 to migrate from the reservoir. The very latest calcite generation (a thin outer coating on these crystals) precipitated from CO_2-rich fluids moving through the fractures. In addition, evidence from characterisation of the tiny fluid inclusions trapped in the fracture calcite indicates that the fluids moving through these fractures also contained hydrocarbons. This provides some evidence for the potential of CO_2 to mobilise and carry hydrocarbons. This ability is, of course exploited in the oil production industry during enhanced oil production.

The overlying Rhaetian and Hettangian limestones and sub-reservoir basement lithologies provided exceptionally good evidence for the microfracture-controlled migration of supercritical CO_2 fluids (Figure 3.1). In two of the three boreholes at Montmiral where CO_2 accumulations have been discovered in Triassic sandstones, the overlying Rhaetian and Hettangian cap rock limestones display *prima facie* evidence for the migration of supercritical CO_2 along reactivated carbonate-anhydrite cemented fractures. Furthermore, the CO_2 has remobilised pre-existing liquid hydrocarbons giving rise to a wide range of mixed hydrocarbon-CO_2 fluids that simulate the fluids generated during commercial EOR experiments. CO_2 migration through the cap rocks is not accompanied by significant new mineral deposition but is characteristically associated with millimetric calcite veinlets that post-date all previous generations of veining. Thus, where evidence for CO_2 breakthrough is sought, as would be required for storage risk assessment, Montmiral demonstrates that careful investigation is needed to justify the integrity of the cap rocks. Since the sampling intervals (<118m) were controlled by the availability of borehole core, the upper limits of CO_2 migration have not been defined. It remains to be proven whether such hydrocarbon-enriched CO_2 fluids ever reached higher level groundwaters.

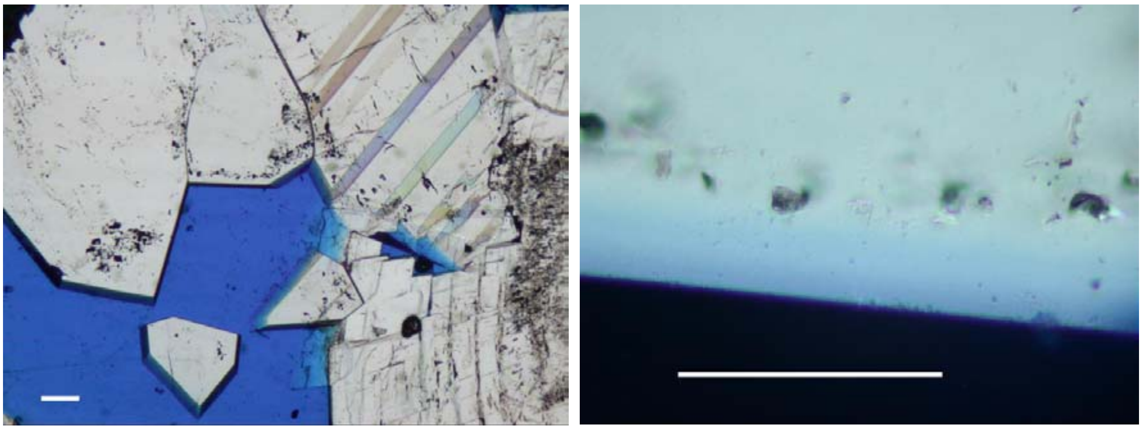

Figure 3.1: Left: Optical microscopic view of late stage calcite with very late stage growth zones containing supercritical CO_2 and hydrocarbon inclusions. Scale bar is 100 microns. Right: Close up of late stage calcite with very late stage growth zones containing supercritical CO_2 and hydrocarbon inclusions. Scale bar is 100 microns.

Reconstruction of the conditions prevailing during charging of the Montmiral reservoir is very dependant upon the time of CO_2 migration. In the absence of absolute dates only relative timing can be modelled. Assuming charging occurred soon after maximum burial, isochoric data for the inclusion fluids suggests ≈150 °C and 50 MPa. If this applies then the reservoir has since undergone significant decompression and cooling in response to uplift; the current conditions being ≈100 °C and 36 MPa. However, if the charging was much younger then the initial conditions would lie somewhere between these two end states. Isochoric data for CO_2 inclusions in the sub-reservoir basement also indicate that the Montmiral reservoir and its enclosing rock envelope have undergone periodic decompression. One explanation could be that during uplift, fracturing in response to tectonic events has caused switching between hydrostatic and lithostatic conditions. Whilst the temporal relationship between reservoir charging and CO_2 migration through the cap rocks cannot be established, the evidence for decompression tends to support the idea that the cap rocks have been breached by hydraulic fracturing with the consequent loss of CO_2 from the reservoir. If this is true then the cap rocks have not behaved as a proper seal.

A stable isotope study of carbonate fracture-fills occurring in the Rhaetian-Hettangian limestones overlying the Montmiral CO_2 reservoir was undertaken in order to constrain the nature and origin of water responsible for calcite precipitation in fractures, in particular in relation with CO_2 migration events through the cap-rock. The $\delta^{13}C$, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$ values of bulk-rock and late-fracture calcite were determined for a selection of 21 representative samples from two wells. Particular emphasis was placed on two distinctive generations of fracture-fill calcite, referred to as early calcite and late calcite. Based on fluid inclusions evidence, precipitation of early calcite and late calcite is considered to have occurred, respectively, prior to and concomitant with CO_2 migration in the limestones.

Bulk-rock (matrix) calcite exhibits $\delta^{13}C$-$\delta^{18}O$ values within the expected range for primary marine carbonates of Trias-Jurassic age, averaging 0 ±1 ‰ PeeDee Belemnite (PDB) for $\delta^{13}C$ and 26 ±2 ‰ Standard Mean Ocean Water (SMOW) for $\delta^{18}O$ (Figure 3.2). This indicates that the original isotopic composition of the bulk cap-rock limestones was not significantly modified by post-depositional water-rock interactions, whether related to burial diagenesis and/or to CO_2 migration. It further implies that water-interaction processes that affected the limestone cap-rock were mainly restricted to fractures.

Fracture-fill calcite exhibits consistent $\delta^{13}C$ values, averaging -1 ±2 ‰ PDB, similar to those of host limestones. In contrast, $\delta^{18}O$ values of fracture calcite are variable, ranging from 13 to 23 ‰ SMOW, and significantly lower than those of bulk-rock calcite. Within the documented range, the results of high resolution *in situ* isotope micro-analyses performed by SIMS (Secondary Ion Mass Spectrometry) reveal that late calcite is, on average, less depleted in ^{18}O than early calcite ($\delta^{18}O$ late calcite = 18 ±2 ‰; $\delta^{18}O$ early calcite = 15 ±2 ‰). The observations above lead to the following conclusions:

1. The carbon involved in the precipitation of early and late fracture calcite appears to be predominantly of marine origin and derived from the surrounding host limestone.
2. The generally low $\delta^{18}O$ values exhibited by fracture calcites reflect their high temperature of formation (100-140 °C according to fluid inclusions and geological evidence).
3. The less-depleted $\delta^{18}O$ value of late calcite relative to early calcite may reflect either a slightly lower temperature of formation for late calcite or, more probably, the imprint of an elevated CO_2/water ratio on the isotopic composition of water during the CO_2 migration event.

The reconstructed isotopic composition of water from which fracture calcite precipitated is consistent with a marine or basinal brine source. Calcite-forming water most likely represents a brine component present in the reservoir prior to CO_2 emplacement, whose existence is evidenced from other geochemical and isotopic data (production water).

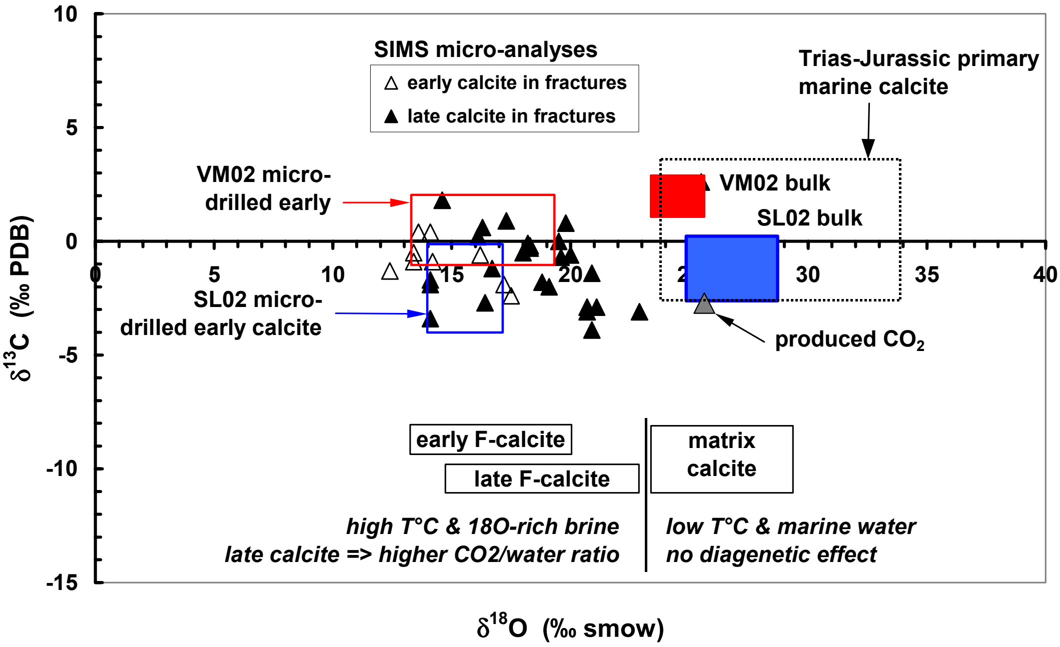

Figure 3.2: In situ $\delta^{13}C$-$\delta^{18}O$ SIMS micro-analyses of early and late calcite occurring in late fractures (III) in SL02 and VM02 wells, and comparison with $\delta^{13}C$-$\delta^{18}O$ values of bulk fracture (early) calcite (open squares) and bulk-rock calcite (solid squares) in the same wells.

The elevated $^{87}Sr/^{86}Sr$ ratios (0.7108-0.7118) exhibited by fracture calcites constitute further evidence of the presence of a significant brine component in the studied system. The highly radiogenic Sr signature of calcite-forming brine is most likely derived from dissolution of detrital feldspar in the reservoir or detrital clays in the interbedded shales.

The circumstances under which calcite precipitation, linked to CO_2 breakthrough in the cap rock fractures, could occur was investigated by geochemical modelling interactions between the *Montmiral cap rock* and CO_2-saturated reservoir fluids. Therefore, the influence of pressure and temperature and the interactions with other minerals present in the caprock fractures were investigated. Based on the modelling it was concluded that the precipitation of the calcite is very unlikely to be the result of a drop in pressure only, which could have occurred when the fractures in the cap rock were reactivated and dissolved CO_2 from the reservoir enters the cap rock. However, a decrease in temperature (within the range of 150 °C-80 °C) would induce the precipitation of calcite if it were allowed to re-equilibrate with dolomite. The impact of these calcite-dolomite re-equilibration reactions is minor and the amounts of calcite that can precipitate are very little. This is in agreement with the observations showing only tiny formation of the late calcite.

3.4. WHAT MAKES A GOOD SEAL?

Apart from events like *seismically induced seal rupture or tectonic deformations* resulting in the formation of conducting faults (which may persist only over limited periods of geologic time) the retention of hydrocarbons by overlying seals is controlled by the *capillary entry pressure*, the *permeability* and *relative permeability* and the extent of *diffusive losses* (molecular transport) through the fluid-saturated pore space.

Capillary forces inhibit volume flow of a non-wetting hydrocarbon phase through a seal until the pressure of the underlying hydrocarbons exceeds the capillary entry pressure. Leakage occurs when an interconnected flowpath of the hydrocarbon phase forms across the pore system of the cap rock. In an analysis of various cap rock and fault seal situations Watts (1987) denotes these seals as membrane seals. The capillary sealing efficiency of membrane seals depends critically on the wettability of the cap rock. Problems relating to wettability changes during hydrocarbon leakage and the reversibility of seal failure are largely unexplored. Under hydrostatic conditions a hydrocarbon column of a certain height is required to create the buoyancy pressure which can eventually compensate and exceed the capillary entry pressure. The dependence of the capillary sealing efficiency on the petroleum fluid phases (gas and oil) has been discussed by Watts (1987). Gas-water interfacial tension is larger by around one order of magnitude than oil-water interfacial tension. Therefore, a gas cap on top of an oil column will enhance the sealing efficiency. Due to its lower density, a gas column will exert a higher buoyancy pressure than an oil column of equal height. Gas density is, however, strongly pressure dependent and at greater depth the buoyancy forces exerted by gas columns decrease substantially. It should be noted in this context that a CO_2 column replacing a natural gas (methane) column of equal height in an exhausted reservoir will exert a significantly lower capillary pressure on the overlying seal (Figure 3.3).

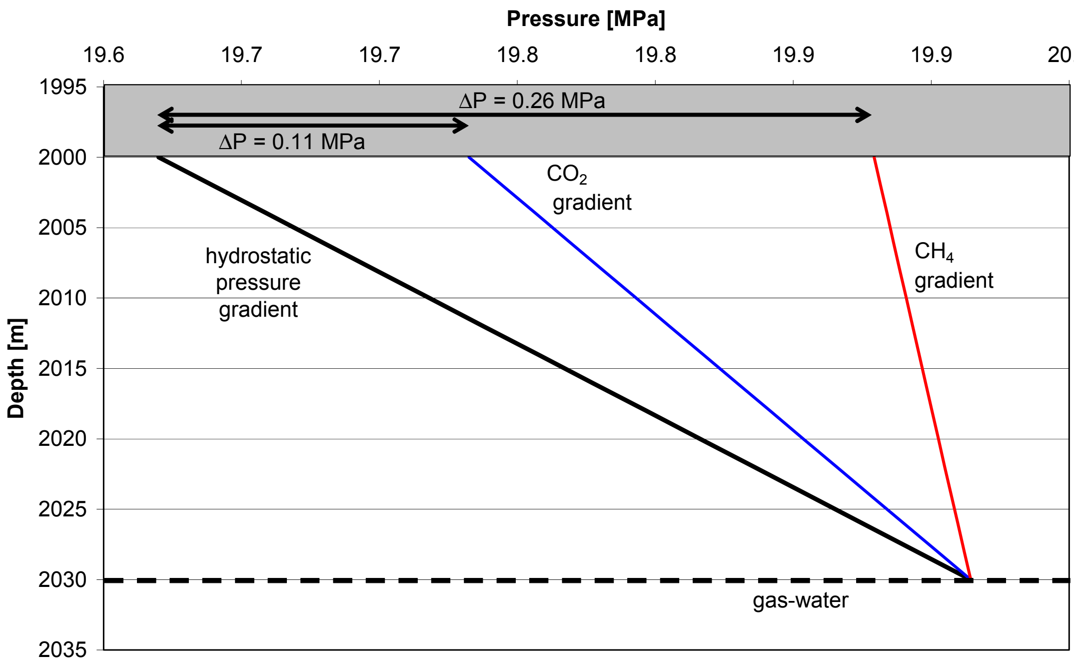

Figure 3.3: Comparison of gas pressure gradients for CO_2 and CH_4 in a 30 m gas reservoir underlying a seal at 2000 m depth. Buoyancy pressures at the caprock/reservoir interface are 0.11 MPa and 0.26 MPa for CO_2 and CH_4, respectively.

In the case of overpressured reservoir compartments, capillary seal failure cannot be related to absolute hydrocarbon column height, but buoyancy pressures will still represent a factor in controlling sealing efficiency in this case. Lithologies with extremely high or "infinite" capillary entry pressures are referred to as hydraulic seals (Watts 1987). Here seal failure is only possible by mechanical fracturing due to build-up of excessive fluid pressure or tectonic events (cf. Caillet, 1993).

Permeability and relative permeability will control fluid transport through the seal once the capillary entry pressure has been exceeded. The gas (or oil) column heights within a reservoir will then be determined by the relative rates of charge and leakage. For the assessment of gas leakage through initially water-saturated seal rocks the *effective permeability* for the gas phase after breakthrough is the key parameter. Because the non-wetting (gas) phase uses only a portion of the interconnected pore network as transport pathway the effective permeability will always be lower than the absolute (single-phase) permeability. The effective permeability depends on the relative portion of the pore system used for non-wetting phase transport and thus on the non-wetting phase saturation of the rock. For porous petroleum and gas reservoir rocks, the concept of relative permeability is used to describe the two-phase transport of fluids. For fine-grained caprocks with low porosities, the gas- and/or water-saturation cannot be readily determined and other approaches have to be used to describe the variation in effective permeability after gas breakthrough. The concept proposed here relates the effective permeability directly to the pressure difference between non-wetting (gas) and wetting (water) phase, i.e. the “capillary pressure”.

Diffusion is a perpetual and ubiquitous process in sedimentary basins and its role in hydrocarbon migration has been analysed by several workers (e.g. Antonov, 1954, 1958, 1964, 1970; Smith et al., 1971; Nesterow and Uschatinskij, 1972; Leythaeuser et al., 1980, 1982; Krooss and Schaefer, 1987; Krooss and Leythaeuser, 1988; Krooss et al., 1992a, b; Nelson and Simmons, 1992, 1995; Montel et al., 1993). The efficiency of diffusive leakage from gas reservoirs depends on seal properties, seal thickness and caprock/reservoir area available for transport. In most cases, this transport mechanism can be considered negligible even on longer geologic time scales (millions of years). However, the penetration of a CO_2 diffusion front into a seal layer may represent the initial and rate-controlling step in the geochemical degradation of the seal and therefore deserves special attention.

3.4.1. Laboratory experiments

Two basic types of caprock/seal failure can be envisioned to occur in natural gas systems and, by analogy, in geologic systems designed for anthropogenic CO_2 storage (Figure 3.4). Seal failure due to *seismically induced seal rupture or tectonic events* constitutes a potential leakage risk that is essentially unpredictable in terms of specific time of occurrence and leakage intensity and duration. These processes are, by nature, not amenable to studies on the laboratory scale and therefore have not been considered in this study. However, through studies of fracture architecture and history of development at specific sites, probability functions can be created that allow some prediction over geological timescales of seal rupture through seismic events.

The second category of seal/caprock leakage processes, involving the undisturbed rock matrix, comprises pressure-driven volume flow and molecular transport (diffusion). These two processes have been investigated in the Nascent project in laboratory experiments on selected rock samples from different locations. The main results of this experimental work have been published as peer-reviewed papers (Hildenbrand et al.

2002, Hildenbrand et al. 2004). Qualitative and quantitative aspects of molecular migration processes on the chemical and isotopic composition of natural gas accumulations have been addressed recently by Schloemer & Krooss (2004).

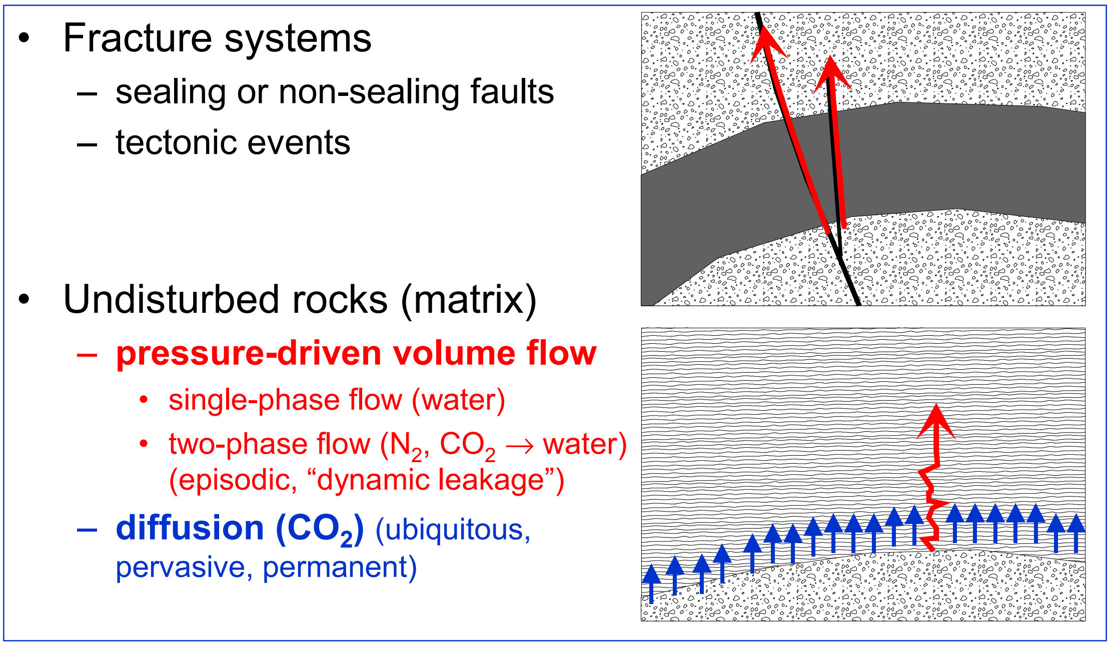

Figure 3.4: Types of caprock /seal failure envisaged in natural gas reservoirs and CO_2 storage.

3.4.1.1 Gas breakthrough experiments:

The concept of capillary gas breakthrough in initially water-saturated rocks is shown in Figure 3.5. The buoyancy pressure of a gas phase underlying a cap rock will increase with increasing gas column height and may ultimately exceed the capillary entry or breakthrough pressure of the seal. This will result in gas leakage along the largest interconnected pathways in the pore system. With increasing gas pressure, an increasingly larger portion of the pore system will become saturated with gas (due to displacement of water) and participate in gas transport. Consequently, the effective gas permeability of the seal rock will increase. If the gas pressure decreases due to depletion of the reservoir, the effective permeability will decrease due to re-imbibition of water into successively larger pores. Gas flow will cease completely when the last interconnected pathway is shut off by the imbibing water. Theoretically, a natural gas reservoir may run through repeated cycles of capillary leakage and re-sealing of the caprock associated with depletion and replenishment of the reservoir. This aspect of dynamic leakage has been a focus of the experimental and conceptual work conducted in this project.

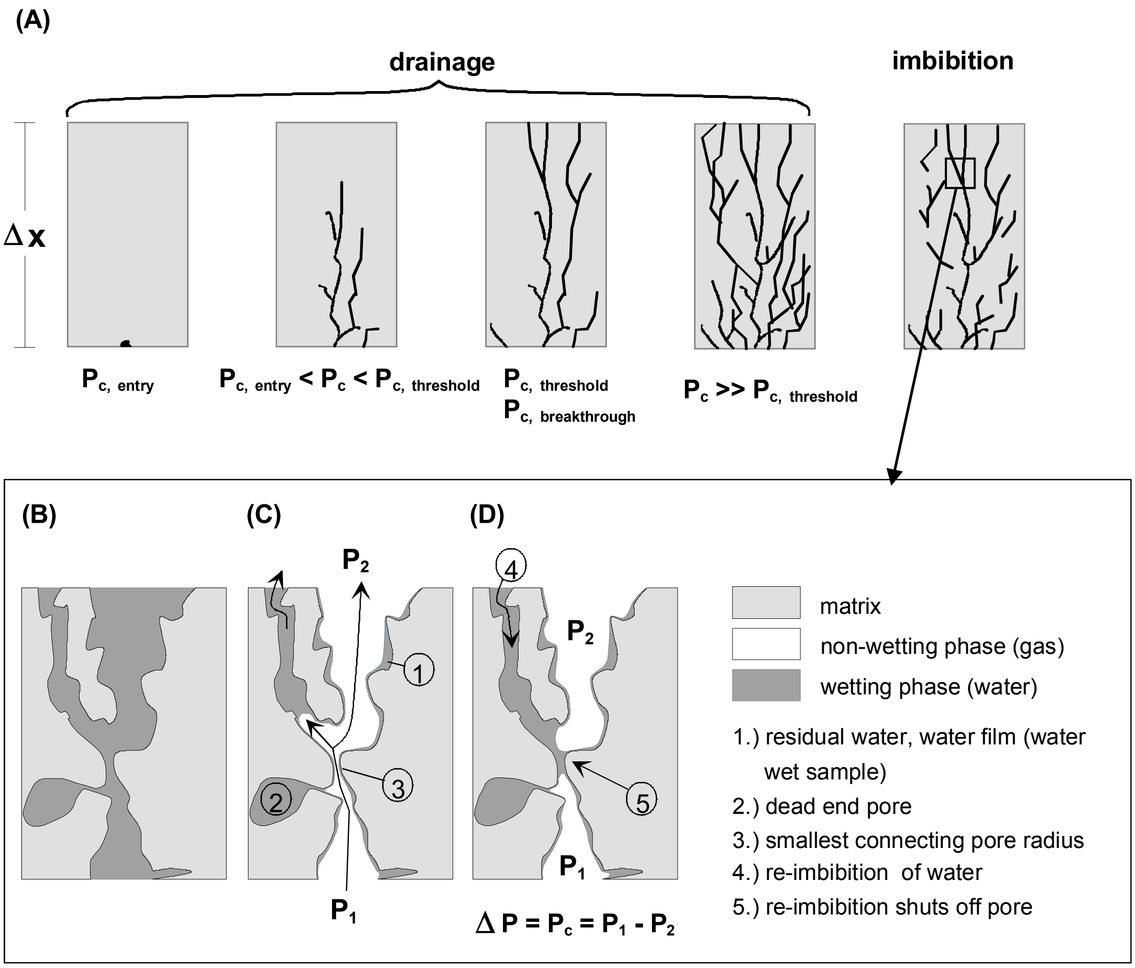

Figure 3.5: (A) Stages of capillary gas breakthrough (drainage) and re-imbibition process in fine-grained rocks (schematic); (B) initially water-saturated sample; (C) gas breakthrough, (D) re-imbibition.

The scheme of the experimental work on gas breakthrough is shown in Figure 3.6. A detailed description of the experimental procedure and the conceptual background is given in Hildenbrand et al. (2002).

In the initial phase of the laboratory work, before field samples from any of the NASCENT locations were available, fundamental work was carried out to study the capillary sealing efficiency of well-characterised fine-grained sedimentary rocks.

The initial set of gas breakthrough experiments was conducted with nitrogen (N_2) on fully water saturated claystones and siltstones from Belgium (Boom Clay), Switzerland (Opalinus Clay) and offshore Norway Tertiary mudstones of different lithological compositions. Sand contents of the samples were consistently below 12%, major clay minerals were illite and smectite. Porosities determined by mercury injection lay between 10 and 30% while specific surface areas determined by nitrogen adsorption (BET method) ranged from 20 to 48 m^2/g. Total organic carbon contents were below 2%.

Prior to the gas breakthrough experiments, the absolute (single phase) permeability (k_{abs}) of the samples was determined by steady state flow tests with water or NaCl brine. The k_{abs} values ranged between 3 and 550 nDarcy (3×10^{-21} and 5.5×10^{-19} m^2). The maximum effective permeability to the gas-phase (k_{eff}) measured after gas breakthrough on initially water-saturated samples extended from 0.01 nDarcy (1×10^{-23} m²) up to 1100 nDarcy (5×10^{-18} m²). The residual differential pressures after re-imbibition of the water phase, referred to as the "minimum capillary displacement pressures" (P_d), ranged from 0.06 to 6.7 MPa. During the re-imbibition process the effective permeability of the gas phase decreases with decreasing differential pressure. The recorded permeability/pressure data were used to derive the pore size distribution (mostly between 8 and 60 nm) and the transport porosity of the conducting pore system (10^{-5} - 10^{-2}%) (Hildenbrand et al., 2002).

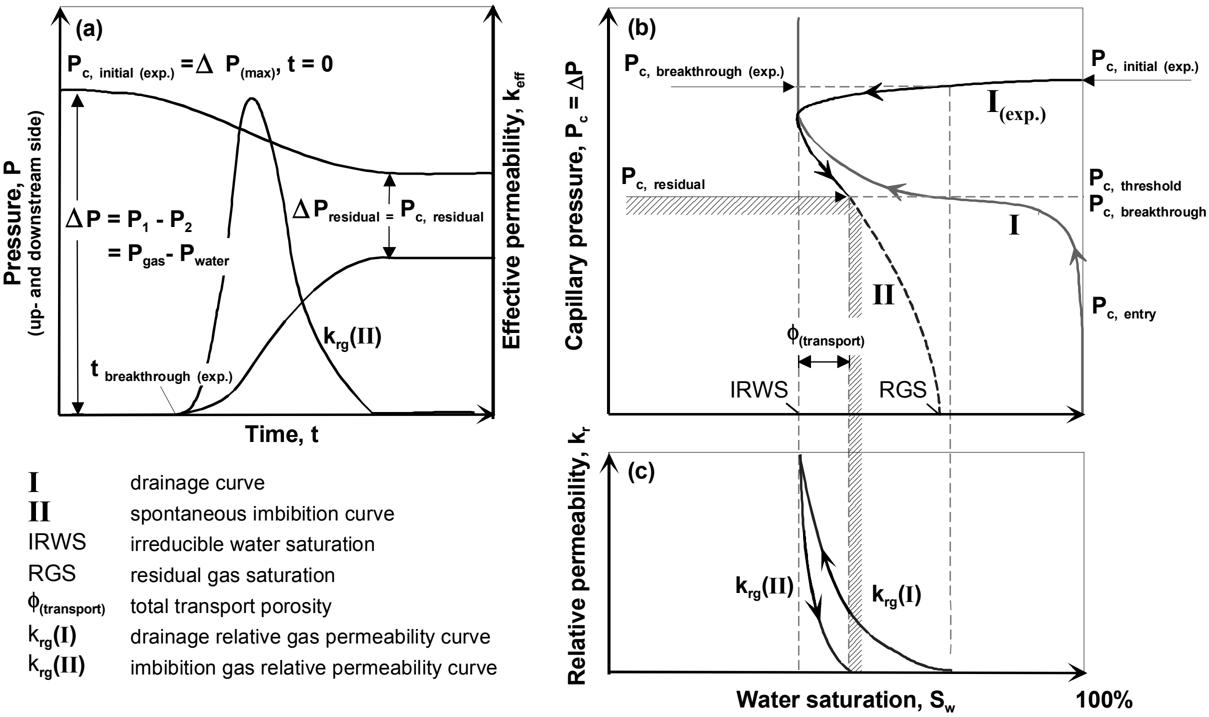

Figure 3.6: Scheme of the experimental parameters recorded in this study and their interpretation in terms of capillary processes: (a) pressure history of a gas breakthrough experiment; (b) capillary pressure of the gas phase as a function of water saturation; (c) relative permeability curve for the gas phase as a function of water saturation during drainage (I) and imbibition (II).

In a comparative study, the capillary sealing efficiency of intermediate to low permeability sedimentary rocks was investigated by N_2, CO_2 and CH_4 breakthrough experiments on initially fully water-saturated rocks of different lithological compositions. Differential gas pressures up to 20 MPa were imposed across samples of 10 - 20 mm thickness, and the decline of the differential pressures was monitored over time. Absolute (single phase) permeability coefficients (k_{abs}), determined by steady state fluid flow tests, ranged between 10^{-22} and 10^{-15} m^2. Maximum effective permeabilities to the gas-phase (k_{eff}), measured after gas breakthrough at maximum gas saturation, extended from 10^{-26} m² to 10^{-18} m².

Correlations were established between (i) absolute and effective permeability coefficients and (ii) effective or absolute permeability and capillary displacement pressure. The results shown in Figure 3.7 indicate systematic differences in gas breakthrough behaviour of N_2, CO_2 and CH_4 reflecting differences in wettability and interfacial tension. For equal permeability values, CO_2 tends to show lower capillary displacement pressure values than methane, while even higher capillary pressures are found for N_2.

Based on the experimental results, a simple dynamic model for gas leakage through a capillary seal was developed, taking into account the variation of effective permeability as a function of buoyancy pressure exerted by a gas column underneath the seal. It could be demonstrated that this model predicts significantly lower leakage rates than models assuming a constant effective gas permeability value after gas breakthrough (Hildenbrand et al. 2004).

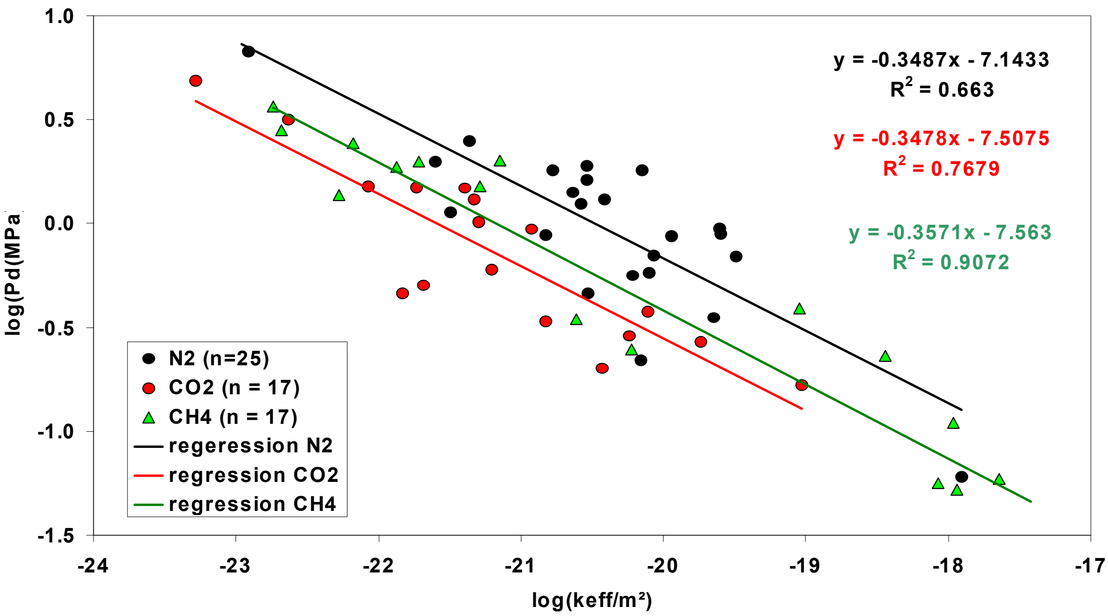

Figure 3.7: Correlations between capillary displacement pressures (Pd) and effective permeability coefficients (K_{eff}, maximum values after gas breakthrough) for nitrogen, methane and carbon dioxide.

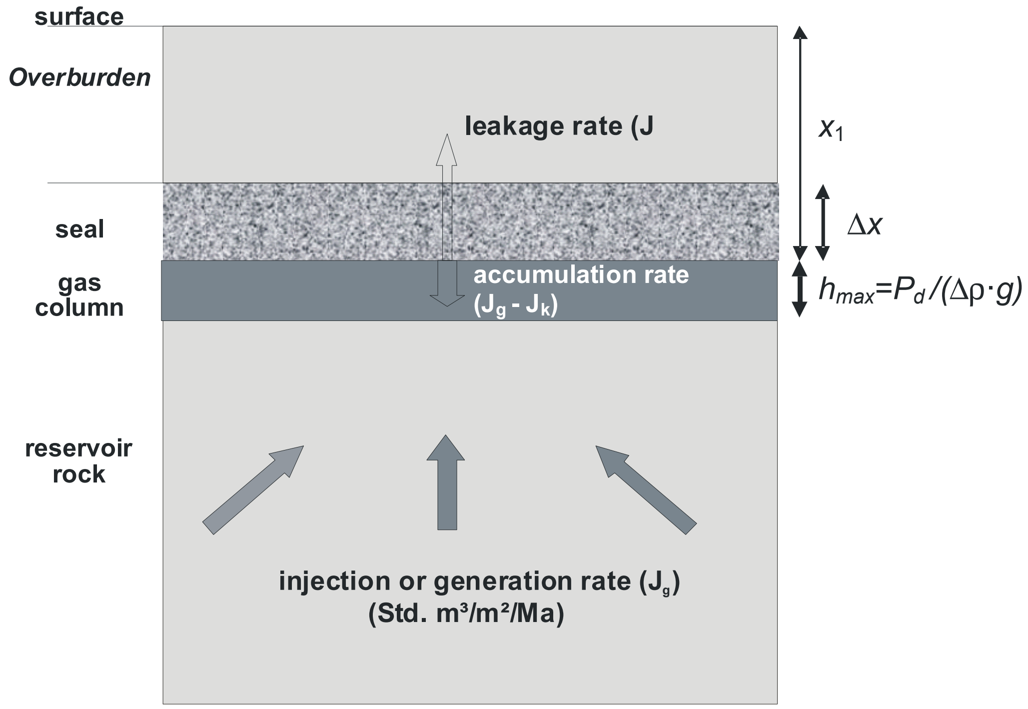

Figure 3.8: Scheme of the dynamic capillary gas leakage model taking into account the dependence of effective permeability on the capillary pressure (difference between gas and water pressure) (Hildenbrand et al. 2004).

3.4.1.2 CO_2 diffusion experiments:

To investigate the rate and intensity of molecular diffusion of CO_2 in water-saturated sedimentary rocks, an experimental set-up was constructed in this project to measure CO_2 diffusion coefficients at simulated subsurface conditions. Due to the specific physical and chemical properties of CO_2, this experimental work faced significant technical challenges, which were mostly overcome. Nevertheless, the poor reproducibility of many measurements is indicative of the complexity of the processes involved (pressure-dependence of CO_2 solubility, pH changes, chemical reactions) and the need for further refinement of the measuring technology.

Evaluation of effective diffusion coefficients

Diffusion is the result of the random Brownian motion of atoms or molecules in liquids, gases or solids. Fick's first law of diffusion describes the diffusive flux rate JD [mass/area/time] as a function of the concentration gradient grad c [mass/length4]:

$$J_D = -D \cdot grad\ c \tag{1}$$

where *D* denotes the diffusion coefficient [length^2/time].

In this work the effective diffusion coefficient is defined as:

$$J_D = -D_{eff} \cdot grad\ c_{bulk} \tag{2}$$

Here D_{eff} denotes the effective diffusion coefficient [length^2/time] and c_{bulk} is the bulk concentration of the species under consideration in the (water-saturated) porous medium (mass per volume of bulk rock). Gas diffusion through the rock samples under the experimental conditions can be described as non-stationary diffusion through a plane sheet.
For the evaluation of the diffusion experiments, equation (3) is fitted to the experimental cumulative total amount of gas that has passed through the sample (*Q(t)*) by means of a least squares procedure and variation of the initial concentration (Q_0) and the lag time (t_0):

$$Q(t) = Q_0 \cdot \left(1 - \frac{t}{t_0} + \frac{12}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \cdot e^{\frac{-n^2 \cdot \pi^2 \cdot t}{6 t_0}} \right) \tag{3}$$

Figure 3.9 illustrates an experimental cumulative diffusion curve (data points) with the fitted diffusion function according to equation (3). The cumulative curve represents the total amount of CO_2 that has diffused across the sample slice since the start of the diffusion experiment. The CO_2 gas reaches the downstream side of the sample and is recorded there only after an initial time. This lag time (t_0) is defined by the intercept of the tangent to the steady-state cumulative curve with the time axis. Also shown in this diagram is the parameter Q_0, which is the intercept of the tangent with the concentration axis.

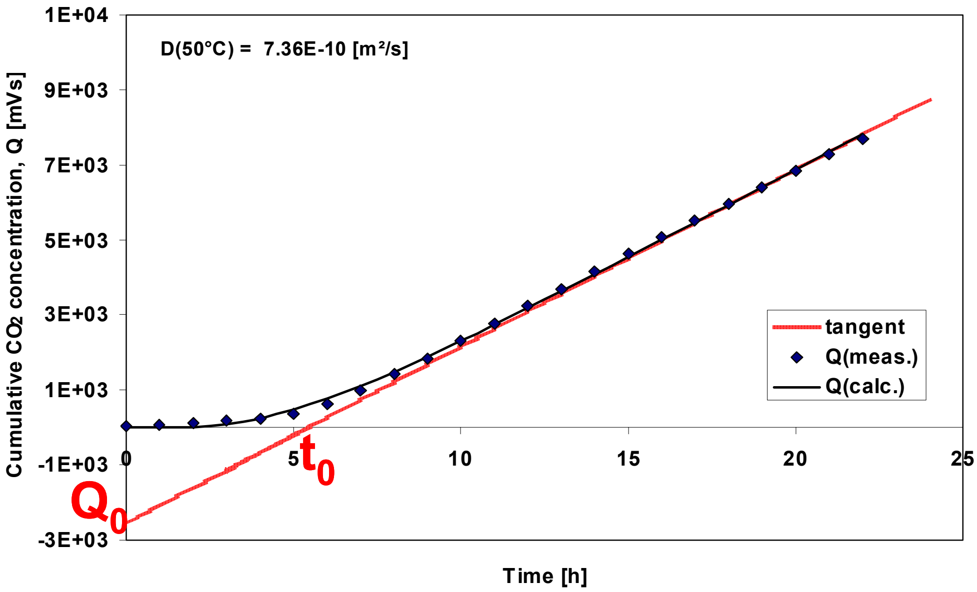

Figure 3.9: Example of a cumulative diffusion curve (measured values and least-squares fit), the tangent defining the lag-time (t_0) and the Q_0 value of the diffusion experiment.

Results

A first series of diffusion experiments was performed on a range of samples of fine-grained caprocks from Montmiral, Thuringia and Florina, plus other previously well-characterised test samples. The diffusion coefficients range between 10^{-9} and 10^{-11} m²/s and show fluctuations of more than one order of magnitude for multiple experiments on the same sample. It is likely that these fluctuations reflect chemical changes in the mineral matrix of the samples during the diffusion experiments.

One remarkable feature are the extremely high C_1 values observed for the Boom clay samples, indicating a very high CO_2 storage capacity of this material. At the same time, consistently low diffusion coefficients are observed for this clay. These results have prompted us to conduct further investigations in the diffusive transport of CO_2 in clays and shales.

3.4.1.3 Petrophysical measurements and fluid transport experiments on Samples from the Florina Basin (Greece)

Seventeen samples were collected from the M1 well at Messokampos in the Florina Basin, Northern Greece. Mercury injection porosimetry was performed successfully on four of these samples. Although their absolute porosity values are similar, the four samples exhibited significant differences in their pore-size distributions.

Among the samples from the Florina well, one was selected for permeability tests and CO_2 diffusion experiments. This sample appeared to be very clay-rich and the pore-size distribution indicated a considerable amount of microporosity. Sample plugs were drilled both perpendicular and parallel to the bedding plane.

Permeability coefficients perpendicular to the bedding plane were initially in the 5 – 10 nDarcy (5 – 10×10^{-21} m²) range. After the first two CO_2 diffusion experiments, a significant increase in permeability coefficients, up to > 300 nDarcy, was noticed. The last permeability test yielded a coefficient of 76 nDarcy. The effective diffusion coefficients (D_{eff}) measured in the experiments are in the range of 10^{-10} m²/s. Within the first three measurements they show an increase from 0.84×10^{-10} m²/s to 1.5×10^{-10} m²/s, while the final value is lower again, thus following the permeability trend. The reasons for the observed behaviour could not be established on the basis of the limited number of experiments. Chemical reactions of the CO_2 with the mineral matrix of the sample might be one explanation, but mechanical damage of this very brittle and poorly consolidated sample during the fluid pressure changes between the individual experiments cannot be excluded.

The results of the permeability and diffusion tests, conducted with the plug drilled parallel to the bedding plane, also showed a slight increase in permeability after the first two CO_2 diffusion experiments. These experiments could not be evaluated due to technical problems. The final diffusion experiment yielded a diffusion coefficient of 1.7×10^{-10} m²/s, i.e. slightly higher than for the perpendicular plug. The C_1 values (representing the CO_2 storage capacity under the experimental pressure and temperature conditions) for this shaly sample were significantly higher than those observed for most other samples from the first series but not as high as those found for the Boom clay sample. The observations indicate that clay/shale content in poorly compacted lithotypes could play a significant role in the retention or storage of CO_2. Future studies should focus on clay content and cation exchange capacity as parameters controlling sealing efficiency for CO_2.

3.5. FURTHER READING

NASCENT REPORTS:

HILDENBRAND A., SCHLÖMER S., AND KROOSS B. M. (2002) Gas breakthrough experiments on fine-grained sedimentary rocks. *Geofluids* **2**, 3-23.

HILDENBRAND A., SCHLOEMER S., KROOSS B., AND LITTKE R. (2004) Gas breakthrough experiments on pelitic rocks: comparative study with N_2, CO_2 and CH_4. *Geofluids* **4**, 61-80.

OTHER REFERENCES

ANTONOV, P.L. (1954) On the diffusion permeability of some claystones *Trudy NIIGGR* **2**, 39-55. Sb. Geokhim. Met. Poisk. Nefti i Gaza. Gostoptekhizdat, Moscow. (in Russian)

ANTONOV, P.L. (1958) On the investigation of the principles of gas saturation of sedimentary rocks with depth *Trudy VNIGNI* **10**, 241-256, Gostoptekhizdat, Moscow. (in Russian)

ANTONOV, P.L. (1964) On the extent of diffusive permeability of rocks. In: *Direct Methods of Oil and Gas Exploration*, Nedra, Moscow, 5-13. (in Russian)

ANTONOV, P.L. (1970) Results of the investigation of diffusive permeability of sedimentary rocks for hydrocarbon gases, *Trudy VNIIYaGG*, **8**, 51-79. (in Russian)

BERG R.R. (1975) Capillary pressures in stratigraphic traps *AAPG Bulletin* **59**, 939-956.

BREDEHOEFT, J.D. AND HANSHAW, B.B. (1968) On the Maintenanace of Anomalous Fluid Pressures: I. Thick Sedimentary Sequences, *Geological Society of America Bulletin*, **79**., 1097-1106.

CAILLET, G. (1993) The caprock of the Snorre Field, Norway: a possible leakage by hydraulic fracturing, *Marine and Petroleum Geology*, **10**, 42-50.

CRANK J. (1975) The Mathematics of Diffusion. Oxford, Clarendon Press

DOWNEY, M.W. (1984) Evaluating seals for hydrocarbon accumulations, *AAPG Bulletin* **68**, 1752-1763

HANTSCHEL, T., KROOSS, B.M., WYGRALA, B.P. AND MUSCIO, G.P.A. (1995) Comparative Study of Separate Phase Flow and Diffusion of Light Hydrocarbons, *EAGE 57th Conference and Technical Exhibition - Glasgow, Scotland, Extended Abstract* **2**, no. F040

HUBBERT, M.K. (1953) Entrapment of petroleum under hydrodynamic conditions, *AAPG Bulletin.* **37**, 1954-2026.

KROOSS, B.M. AND SCHAEFER, R.G. (1987) Experimental measurements of the diffusion parameters of light hydrocarbons in water-saturated sedimentary rocks - I. A new experimental procedure, *Organic Geochemistry*, **11**, 193-199

KROOSS, B.M. AND LEYTHAEUSER, (1988) Experimental measurements of the diffusion parameters of light hydrocarbons in water-saturated sedimentary rocks - II. Results and geochemical significance, *Organic Geochemistry*, **12**, 91-108

KROOSS, B. M. AND LEYTHAEUSER D. (1997) Diffusion of methane and ethane through the reservoir cap rock: Implications for the timing and duration of catagenesis: Discussion. *The American Association of Petroleum Geologists Bulletin*, **81**, 155-161

KROOSS, B.M., LEYTHAEUSER, D. AND SCHAEFER, R.G. (1992a) The quantification of diffusive hydrocarbon losses through cap rocks of natural gas reservoirs - a reevaluation, *AAPG Bulletin*, **76**, 403-406

KROOSS, B.M., LEYTHAEUSER, D. AND SCHAEFER, R.G. (1992b) The quantification of diffusive hydrocarbon losses through cap rocks of natural gas reservoirs - a reevaluation: reply, *AAPG Bulletin*, **76**, 1842-1846

LEYTHAEUSER, D., SCHAEFER, R.G. AND YÜKLER, A. (1980) Diffusion of light hydrocarbons through near-surface rocks, *Nature*, **284**, 522-525

LEYTHAEUSER, D., SCHAEFER, R.G. AND YÜKLER, A. (1982) Role of diffusion in primary migration of hydrocarbons. *AAPG Bulletin*, **66**, 408-429

MONTEL, F., CAILLET, G., PUCHEU, A. AND CALTAGIRONE, J.P. (1993) Diffusion model for predicting reservoir gas losses, *Marine and Petroleum Geology*, **10**, 51-57

NELSON, J.S., AND SIMMONS, E.S. (1992) The quantification of diffusive hydrocarbon losses through cap rocks of natural gas reservoirs - a reevaluation: discussion, *AAPG Bulletin*, **76**, 1839-1841

NELSON, J.S. AND SIMMONS, E.S. (1995) Diffusion of methane and ethane through the reservoir cap rock: Implications for the timing and duration of catagenesis, *AAPG Bulletin*, **79**, 1064-1074

NESTEROW, I.I., AND USCHATINSKIJ, I.N. (1972) Seal properties of claystones above oil and gas accumulations in Mesozoic sediments of the western Siberian depression, *Zeitschrift für angewandte Geologie*, **18**, 548 - 555. (in German)

SCHLOEMER S. AND KROOSS B. (2004) Molecular transport of methane, ethane and nitrogen and the influence of diffusion on the chemical and isotopic composition of natural gas accumulations. *Geofluids* **4**(1), 81-108.

SCHOWALTER, T. T. (1979) Mechanics of secondary hydrocarbon migration trapping, *AAPG Bulletin*, **63/5**, 723-760

SMITH, J.E., ERDMAN, J.G. AND MORRIS, D.A. (1971) Migration, accumulation and retention of petroleum in the earth, *Proceedings of the 8th World Petroleum Congress*, **2**, 13-26

WATTS, N. L. (1987) Theoretical aspects of cap-rock and fault seals for single- and two-phase hydrocarbon columns. *Marine and Petroleum Geology*, **4**, 274-307

Chapter 4. Migration in the shallow subsurface

4.1. SUMMARY AND CONCLUSIONS

As the shallow subsurface may be the last barrier against CO_2 escape to the atmosphere, a detailed understanding of gas migration in this environment is important to assess risk to human health and the environment. Results presented in this chapter indicate how various mechanisms in the near surface can attenuate CO_2. However, the physical and chemical characteristics of the site, as well as the size and intensity of any eventual leak, fundamentally control the effectiveness of these processes.

The study included detailed soil gas surveys in areas of natural CO_2 vents, a shallow gas injection test, gas bubble migration experiments and studies of shallow natural gas (methane) leaking offshore in the North Sea.

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. The influence of the unsaturated zone was also observed in a detailed examination of other, unstable gas species transported by the CO_2, such as hydrogen sulphide (H_2S) and hydrogen (H_2). Elevated concentrations of these gases are restricted to zones of high flux rates in the centre of the vents, as lateral diffusion results in their oxidative destruction. The association of these trace gases, which also present a health (H_2, H_2S) or greenhouse (CH_4) hazard, with the vent indicates that even if only CO_2 is sequestered at depth a future leak may also result in the mobilisation of other gaseous species due to their transport within the higher volume CO_2 stream. Soil gas surveys, including the determination of the mobile noble gases helium (He) and radon (Rn) around known fault systems over a natural CO_2 accumulation in the Vorderrhön area, Thuringia, Germany, helped to identify the optimal position for the installation of continuously operated monitoring systems.

The results of the injection of a helium (He)/ argon (Ar)/ CO_2 gas mixture at around 10 m depth and subsequent monitoring of soil gas concentrations clearly demonstrated how the chemical characteristics of each gas species can control its migration in the shallow subsurface. Data indicated that the non-reactive, low-solubility, highly-mobile gas He escaped to the surface immediately, at high concentrations and near the injection well. In contrast, the soluble, reactive and dense gas CO_2 arrived at the surface at much lower concentrations and at a much later time, due to its dissolution in groundwater (and transport in this phase) as well as its lateral diffusion in the unsaturated zone due to density differences. The laboratory column experiments conducted to examine the migration characteristics of ascending bubbles in the shallow environment support these results, as rapid dissolution was observed once bubble sizes decreased below a certain threshold.

These results indicate that gas migration and possible release to the atmosphere is controlled by the physical and chemical characteristics of the migrating gases and the geology and hydrogeology of the shallow subsurface. Clearly, a major difference between the natural CO_2 vent and the gas injection test results, however, is the gas volume and time scale. For example, the gas vent has probably existed for tens (or perhaps hundreds) of years with an essentially unlimited source of CO_2 due to the continual formation of the gas by thermal metamorphic reactions. This, combined with the high flux rates, has resulted in a system at steady-state which provides a continual and significant transfer of CO_2 to the atmosphere. In contrast, the short-term injection of a finite amount of CO_2 into the shallow environment resulted in little transfer of this gas to the atmosphere due to the attenuating capabilities of the local system. The scale of any eventual leak from a CO_2 storage reservoir would lie between these two extremes, as the amount of gas available at depth would be large but finite, and would be limited further by attenuation reactions during its upward migration. This smaller quantity of gas would then be further decreased within the near-surface environment through the processes of dissolution, dilution, chemical reactions and biological consumption observed in this work. If CO_2 volumes are small enough, advection rates low enough and the appropriate shallow environment exists, the near surface environment may even have the potential to prevent the transfer of deep CO_2 to the atmosphere, acting as the final barrier at the end of a long migration pathway.

Accumulations of shallow gas (mainly composed of methane) are known to occur in various parts of the North Sea. A study area in the northernmost part of the Netherlands North Sea sector was selected at the start of the NASCENT project with the aim of carefully examining the nature, characteristics and more in particular also the surface and subsurface expressions of the gas on different data sets. Reflection seismic and other marine acoustic data can reveal the presence and distribution of the shallow gas in the subsurface and in the water column. Confirmation of the interpretation of the presence of gas can be obtained through chemical analysis of the headspace gas from seabed sediment samples. Although the shallow gas is composed mainly of methane and therefore is chemically different from CO_2, its physical behaviour in the subsurface, including the way it migrates through the near-surface environment and leaks to the surface, can be considered as similar to that of CO_2.

In the Vorderrhön area, 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 showed no evidence for a leak. 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 vegetation period are much larger.

4.2. INTRODUCTION

If CO_2 were to eventually leak from a deep geological reservoir, its migration and release to the surface would be strongly attenuated by many physical and chemical processes occurring along the travel pathway. The final “barrier” through which this ascending gas must pass is the shallow subsurface, an interval which will be unique for every site but which, in an onshore storage system, may include confined and unconfined fresh-water aquifers, the unsaturated zone, and several interlinked ecosystems including a final interval of plant roots and organic litter.

CO_2 behaviour in the near surface zone has been studied for two reasons. The first reason is to understand how this interval may contribute to reducing, or even completely preventing, the migration of CO_2 to the atmosphere. Various processes occur in the shallow subsurface, which may contribute to the attenuation of CO_2 prior to release at surface:

- Unsaturated zone:
  - Density driven diffusion of CO_2 on top of the water table
  - Lateral gas phase diffusion and dilution
  - Dissolution in percolating rainwater
  - Consumption in biological reactions
  - Entrapment below impermeable barriers
- Saturated zone:
  - Upward bubble advection
  - Gas dissolution into groundwater
  - Acid-base reactions in the aqueous phase
  - Diffusion in the aqueous phase
  - Advection in flowing groundwater
  - Entrapment below impermeable barriers

Many site-specific factors will have a significant control over the effectiveness of any of these processes, such as:

- Groundwater salinity (higher salinity results in lower gas solubility) and alkalinity (higher alkalinity will consume more CO_2-derived acidity)
- Aquifer geology (e.g. silicates vs. carbonates would result in different geochemical reactions that consume CO_2 at different rates)
- Local geology (e.g. less permeable clay versus more permeable sand)
- The thickness, porosity and permeability of the unsaturated zone (gas storage capacity, diffusion potential)
- The density and type of plants occurring on the surface (i.e. tolerance to high CO_2 concentrations)

The combination of these parameters has the potential to greatly influence the timing and quantity of any eventual CO_2 release to the atmosphere.

The second reason for interest in the shallow subsurface is the need to better understand how this zone influences any eventual release points at the surface, and how this in turn affects humans as well as the biosphere as a whole. For example, the risk to human health and the approach used to mitigate these risks, will be greatly influenced if the gas is released as a point source or more diffusely throughout an entire area. Similarly, release patterns will also affect the extent and severity of a CO_2 leak on plant life, on the quality of shallow groundwaters used as drinking water sources and on the possible formation of collapse structures due to karstic reactions.

The principle goal of the work conducted on the shallow subsurface was to better understand the influence of the physical and chemical properties of CO_2 and the geological and hydrogeological environment through which it may pass. The Università di Roma "La Sapienza" addressed this goal through:

- Detailed (2 samples per km^2) and highly-detailed (60 samples per km^2) soil gas and gas flux surveys in areas of natural CO_2 seeps
- Through the field-scale injection of a gas mixture (including CO_2) into a shallow aquifer to monitor the migration of gases having different physical and chemical characteristics
- Through a series of laboratory column experiments which examined the ascent velocities of bubbles in a water-saturated glass-bead "aquifer".

It has been possible to clearly define the importance of various parameters that control near-surface attenuation, consumption and migration of CO_2 using these three approaches.

To accurately determine the CO_2 concentration in the shallow subsurface reliable monitoring tools are required for continuous operation. The Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) developed a new type of monitoring system which was operated at potential point sources for geogenic CO_2 (e.g. in bore holes, fractures in rocks and salt beds). It was operated automatically and controlled remotely. The test site was the Oechsen CO_2 deposit in Thuringia, Vorderrhön. Monitoring of gas emanations from the shallow subsurface for periods of months and years gave no indications of contributions from the underlying CO_2 reservoir. Details for the selection of monitoring sites, the instrumental setup as well as monitoring results are given in detail in Pearce (Ed.) (2003) and Kemp et al. (2003).

4.3. HOW DOES GAS MIGRATE IN THE SHALLOW SUBSURFACE?

4.3.1. Soil gas surveys

Although a number of soil gas surveys were conducted at the four Italian sites, the detailed work performed within the Latera area gave the most information regarding gas migration in the shallow subsurface.

The studied area was a small field within the Latera study site where a number of gas vents could be seen on the surface due to the adverse effect of CO_2 and other gases on the local vegetation. In this area, the water table is located at a depth of around 4 m, with most of the shallow geological units consisting of volcaniclastic sediments and fluvial deposits. Two types of survey were conducted at this site:

i) A reconnaissance survey consisting of a series of radiating sampling points around a number of recognised gas vents using field based analytical instruments; and

ii) A second survey consisting of a highly detailed horizontal profile of samples (1 to 2 m apart) across vents with reactive gases analysed both in the field and a full suite of stable gases analysed in the laboratory.

The first survey showed that the CO_2 distribution was sub-circular and symmetrical above isolated vents but was elongated and irregular where near-by vents coalesced (Figure 4.1). Although the highest CO_2 concentrations were observed in areas with stressed or no vegetation, elevated values extended far beyond that observed on the surface. The width of the vents was highly variable, ranging from less than 10 to over 40 m wide (defined by a threshold CO_2 concentration of >8%). As outlined in a previous report (Annunziatellis et al., 2003a), the flux rates of CO_2 are also highly variable, both from one vent to another and within a single vent, with flux rates varying by more than two orders of magnitude within a metre. Gas release therefore occurs within a number of relatively small points on the surface, implying that gas flow at depth is likely to be highly channelised along irregular gas-permeable pathways within the fault zone identified in geophysical surveys.

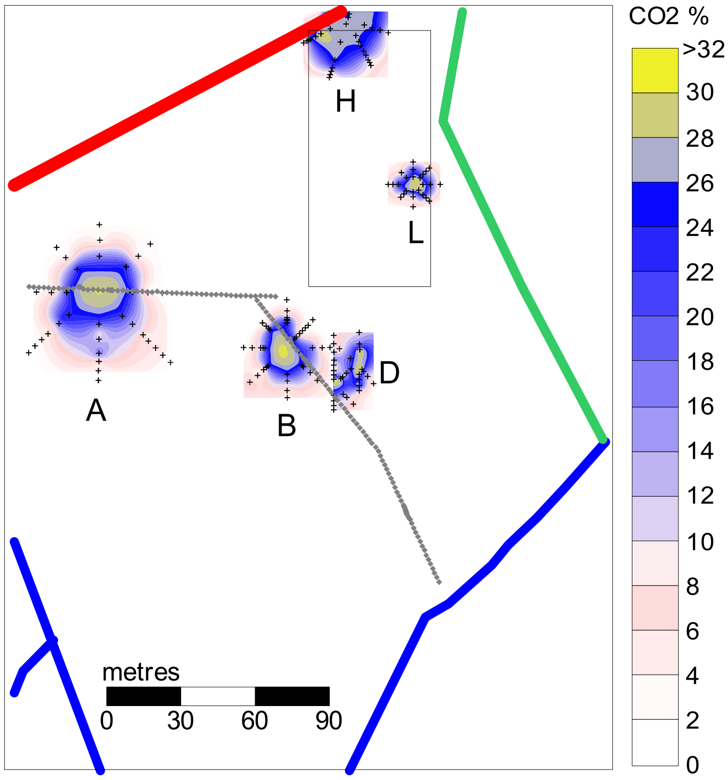

Figure 4.1: Radiating soil gas surveys highlighting various gas vents (note field sensor maximum was 32%). Trace of horizontal profile (results given in Figure 4.2) is shown as grey dots.

In order to better interpret the results of these radial surveys a second, horizontal profile survey was performed across a number of vents, with samples being analysed immediately in the field for H_2S and H_2 while CO_2, oxygen (O_2), N_2, He and light hydrocarbons were analysed in the laboratory. CO_2 and He have essentially the same distribution and have the widest and largest number of peaks in concentration of any of the measured species (Figure 4.2). The gases H_2S, H_2, CH_4 and C_2H_6 show far fewer peaks but their distributions are very similar to each other, with the two main peaks for these gases corresponding with the two largest CO_2 peaks (Figure 4.2). If one assumes that all the gases come from a similar depth and are transported to the surface by CO_2, which acts as a "carrier gas", then the variability observed on the surface is likely to be due to the different reactivity of each gas in the near surface environment. For example, He is a highly mobile and non-reactive element, and therefore shows a large number of wide peaks along the entire profile. CO_2, on the other hand, which has essentially the same distribution, is far more reactive due to its high solubility in water and its involvement in acid-base reactions. The similarity of the reactive CO_2 and the conservative He implies that:

- The system is approaching a steady state such that minerals involved in the reactions have been consumed allowing for lateral diffusion of the gas;
- The high CO_2 flux supplies an excess mass of CO_2 at a rate which is greater than the kinetics of dissolution and eventual reaction;
- CO_2 dissolution is greatly reduced within the relatively thick unsaturated zone (4 m), thereby allowing for lateral diffusive and advective transport with minimal loss due to reactions; or
- A combination of some of these processes.

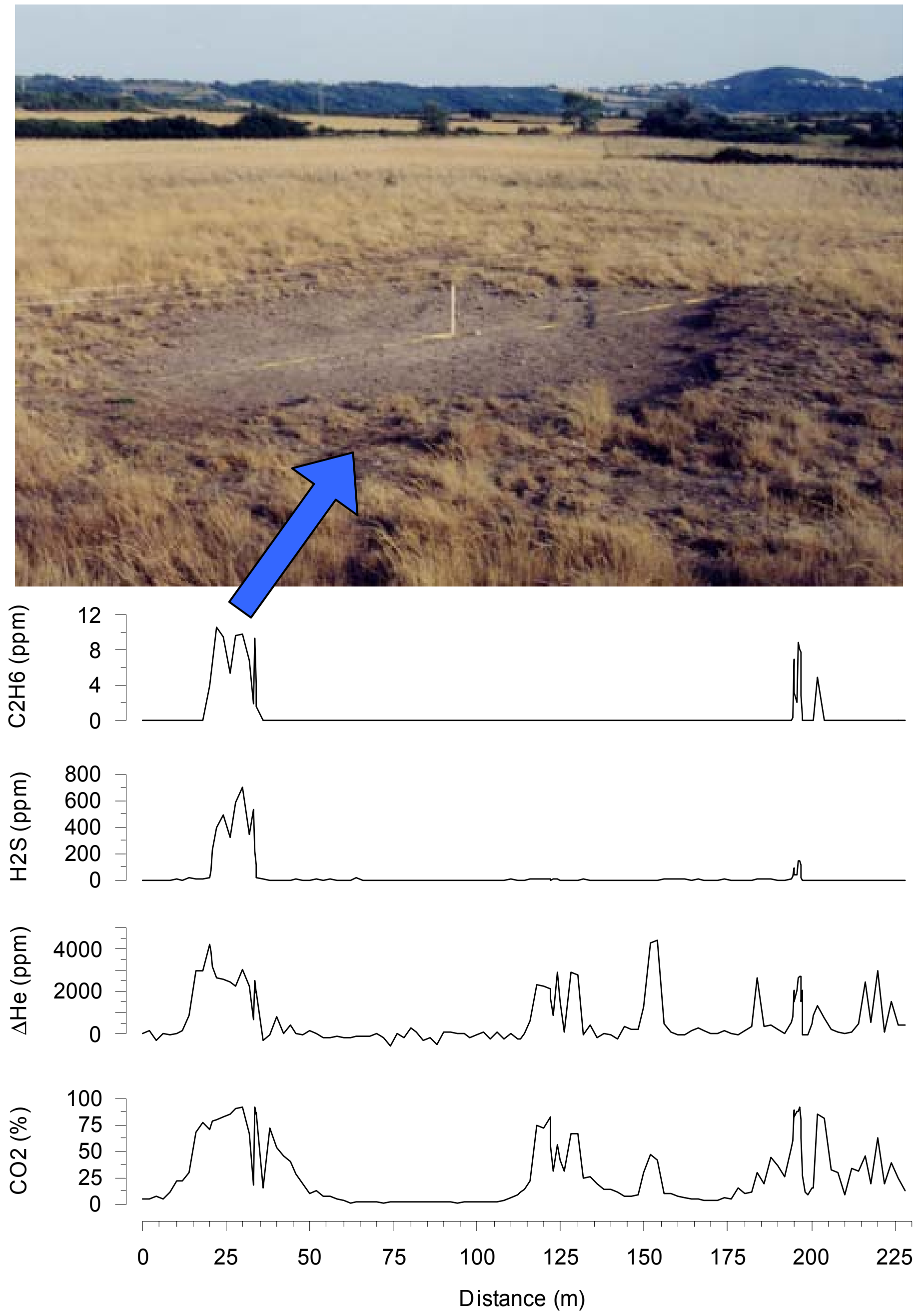

Figure 4.2: Gas vent (top) and results from a soil gas profile conducted in the same area (bottom); the elevated values at 25 m are located above the pictured vent. Note that CO_2 and He have a very similar distribution, whereas H_2S and C_2H_6 have elevated values only at two points with high fluxes.

Interestingly the thick unsaturated zone may also contribute to the rather limited number of narrower peaks observed for the other gas species. For example, the highly reduced H_2S is not only soluble and involved in acid-base and redox reactions in the aqueous phase, but it may also be involved in gas-phase redox reactions with O_2. As such, once the gas bubbles burst from the surface of the water table, H_2S and the other species are transported advectively in the gas phase and are free to react with soil gas that is in equilibrium with atmospheric air. It is likely that a redox reaction pathway involving O_2 consumes such reduced species as H_2S, H_2 and CH_4, and thus only narrow peaks are observed for these species in the cores of gas vents having a high flux rate. This is because in the centre of these vents the reactive gases do not encounter high O_2

concentrations, due to the high CO_2 levels, nor do they have time to react, due to the high velocities.

The soil gas survey results from Ciampino were similar to those of Latera, with this site showing areas of dead or “stressed” vegetation due to the occurrence of gas vents, as well as a clear association between the “carrier” gas CO_2 and other trace toxic gases like H_2S and radon (Rn). This similarity is perhaps not surprising considering that both are quiescent volcanic areas. In contrast, the San Vittorino site, which is a sediment filled intramontane basin with a very shallow water table, does not show patches of dead vegetation but rather the development of sinkholes. At this site gas bubbles arrive at the ground surface in water-filled sinkholes and springs, indicating that the unsaturated zone plays a minor role in attenuation. Although detailed sampling was not conducted around the vents it is expected that the lateral influence of the vents in the soil gas horizon would be much smaller than that observed at Latera. This idea is supported by gas flux measurements around one major vent which showed extremely low values, indicating channelled gas flow and the local sealing capability of the clay-rich fluvial sediments filling the valley.

From the soil gas surveys, two important conclusions can be reached regarding CO_2 storage applications. First, although it is foreseen that only CO_2 will be injected into a geological reservoir at depth it must be remembered that if there is an eventual leak to the surface the CO_2 may also transport other trace gases with it. Second, the different distributions of the various gas species in the shallow soil environment indicate the importance of this horizon in acting as a buffer against the transfer of gas species to the atmosphere. The efficiency of this buffer will depend on the characteristics of the zone itself, such as the unsaturated zone thickness, mineralogy and gas permeability, as well as on the characteristics of the vent, such as flux rates and gas composition (see Annunziatellis et al., 2003a, for more details of the highly detailed sampling at the Latera gas vents.)

4.3.2. Gas injection test

In order to understand the influence of a fault structure on gas migration, a gas injection test (Figure 4.3) was conducted at the Latera location described above, slightly to the north of the majority of the gas vents. This site was chosen because geophysical surveys and vent alignment indicated the presence of a fault crossing the area at depth. During this experiment, a total of 6400 L of gas (40% Ar, 40% He and 20% CO_2) was injected into a non-recoverable interval (possibly a fault) between 9 and 12 m below ground surface. Soil gas samples were collected around the injection borehole from a grid of 64 fixed sample points, spaced 1 m apart, near the well and 10 to 20 m apart further away. All points were sampled as a group at specific times (e.g. 1, 5, 12, 24 etc. hours after the start of injection) and the samples were analysed both in the field and the laboratory for the injected gas species. In order to monitor for breakthrough of the highly soluble CO_2 in the dissolved phase, ground water samples were also collected from six piezometers, drilled to 5 m depth into the shallow aquifer.

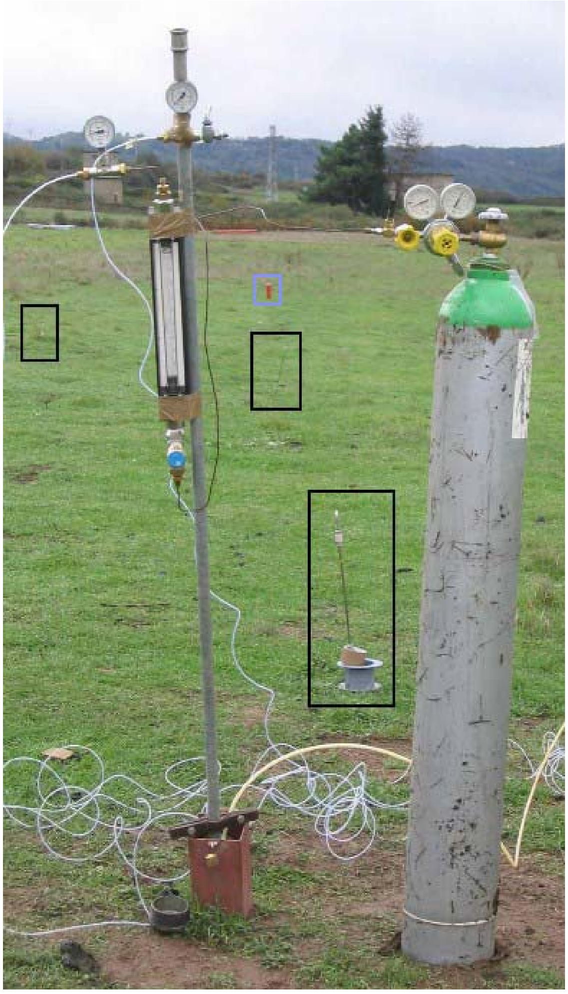

Figure 4.3: Gas injection set up showing the gas canister, gauges for up-stream and down-hole pressure readings and the gas flow meter. Black squares out-line soil gas probes and the blue square marks an observation piezometer

Results from the gas injection test (Figure 4.4) highlight the importance of understanding the chemical and physical characteristics of the gases being monitored, as aqueous solubility, gas density and both aqueous- and gas-phase diffusivities play a role in the travel times and mass attenuation features of migrating gases. The gas mixture injected at the Latera test site consisted of three rather different species, ranging from the highly insoluble, highly mobile, low density He to the very soluble, reactive and dense gas CO_2, while Ar has characteristics which lie between these two extremes but closer to He.

These differences were reflected in the results obtained during the test. He arrived between 1 and 5 hours over a 10×10 m area around the injection well. At 5 hours, the average He concentration was 60 ppm, rising to a maximum of 150 ppm after 24 hours and then decreased to background levels (between 6×10^3 and 3×10^4 ppb over the next 3 to 4 weeks). In contrast, it is the CO_2 first arrived after 24 hours (c. 7%) at one point about 30m from the injection well along the groundwater flow direction and a recognised fault system, however as the background values of CO_2 are high and somewhat variable at this site it is difficult to pinpoint an exact arrival time. Over the duration of the monitoring, a number of scattered points located 20 to 40 m from the injection well showed elevated CO_2 values (up to 10%), however high concentrations were never observed near the well as was seen for He and, to a lesser extent, Ar. Ar had a distribution that was more similar to He, as Ar also had a sharp increase (5.1%) after 5 hours, at one site near the injection well. Subsequent sampling indicated values up to 6.1% Ar, however elevated concentrations were only observed in three or four sites around the injection well, compared to twelve sites for He.

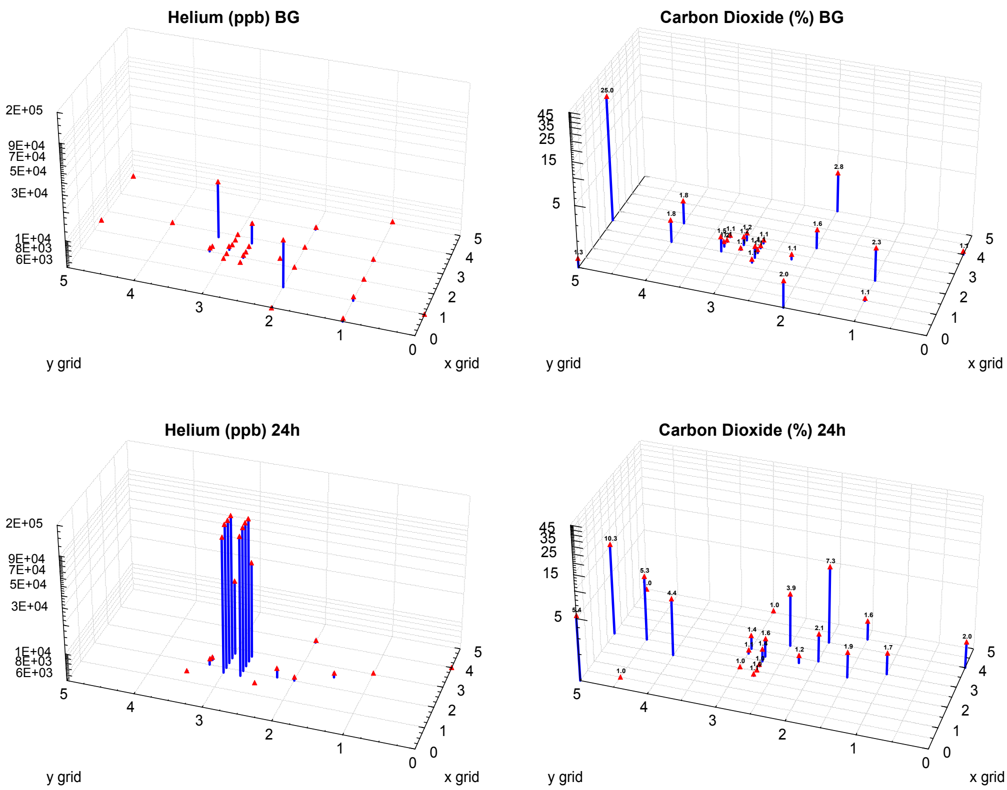

Figure 4.4: 3D representation of soil gas helium and carbon dioxide before (background) and after the injection of 6400 L of gas mix (40%Ar, 40% He, 20% CO2) at a depth of 9-12 m below surface into a faulted interval. The Y axis runs essentially north-south

A mechanism to explain these results is proposed whereby initially the more soluble gases are stripped from the gas bubbles, enriching them in He, and that this gas phase, upon reaching the water table, migrates rapidly through the unsaturated zone to the surface due to its low density and high diffusivity. Subsequently the groundwater in the bubble flow path becomes progressively saturated in CO_2, resulting in less transfer to the dissolved phase and more of this gas reaching the water table. Once in the unsaturated zone, the denser CO_2 moves laterally on top of the water table, resulting in the observed lateral dispersion, temporal attenuation and lower concentrations (due to both dilution by soil gas and removal into the aqueous phase) observed in the soil gas surveys. Lateral migration of CO_2 saturated groundwater, and eventual release of this gas to the unsaturated zone via vent activity, is also a possible mechanism. However, this can only explain anomalies observed down gradient from the injection point.

These results, like the soil gas surveys discussed above, indicate the importance of the physico-chemical characteristics of the studied gases as well as the geology and hydrogeology of the shallow subsurface, in controlling gas migration and possible release to the atmosphere. In particular, the temporal and mass-transfer attenuation of CO_2, as compared to the tracer He, indicates that the shallow sub-surface acts as a final barrier which can reduce the amount of leaking CO_2 that is released to the atmosphere.

4.3.3. Laboratory microbubble flow experiments

Well-constrained laboratory microbubble flow experiments were conducted to simulate natural CO_2 migration through the near-surface saturated zone. This work involved measuring the time required for a He slug in a constant flow of N_2 gas bubbles to travel the length of a 110 cm high Plexiglas column (Figure 4.5), with a number of experiments being conducted on bubbles of different sizes (see Annunziatellis et al., 2003a, Chapter 5 for more details). N_2 was chosen for these tests due to its low solubility, compared to CO_2, while He was used as a tracer within the N_2 due to its high mobility and laboratory analytical applicability. The experimental set-up consisted of two Plexiglas columns, one inside the other, held together by upper and lower grooved Plexiglas plates containing various inlet and outlet ports. The inner tube was used as the sample column, and it is here that the bubbles migrated through either free water or water-saturated glass beads. Heated water was then circulated between the two tubes to maintain the experiment at a constant temperature, while a gas canister was used to maintain constant pressure. A mass flow controller was used to regulate the amount of gas transferred to the base of the column, an injection port was located down-gradient for the introduction of the He tracer slug and bubbles were produced via oscillating glass capillary tubes. Software, written exclusively for the experiment, controls the valves and receives input from the other sensors, thereby automating control and data collection once an experiment is begun. Travel time experiments were conducted by establishing a steady state flow of N_2 bubbles through the column and then injecting a known quantity of He at the base. He concentration in the head space at the top of the column is then monitored for breakthrough and gas bubble velocities are calculated.

Data were produced on the travel times of very small bubbles of N_2 through a 1 m long column of saturated glass beads. Results collected on the rise velocity of upwardly migrating bubbles of various sizes, from 0.1 to 2 mm, agreed with theoretical calculations based on Stokes Law. Of particular interest was the experiment conducted on very small bubbles having a diameter of less than 100 μm, as the combination of high surface area to volume ratios and very slow rise velocities resulted in extremely rapid dissolution of the bubbles. This result was seen not only with the low solubility carrier gas N_2 but also with the even less soluble tracer gas He. These results illustrate the buffering capacity of the overlying aquifers, in terms of stripping the rising bubbles of the much more soluble CO_2 as it rises through the aquifers that may overly a reservoir. Although it is not known what the size of bubbles might be from a leaking CO_2 reservoir, the extremely long travel pathway to the surface should provide a significant sink for the gas and greatly attenuate its mass transfer and travel times to surface. These results are in good agreement with those obtained during the gas injection test described above and detailed in Chapter 4 of Annunziatellis et al., 2003a.

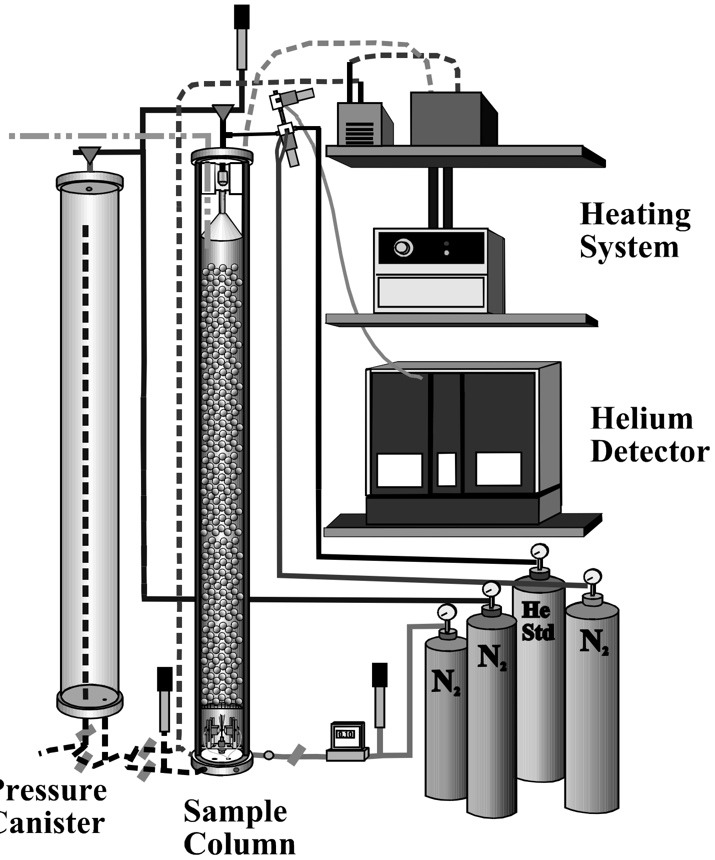

Figure 4.5: Schematic drawing showing the gas bubble experimental set-up.

4.3.4. Offshore shallow methane monitoring

Accumulations of shallow gas (mainly composed of methane) are known to occur in various parts of the North Sea. A study area in the northernmost part of the Netherlands North Sea sector was selected at the start of the NASCENT project with the aim of carefully examining the nature, characteristics and especially the surface and subsurface expressions of the gas by different monitoring techniques. Reflection seismic and other marine acoustic data can reveal the presence and distribution of the shallow gas in the subsurface and in the water column. Confirmation of the interpretation of the presence of gas can be obtained through chemical analysis of the headspace gas from seabed sediment samples. Although the shallow gas is composed mainly of methane and therefore is chemically different from CO_2, its physical behaviour in the subsurface, including the way it migrates through the near-surface environment and leaks to the surface, can be considered as similar to that of CO_2.

During the first phase of the project a detailed literature review and a quick scan of existing seismic and acoustic data of the study area resulted in an inventory of the various indications for shallow gas that occur in the area (Schroot & Schüttenhelm, 2001). Among the features related to the presence or escape of shallow gas described in the literature, the following were found to occur in the study area:

- pockmarks (surface features visible on echo and multi-beam data)
- acoustic blanking and acoustic turbidity (on very high frequency sub-bottom profiler data) and bright spots
- shallow enhanced reflectors
- gas chimneys

Schroot & Schüttenhelm (2002) provided an overview of where these features were encountered. During the second phase of the project a marine data acquisition survey was designed in order to take additional measurements at a few selected sites of interest. Using a Netherlands Government research vessel, one week was spent acquiring acoustic and seismic data and a second week was dedicated to collecting seabed sediment samples using a vibrocorer instrument. These samples were sent to a geochemical laboratory for analysis of their gas content. Methane and ethane concentrations and the carbon isotopic composition of methane were measured in the laboratory. In total 60 cores, with a length varying between 2 and 5.5 m were taken. The 60 sites were distributed over three specific sites of interest.

The first site chosen was that of a previously detected seabed pockmark in the Dutch offshore license block A11. The feature had been reported in 1998 by the Royal Netherlands Navy who had observed it on side-scan sonar. Our marine survey in 2002 confirmed the presence of the crater-like feature. Figure 4.6 shows an image of the seafloor morphology using multi-beam echo data. The diameter of the pockmark is about 140-150 m, the shape being somewhat asymmetric. Maximum depth of the depression is about 2 m. Samples were collected from the cores taken at six different locations in and near the pockmark. Maximum core length was 3.4 m. The samples were used for conventional headspace analysis. Figure 4.6 shows that the highest CH_4 concentration (122.6 ppm) is found in the core from the very centre of the feature. This value is significantly higher than background values. It is remarkable that the location of the anomaly almost coincides with the presence of a smaller, so-called unit pockmark. Unit pockmarks are smaller features of a few meters in diameter, occurring within the larger feature (Hovland & Judd, 1988). Within the larger feature the unit pockmark possibly represents the most recent spasmodic seepage.

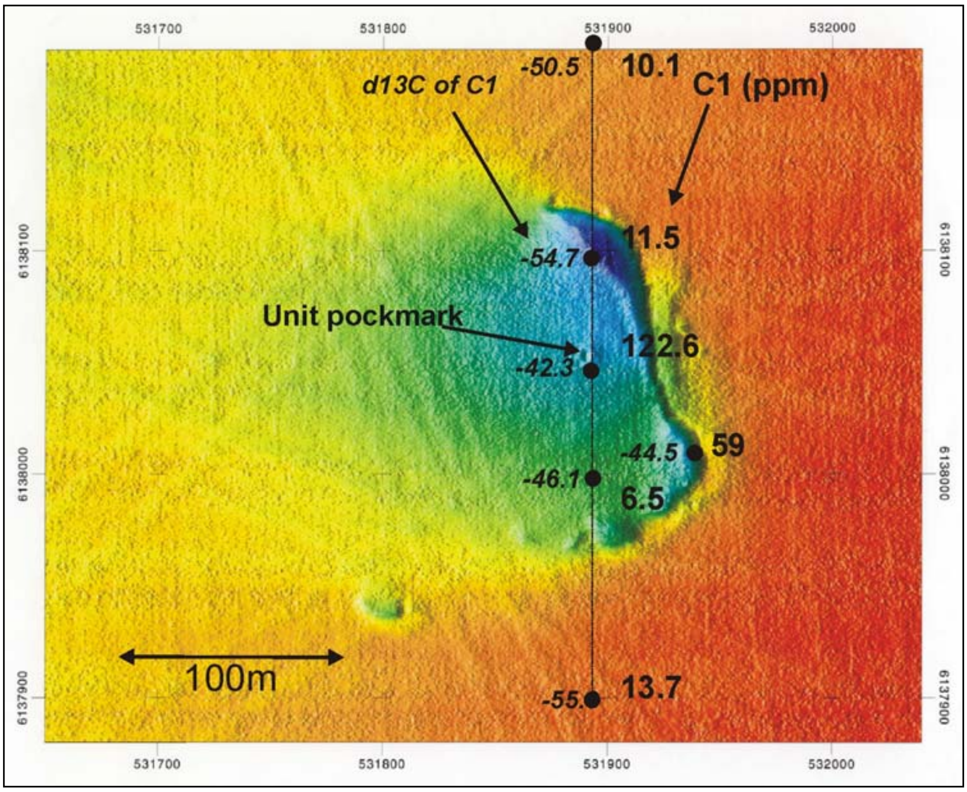

Figure 4.6: Multi-beam image showing seafloor morphology around a 140 m wide pockmark in Dutch license block A11. Methane (C1) concentrations measured in the headspace gas of seabed sediments (maximum depth 3.4 m), as well as carbon isotopic composition of methane are plotted next to the vibrocore locations.

High frequency acoustic data did not reveal any obvious expressions of venting of gas into the water column. The methane concentration anomaly is interpreted to be significant but not high. It is therefore thought that leakage of gas at this site is rather limited, but may have been larger in the past in order to cause the crater.

The second site investigated is the area over the crestal part of a shallow Plio-Pleistocene gas field in Dutch license block B13 (Figure 4.7). In this area, a number of similar gas fields were discovered in the 1980s. These fields can clearly be identified on seismic profiles due to their strong amplitude anomalies (bright spots) resulting from the presence of gas in the Plio-Pleistocene unconsolidated sands at a depth of some 600 m. The outline of the gas field shown in Figure 4.7 reflects one of the large bright spots. The samples of the 2002 marine campaign were taken from the seafloor over the central area of the field. The methane concentrations at the five vibrocore sites are shown in Figure 4.7.

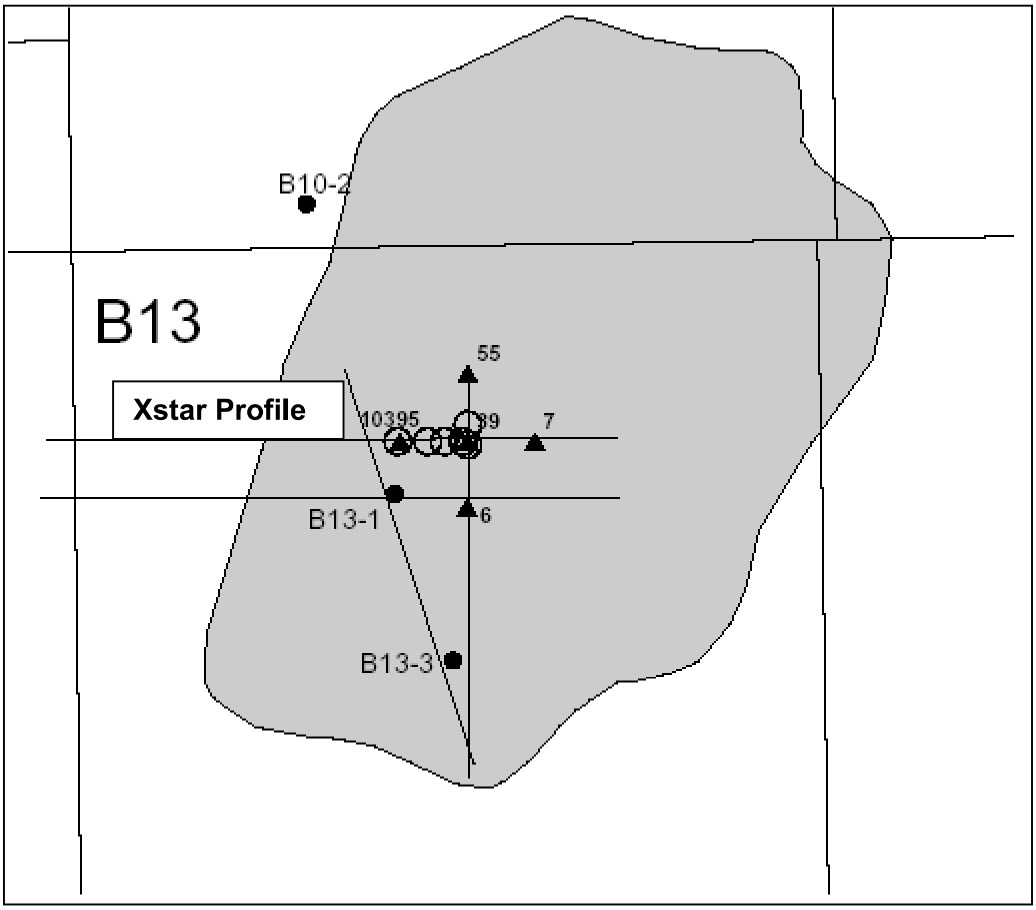

Figure 4.7: Plio-Pleistocene shallow gas field in Dutch license block B13 showing also the locations of four Xstar sub-bottom profiler lines and four vibrocore locations (triangles). Methane concentrations (vppm) are annotated next to the locations. Circles indicate plumes in the water column observed on the profiles.

Part of the northernmost east-west running sub-bottom profiler (Xstar) line is shown in Figure 4.8. The section shown includes the location of vibrocores 261 and 265 where methane concentrations of 39 and 10395 ppm were found respectively. Both positions are close to gas plumes observed in the water column. These plumes are very clear acoustic expressions only visible on this kind of high frequency acoustic data. They cannot be found on regular seismic data. In view of the very high geochemical anomaly in one of the samples and the very strong acoustic anomaly close to the other, it seems likely that we are dealing with substantial seepage of gas from the shallow subsurface into the water here. Flux rates have not been measured but are expected to be locally high. The fact that close to the strong acoustic anomaly methane concentrations already drop to 39 ppm suggests that the lateral variation in concentrations and fluxes is high. Carbon stable isotope analysis of the captured methane revealed that the gas is most probably of biogenic origin, since the $\delta^{13}C_{CH_4}$ values range from –58.8 to –88.3. Nevertheless, it is remarkable that in some of the samples ethane concentrations of up to 2.2 ppm were found. Examination of the multi-beam echo data over the same area did not show any pockmark like seafloor morphology.

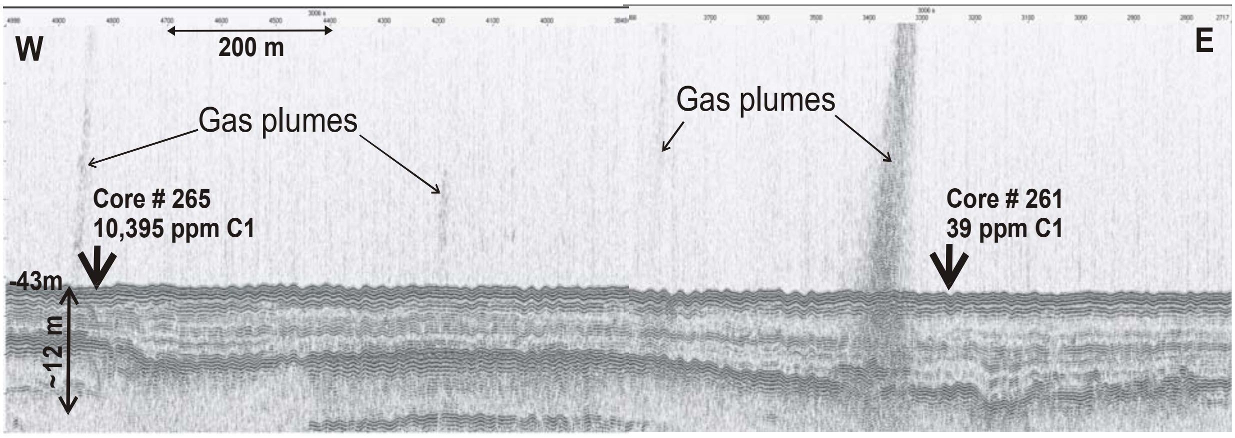

Figure 4.8: High frequency acoustic profile across gas seeps in block B13. Two vibrocore locations are shown with the methane concentration in the headspace gas of sediment samples from 3.5 m below seabed.

When comparing the findings in blocks sites A11 and B13, it is concluded that in this particular setting the occurrences of pockmarks and active venting as indicated by plumes in the water column are not mutually linked.

The third area, which was investigated during the 2002 marine campaign, was Dutch license block F3 at the eastern margin of the Dutch Central Graben. A number of different features were sampled with the vibrocore method. One of the most interesting features is that of a shallow gas chimney in the very south of the block. The shallow seismic chimney is the response of leakage of hydrocarbons from a small shallow Upper Pliocene reservoir at a depth of about 500 m to the seabed. Although Figure 4.9 seems to indicate that the gas moves up all the way to the seabed, the methane concentrations in the samples of the cores are low. The highest value found here was only 15 ppm, which can be regarded as only slightly elevated. A possible explanation would be that the gas is trapped underneath a very shallow clay layer, not visible on the seismic profile.

The fact that the seismic amplitudes within the chimney are higher than outside the disturbance and that reflector continuity is maintained, is interpreted to imply that sedimentary bedding was not disturbed too much by the migration of the gas or fluids (Schroot, 2002). No pockmarks were found at the seafloor. Very close to where the upward continuation of the chimney would intersect with the seafloor a weak indication of a gas plume in the water column, similar to the ones in B13, was found on an east-west running XStar profile. Finally, another observation from profiles such as Figure 4.9 is that indications on seismic data of upward migration of hydrocarbons are often related to faults that are providing a migration pathway.

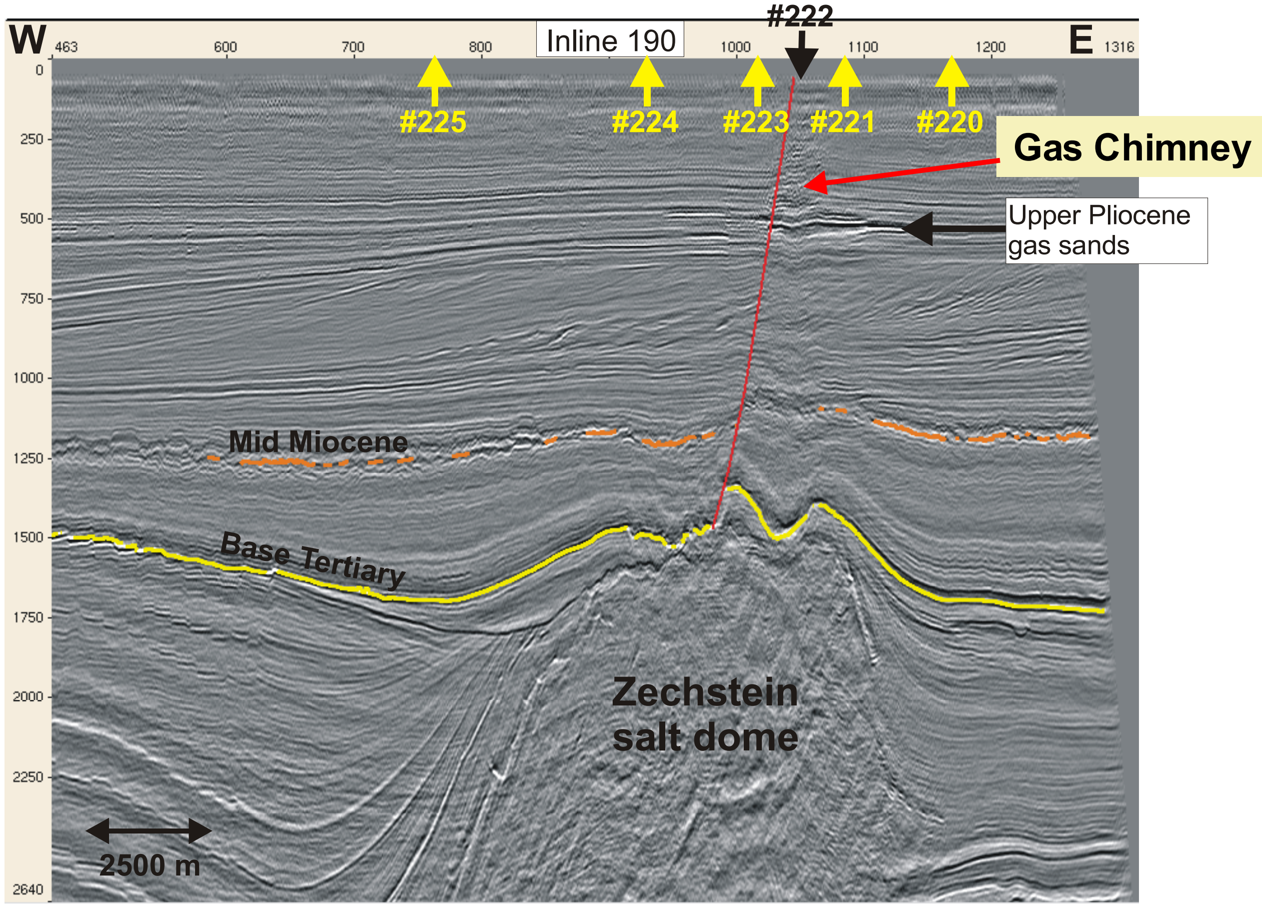

Figure 4.9: Seismic profile near the border of Dutch license blocks F3 and F6 showing a shallow gas chimney over a Pliocene bright spot and a normal fault, which has most likely played a role in the upward migration of the gas.

4.4. CONCLUSIONS

Results presented in this chapter indicate how various mechanisms in the near surface can attenuate CO_2. However, the physical and chemical characteristics of the site, as well as the size and intensity of any eventual leak, fundamentally control the effectiveness of these processes.

The study included detailed soil gas surveys in areas of natural CO_2 vents, a shallow gas injection test, gas bubble migration experiments and studies of shallow natural gas (methane) leaking offshore in the North Sea.

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. The influence of the unsaturated zone was also observed in a detailed examination of other, unstable gas species transported by the CO_2, such as hydrogen sulphide (H_2S) and hydrogen (H_2). The association of these trace gases, with the vent indicates that even if only CO_2 is stored at depth a future leak may also result in the mobilisation of other gaseous species. Soil gas surveys around known fault systems over a natural CO_2 accumulation in the Vorderrhön area, Thuringia, Germany, helped to identify the optimal position for the installation of continuously operated monitoring systems.

The results of the injection of a helium (He)/ argon (Ar)/ CO_2 gas mixture at around 10 m depth clearly demonstrated how the chemical characteristics of each gas species can control its migration in the shallow subsurface. Data indicated that the conservative gas He escaped to the surface immediately, at high concentrations and near the injection well. In contrast, the soluble, reactive and dense gas CO_2 arrived at the surface at much lower concentrations and at a much later time, due to its dissolution in groundwater (and transport in this phase) as well as its lateral diffusion in the unsaturated zone due to density differences.

These results indicate that gas migration, and possible release to the atmosphere, is controlled by the physical and chemical characteristics of the migrating gases and the geology and hydrogeology of the shallow subsurface.

The scale of any eventual leak from a CO_2 storage reservoir would depend on the amount of gas available at depth and would be limited further by attenuation reactions during its upward migration. This smaller quantity of gas would then be further decreased within the near-surface environment. If CO_2 volumes are small enough, advection rates low enough and the appropriate shallow environment exists, the near surface environment may even have the potential to prevent the transfer of deep CO_2 to the atmosphere, acting as the final barrier at the end of a long migration pathway.

A study area in the northernmost part of the Netherlands North Sea sector was selected at the start of the NASCENT project with the aim of carefully examining the nature, characteristics and more in particular the surface and subsurface expressions of the shallow gas (mainly composed of methane) on different data sets. Reflection seismic and other marine acoustic data can reveal the presence and distribution of the shallow gas in the subsurface and in the water column. Confirmation of the interpretation of the presence of gas can be obtained through chemical analysis of the headspace gas from seabed sediment samples. Although the shallow gas is composed mainly of methane and therefore is chemically different from CO_2, its physical behaviour in the subsurface, including the way it migrates through the near-surface environment and leaks to the surface, can be considered as similar to that of CO_2.

In the Vorderrhön area, continuous monitoring over deep-seated fault systems, the overlying cap rock and near former production wells of a natural CO_2 accumulation showed no evidence for a leak. 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 vegetation period are much larger

4.5. FURTHER READING

NASCENT REPORTS:

ANNUNZIATELLIS A., BEAUBIEN S.E., CIOTOLI G. AND LOMBARDI S. (2004) Allaying public concern regarding CO_2 geological sequestration through the development of automated stations for the continuous geochemical monitoring of gases in the near surface environment. Submitted to the GHGT7 conference, Vancouver, Sept. 5-8 2004.

ANNUNZIATELLIS A., BEAUBIEN S.E., CIOTOLI G. AND LOMBARDI S. (2003) NASCENT Work Package 1 report. Geological setting of the Latera geothermal field.

ANNUNZIATELLIS A., BEAUBIEN S.E., CIOTOLI G. AND LOMBARDI S. (2003) NASCENT Work Package 2 report. Soil gas surveys, field sampling and sample analysis of the Italian study sites.

ANNUNZIATELLIS A., BEAUBIEN S.E., CIOTOLI G. AND LOMBARDI S. (2003) NASCENT Work Package 3 report. Gas migration experiments.

ANNUZIATELLIS A., CIOTOLI G., PETTINELLI E., BEAUBIEN S.E., LOMBARDI S. (2004) Geochemical and geophysical characterisation of an active CO_2 gas vent near the village of Latera, central Italy. Submitted to the GHGT7 conference, Vancouver, Sept. 5-8 2004.

ANNUNZIATELLIS A., BEAUBIEN S.E., CIOTOLI G. AND LOMBARDI S. (2003) NASCENT Work Package 1 report. Geological setting of the Latera geothermal field.

ANNUNZIATELLIS A., BEAUBIEN S.E., CIOTOLI G. AND LOMBARDI S. (2003) NASCENT Work Package 2 report. Soil gas surveys, field sampling and sample analysis of the Italian study sites.

ANNUNZIATELLIS A., BEAUBIEN S.E., CIOTOLI G. AND LOMBARDI S. (2003) NASCENT Work Package 3 report. Gas migration experiments.

CIOTOLI, G., ETIOPE G., GUERRA M., LOMBARDI S., DUDDRIDGE G.A. AND GRAINGER P. (in submission) Migration and behaviour of gas injected into a fault in low permeability ground. Submitted to the Quarterly Journal of Engineering Geology and Hydrogeology.

LOMBARDI S., BEAUBIEN S.E., CIOTOLI G., HATZIYANNIS G., METAXAS A., PEARCE J. (2004) Potential hazards of CO_2 leakage - learning from nature. Submitted to the GHGT7 conference, Vancouver, Sept. 5-8 2004.

LOMBARDI S., BEAUBIEN S.E., CIOTOLI G., HATZIYANNIS G., METAXAS A., PEARCE J. (2004) Potential hazards of CO_2 leakage - learning from nature. Submitted to the GHGT7 conference, Vancouver, Sept. 5-8 2004.

PEARCE, J. (ed), 2003. Natural Analogues for the Storage of CO_2 in the Geological Environment. Report on Field Characterisation including Soil Gas Surveys, Characterisation of Offshore Shallow Gas Seeps, Hydrochemistry and Diagenetic Studies. British Geological Survey, External Report CR/03/147.

SCHROOT, B.M. & R.T.E. SCHÜTTENHELM, 2001. Shallow gas in the Southern North Sea – an inventory for the NASCENT project. TNO report NITG 01-098-A.

SCHROOT, B.M., 2002, North Sea shallow gas as a natural analogue in feasibility studies on CO2 sequestration, *in* Extended Abstracts of the 64th EAGE meeting and Technical Exhibition, Florence, paper H010, 4 p.

SCHROOT, B.M. AND R.T.E. SCHÜTTENHELM, 2003, Expressions of shallow gas in the Netherlands North Sea, Netherlands Journal of Geosciences / Geologie en Mijnbouw, v.82(1), p. 91-105.

OTHER REFERENCES

HOVLAND, M. AND A.G. JUDD, 1988, Seabed pockmarks and seepages, impact on geology, biology and the marine environment. Graham and Trotman, London: 293 p.

Chapter 5. Assessing the potential impacts of a leak

5.1. SUMMARY AND CONCLUSIONS

Although the concept of geological CO_2 storage is sound, and any eventual project will be engineered to the highest level in order to prevent the leakage of the injected CO_2 to the surface, a clear understanding of any possible risks is needed in order to best inform policy makers and the public at large. This chapter uses examples from San Vittorino and Ciampino, central Italy to illustrate the effects of natural CO_2 leakage to the ground surface, examines what can be done to minimise any risks from man-made CO_2 storage repositories, and describes techniques and instruments that could be used to provide an early warning should a leak occur.

5.1.1. San Vittorino Plain

The San Vittorino Plain to the north of Rome 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 series of soil-gas, bubble-gas, dissolved-gas and groundwater-chemistry surveys throughout the plain showed a clear correlation between high concentrations of CO_2 (and associated trace species like H_2S), anomalous inorganic species concentrations in the groundwater 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. A hypothesised deep water, associated with the migrating gas, may have also contributed to an increase in some elements which are typically indicative of brines or marine connate waters. In spite of the increased ionic content of these altered groundwaters a comparison with drinking water standards indicates that they are still safe for human consumption. At this site therefore CO_2 leakage has not reduced water quality to below international standards. At other sites of geological storage, the effects of subsequent leakage will depend on the specific conditions at each site.

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 groundwater, 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. In an effort to monitor for possible future collapse events, linked to the flow of acidic waters, a geochemical monitoring station was developed which continually measures the concentration of CO_2 and H_2S dissolved in groundwater, 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.

5.1.2. Ciampino

Ciampino is a rapidly growing city, located 30 km to the south-east of 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 which were always less than 1%. These relatively low values, compared to the surrounding soil gas concentrations, 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 which control the generation, migration and accumulation at toxic 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 samples that were collected in this area should allow for a calibration between the generated risk/hazard models and the measured distribution of toxic gas species at surface. The approach used during this study consisted of three general stages. First data was digitally organised into thematic layers, then software functions in the GIS program "ArcView" were used to compare and correlate these various layers, and then finally the produced "potential-risk" map was compared with soil gas data in order to validate the model and/or to select zones for further, more detailed soil gas investigations. It is expected that the method developed here could be applied for site assessment of locations being considered for CO_2 storage.

5.2. INTRODUCTION

Although the ultimate goal of geological storage of CO_2 is the "permanent" isolation of this greenhouse gas from the biosphere and atmosphere, a clear understanding of all possible impacts of a leak to the surface is required in order to assess the risks associated with this proposed technology. In the present chapter, natural analogues where CO_2 is already leaking to the surface have been studied to better understand the effects of gas release in the near-surface and surface environment and how local inhabitants deal with these issues. Four sites were studied in Italy (Figure 5.1), three where large fluxes of CO_2 have been released to the atmosphere for hundreds, perhaps thousands, of years (i.e. San Vittorino, Ciampino and Latera) and one where a known CO_2 reservoir does not leak to the surface (Sesta). The inhabitants of the first three sites have had to deal with health hazards related to CO_2 (and other trace gases transported with it), altered chemistry of their groundwater resources, the formation of sinkholes due to water-rock-gas interactions, vegetative die-off due to high gas concentrations, and nuisance odours related to associated gases like H_2S. People have overcome the various risks and collateral effects of the leaking gas. A comparison of the values and statistical distribution of soil-gas CO_2 concentrations found at all four sites is presented in Figure 5.2, however only the San Vittorino and Ciampino sites are discussed here due to their more significant impacts on the local inhabitants.

Figure 5.1: Map of central Italy showing the location of the four study sites

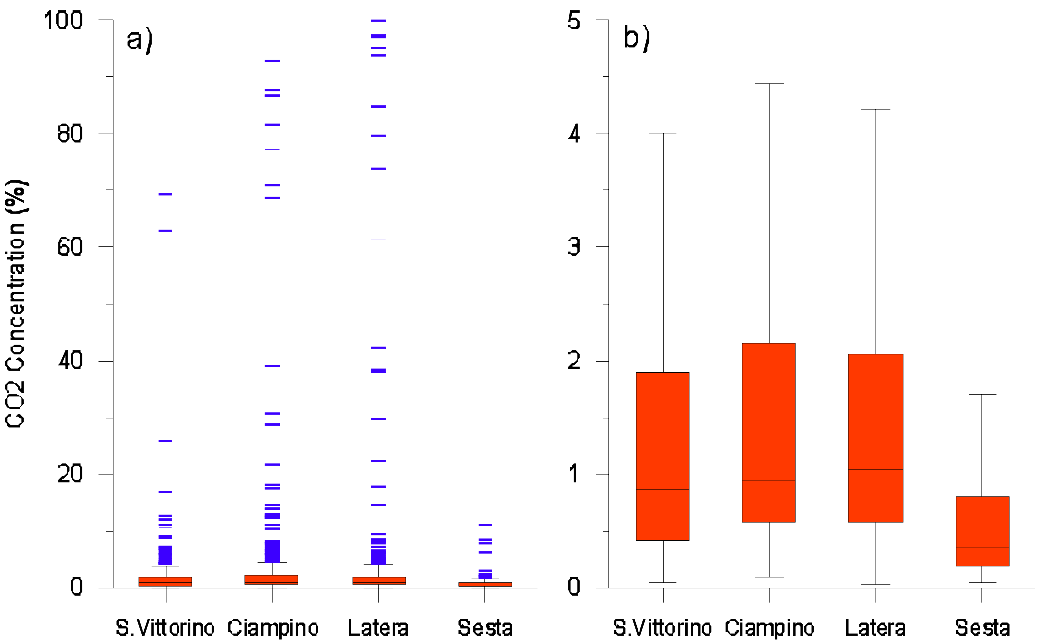

Figure 5.2: Box and whisker plots of soil gas CO_2 data from the four studied sites. The red boxes show the upper and lower quartiles (along with the median inside the box), the vertical lines show the normally-distributed minimum and maximum while the horizontal blue lines show outliers. The plot in (a) shows all the data while (b) is the same data but without outliers. Note that the three sites showing CO_2 leakage are very similar whereas that at Sesta, where a CO_2 reservoir at depth is not leaking, has significantly lower values.

The San Vittorino plain is a triangular-shaped, sparsely populated but heavily cultivated intramontane basin located about 100 km to the NE of Rome, in central Italy. The plain is known for the occurrence of mineral water springs, strong gas vents and a number of large sinkholes, many of which now host small circular lakes. This site was examined by the University of Rome to study the effect of the gas vents on the geochemistry of the local groundwaters as well as to better understand the formation of the sinkholes in terms of water-rock-gas interaction. A total of 41 water samples were collected and analysed for major and trace elements, while 12 dissolved gas and 10 bubble gas samples were analysed for major and minor species. Soil gas surveys were also conducted throughout the plain to better understand regional processes and links between geochemistry and faults. In addition to the geochemical surveys performed at San Vittorino, an autonomous geochemical station was developed and installed in a local village in order to monitor for increases in dissolved acid gas fluxes which may be precursors of sinkhole formation.

The densely populated city of Ciampino, located 30 km south east of Rome, is situated on the slopes of the dormant Alban Hills volcanic complex. Although considered quiescent this area is known for its CO_2 gas vents, seismic activity and thermal waters, indicating that the complex is still active and may thus present a health risk for the local residents. Concern was heightened in 1999 when a large volume of CO_2 released during a seismic swarm resulted in the death of 30 cattle held in a field within the city limits. This site was studied by the University of Rome because the release of CO_2 in this densely populated area provides an opportunity to examine some of the hazards associated with the possible leakage of gas from a CO_2 geological repository, as well as how these risks can be mitigated. Both detailed and regional soil gas surveys were conducted in this area, as well as a limited number of gas flux and indoor gas measurements

5.3. WHAT ARE THE POTENTIAL IMPACTS OF A LEAK ON GROUNDWATERS?

5.3.1. San Vittorino

As described above, there was great interest in the San Vittorino site due to the association of mineral springs and gas vents, implying water-rock-gas interaction and the possible alteration of drinking water sources by naturally escaping CO_2. An extensive research program was undertaken which involved the sampling and analysis of water as well as associated gas bubbles and dissolved gas from springs, sinkholes and wells to better understand the mechanisms controlling aqueous geochemistry.

In general the gas bubble samples (Figure 5.3) were enriched in CO_2 (36-85%), CH_4 (150-2100 ppm) and He (6-400 ppm), had variable N_2 concentrations (7-60%) and were impoverished in O_2 (0.5-2%); H_2S is also known to be present in some of the samples based on its characteristic odour, however it could not be detected analytically due to technical difficulties. Dissolved gas samples (collected primarily from the same sites) had CO_2 values ranging from <0.2 to 0.8 litres of gas per litre of water at STP, with the highest values being near the solubility of CO_2 at 20 °C (0.9 l/l). As expected, the samples with the highest dissolved CO_2 values, and with the bubbles having the highest CO_2 concentrations, were found at those locations where the most anomalous aqueous chemistry was observed, as described below.

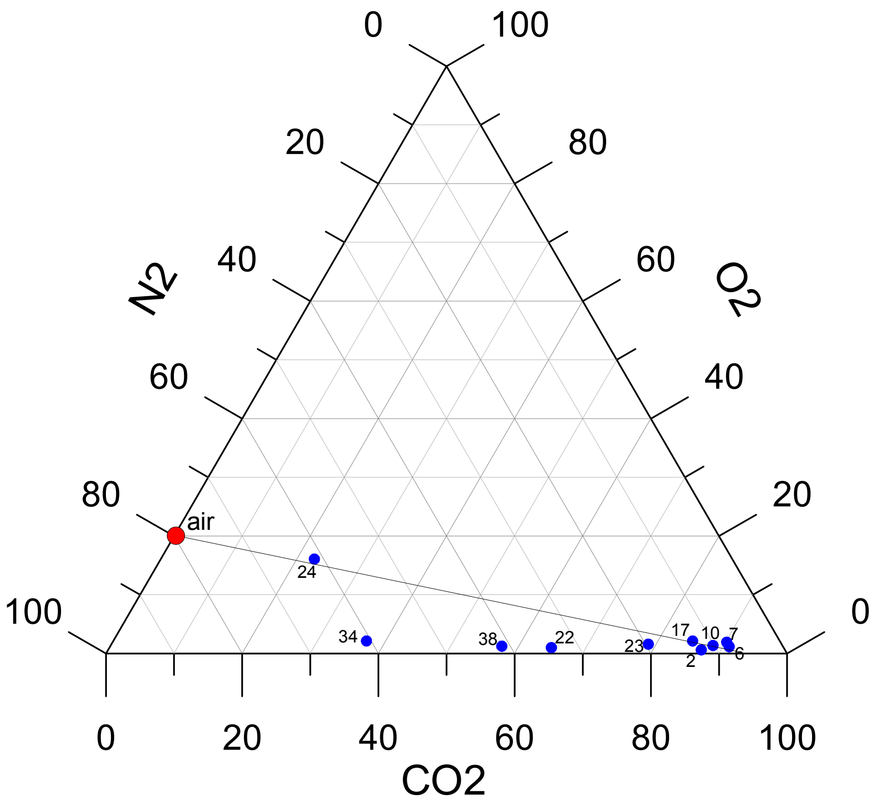

Figure 5.3: Major gas ratios in bubbles collected from gas vents in water. Most samples are enriched in CO_2 while others have progressively higher N_2. Sample 24 was likely contaminated during sampling.

The chemical data indicated that essentially all samples were Ca-HCO_3 waters, with a few being classified as Ca-Mg-HCO_3. Although the water type was consistent due to the constant ratio of the various elements, the total amount of dissolved constituents varied significantly, as shown by total hardness (307 to 1740 mg/L as $CaCO_3$), conductivity (605 to 2520 µS) and Total Dissolved Solids (TDS - 330 to 1843 mg/L). Examination of the individual elemental concentrations showed the same trend, including that for Ca (89-550ppm), Mg (17-97ppm), SO_4 (10-795ppm), Sr (230-2900ppm) and B (43-1945ppm). The extremely high correlations between these components also indicated that most elements were elevated in the same samples, which were located predominately in the north-centre of the plain and were, as mentioned above, associated with bubbling gas.

Although there was a clear association between bubbling acidic gas and increased mineral concentration in the water, a detailed examination of this data indicated that multiple processes may explain the various anomalies, including dissolution, oxidation, precipitation and possibly mixing with other waters. The near-perfect correlation between Ca and HCO_3 implied that the dissolution of carbonate rocks (such as bedrock limestone or near-surface travertines), due to CO_2 and H_2S acidification of the groundwater, was responsible for the observed concentrations. Similarly, an examination of typical trace levels of K, Mg, Ni and Sr in calcite appears to support the idea that the distribution of these elements can be explained by the same mechanism. Although the evidence was not so clear, the dissolution of silicate rocks and/or cation exchange processes may also be responsible for some elevated values (e.g. Mn, Al, Zr, Pd, Rb). The presence of H_2S has also caused a lowering of the Eh, resulting in a decrease in U and Mo concentrations due to insoluble oxide precipitation while at the same time making other elements like Fe and Mn more soluble. Increasing sulphate concentrations, on the other hand, appear to be the result of the (microbial?) oxidation of H_2S, rather than the dissolution of gypsum. This hypothesis was supported by computer modelling, using the geochemical speciation program PHREEQC, that indicated that equilibration with gypsum would result in a change in the Ca/HCO_3 ratio and far higher Mg concentrations than those observed.

Finally there is a group of elements which cannot be explained by the increased aggressiveness of the local groundwater due to the action of added gases, including Cl, Na, Li, I, Br, B and F. Many of these elements (such as B and Li) are associated with deep waters while others (like Cl, I and F) may indicate marine connate waters or brines. A comparison of these elements with those described above appears to indicate the mixing of a second, deeper water with the shallow carbonate aquifers. Although the source of this “deep” water is unknown, the pathway along which it travels (i.e. faults) must be closely related to those of the gas bubbles, perhaps with the bubbles aiding in the lift and mixing of this other water.

The overall effect on water quality in the anomalous springs described above is significant, for example by increasing Mg concentrations in the “Group 2” samples (Figure 5.4). However, a comparison with drinking water standards indicates that these reactions have not made this water un-potable. Even in the most altered waters, trace elements are still below drinking water limits, due possibly to the underlying lithology. For example, if the rocks had been mafic volcanics it is possible that the values of certain elements could have been higher. Finally, while sulphate is not considered a dangerous compound it is outlined as a “nuisance chemical” and given a recommended limit of 250 ppm. The most concentrated water sample collected at San Vittorino had a SO_4 value of 240 ppm.

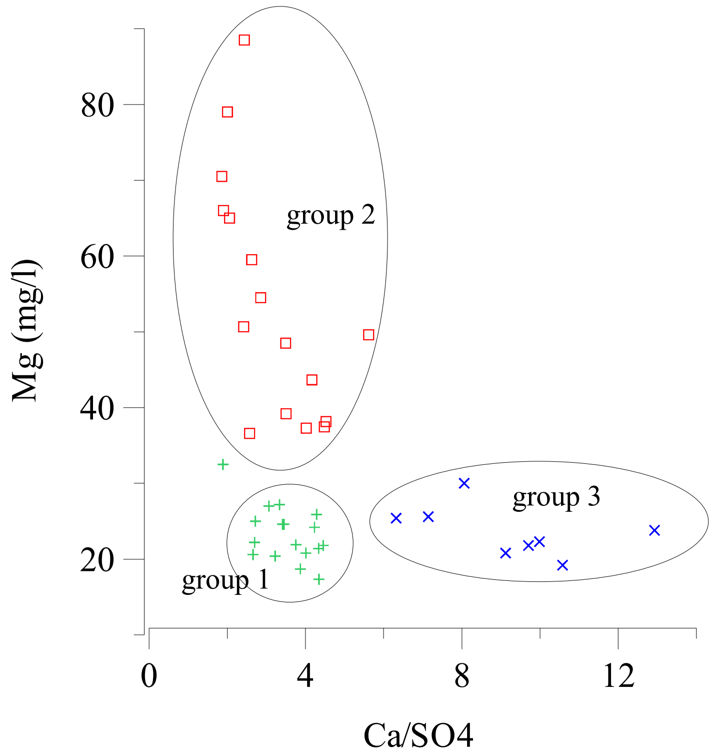

Figure 5.4: Grouping of San Vittorino water samples. Note that Group 2 represents the anomalous samples which are associated with elevated CO_2 concentrations and fluxes.

5.3.2. Hydrogeochemical survey of water quality in the Florina Basin

A detailed hydrogeochemical survey of groundwaters was performed across the whole Florina Basin. The objective was to determine if any changes in water chemistry could be observed in areas containing high CO_2 concentrations. Water samples were collected from wells used for irrigation and potable water supply, water supply boreholes and natural springs, some of which are naturally carbonated.

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 higher concentrations of some elements in a few of those samples. One sample from Limnochori has increased Na, Cl, SO_4 and CO_3 concentrations with a poor water quality, but in fact it is geothermal water with a temperature of 35 ^{o}C.

5.4. WHAT ARE THE POTENTIAL IMPACTS ON PEOPLE?

5.4.1. Ciampino

The population of Ciampino has coped with the existence of CO_2 outgassing over the hundreds of years that the area has been inhabited. However, the recent rapid growth rate of the city, due to its status as a commuter city for Rome, has made the issue more urgent. The rush to enlarge the city has resulted in higher population densities as well as the development of land that previously might have been considered poor quality or even high risk. The present study involved both detailed and regional soil gas surveys throughout the city and surrounding area both to assess risk and to better understand what protocols and procedures could be followed in order to minimise that risk.

Soil gas CO_2 in the Ciampino area (Figure 5.5) ranges from 0.1 to 92.7%, with a statistical examination of the data indicating four populations: i) background values up to 3.2%; ii) low or local anomalies from 3.2 - 8%; iii) high anomalies from 8 –14%; and outliers from 14 - 92.7%. Other gases like Rn, H_2S and CH_4 show a similarly wide range in concentrations, with the spatial distribution of some species, such as Rn, being very similar to that of CO_2. For example, both CO_2 and Rn distributions have a dominant NW-SE alignment which parallels major faults in the area, indicating that these structures provide a vertical pathway for upward gas migration. That said, however, the majority of outlier samples occur as spot anomalies along this alignment, illustrating how gas flow tends to be channelled through more permeable pathways along the faults. This tends to result in highly localised gas vents rather than a diffuse gas release over the entire area. In addition, the similar distributions of various soil-gas anomalies implies the presence of a gas mixture in which CO_2 acts as a “carrier” for trace gases. This fact must be considered when injecting CO_2 in deep reservoirs that may already have other gas species, such as a sour oil field containing H_2S.

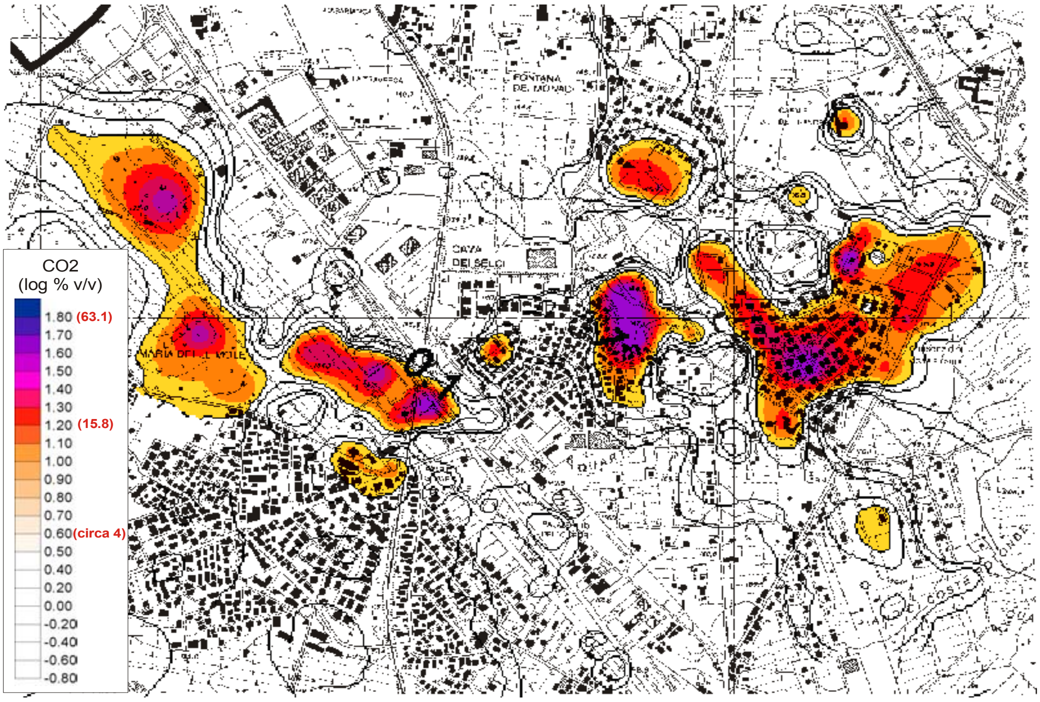

Figure 5.5: Soil gas CO_2 distribution in the Ciampino area. Note the logarithmic scale and the extremely elevated values in some densely populated areas

Only a limited number of gas flux measurements were performed in the Ciampino area, with most being collected around a single major gas vent. These measurements yielded a flux value of around 0.7 kg/m^2/day carbon, although it must be remembered that the flux rates at this site have been known to vary with time. This was dramatically illustrated when in September of 1999 a total of 30 cows being pastured in a small field within the city limits died due to CO_2 asphyxiation. Cattle had been held in this particular field for many years, however an elevated flux of gas was released that day due to seismic activity within the Alban Hills volcanic complex. It is believed that the seismic event caused a decrease in the confining hydrostatic pressure as well as a renewal or temporary opening of the fault structures located in the area. Despite this increased release, however, there were no reported ill effects on the local human population.

The greatest risk for the local population is that CO_2 could migrate from the soil into houses and accumulate in low-lying areas due to its greater density, as CO_2 concentrations above 8% can be fatal. Although this study did find that some new houses were built on ground having soil gas CO_2 concentrations in excess of 70%, a small pilot study of indoor gas concentrations yielded CO_2 values which were always less than 1%. One factor which probably contributes to these relatively low concentrations is the habit of Italians to frequently change the air in their households by opening windows during the day. Obviously in more northern latitudes CO_2 concentrations could increase. That said, although 1% CO_2 is acceptable from a health standpoint it must be remembered that it is much higher than the concentration in atmospheric air (0.035%). Whereas the CO_2 values were reasonably low, some locations did have elevated radon concentrations. As mentioned above, the soil gas distributions of CO_2 and Rn were quite similar in the Ciampino area, implying that Rn is transported within the flow of CO_2. Thus the elevated indoor Rn values may be due to its migration with CO_2 and then entry into the houses as a result of its greater diffusion rate, or it may have been produced in situ by the underlying rocks or the building materials, like volcanic tuffs, used to construct the homes. Where a pathway for CO_2 migration is established, evidence from this study suggests that the CO_2 could act as a carrier gas that may then transport other gases, such as Rn, if Rn was being produced in the rocks through which the CO_2 passed.

Although risks exist in the Ciampino area due to the occurrence of toxic gases, including CO_2, much is being done to greatly minimise any danger to the local inhabitants. In particular, the University of Rome is working together with the regional government of Lazio and the local Civil Protection Agency to develop zoning bylaws and to identify already-existing residential areas which may be at risk. Education programs are also underway to explain to the local inhabitants what low-cost simple things they can do to greatly lower any risk, such as keeping basement and first floor rooms well ventilated.

5.4.2. San Vittorino

As already noted the San Vittorino plain is not as densely populated or confined as the Ciampino area, and thus issues related to CO_2 accumulation are less of a concern for the local inhabitants. In fact, the area has a history of exploiting the local geology and chemistry, with a health spa that uses the local mineralised waters for curative baths. Instead, the major concern in this area is the formation of sinkholes, as inhabitants are worried that future collapse events may result in loss of life, homes or infrastructure. The best example of one such event occurred in the 18th century when a sinkhole formed immediately below a 16th century church, causing irreparable damage which can still be seen today. Many other sub-circular sinkholes occur throughout the plain, varying between 15 and 200 m in diameter and 1 to 45 m in depth (see Figure 5.6 as an example). As there appears to be a close spatial link between the sinkholes and the gas vents the San Vittorino site was chosen for further study into the possible impacts of gas leakage at surface.

Figure 5.6: Example of a water-filled sinkhole in the San Vittorino plain.

The work conducted on the sinkholes was very closely linked to the work described above on shallow groundwater quality. In addition to the aqueous geochemistry sampling, soil gas surveys and a limited number of gas flux measurements were also performed throughout the valley in an attempt to correlate the sinkhole distribution with measurable physical and chemical parameters.

The soil gas surveys showed very high CO_2 concentrations (up to 70%) which were often coupled with very high helium (up to 80000 ppb) and methane (up to 20000 ppm) concentrations; in some cases methane was also associated with other heavier hydrocarbons like ethane (up to 15 ppm) and propane (up to 60 ppm). As discussed previously, CO_2 has probably acted as a carrier gas for other species which may or may not present a hazard. Helium is not a hazard, however its occurrence implies that the source of these gases is deep. The hydrocarbon gases at this level should also not pose any significant risk for the inhabitants, although they do have the potential to change the redox conditions of a shallow aquifer that has a limited oxygen supply. These soil gas anomalies were always located in areas with sinkholes, were found to correlate very well with gravity minimum anomalies identified in a separate study (B. Toro, pers. comm.) and were closely linked to bubbling phenomena, elevated dissolved gas concentrations and anomalous aqueous geochemistry.

These results imply that formation of the sinkholes is closely linked to the interaction of CO_2 (+/-H_2S) leakage with groundwater and the underlying lithology, in particular with travertines and other carbonate-rich sediments. Dissolution combined with flushing out of the resulting fine particles by groundwater flow has resulted in a loss of structural integrity and subsequent collapse during low to medium level seismicity. Finally it is interesting to note that while some sinkholes appear to still be geochemically active, others may be dormant as shown by the lack of significant gas flow and more alkaline conditions. It has been hypothesised that the motion and subsequent collapse which caused the formation of some sinkholes may have also resulted in a change in subsurface permeable pathways, diverting gas flow to another location and re-initialising the entire process elsewhere.

5.4.3. Florina

The following extreme case history depicts both some benefits and the adverse effects to people of leakage of CO_2 to the surface. In the summer of 1990, the Department of Hydrogeology of IGME drilled an exploration well for the location of mineral water in the Florina basin. The existence of CO_2-rich water in the wider basin area had been known since the early 1960’s. The well was completed after drilling to a depth of 559 m. The borehole was cased to the full depth with a steel tube with external diameter of 70 mm. Well completion included the installation of a wellhead with a valve (Figure 5.7. CO_2 shows occurred along the well from a depth of 97 m to a final depth of 559 m.

Figure 5.7: Valve-head of well drilled by IGME, 1990**.**

After the well completion and while the valve of the wellhead was closed, CO_2 leakage was observed at a distance of 100 m from the well. Later on the CO_2 leakage advanced towards the well and created a hole around it having an area of more than 25 m^2 (5x5 m) and a depth of 50 m. The cement base used for the drill rig collapsed and a small lake was created. Access to the hole, for people and animals, was restricted after the installation of a fence.

Some years later, the local authorities created a circular pool with a diameter of 4-5 m with a cement lining, around the leaking well. The pool was used by local people as curing baths by immersion of their feet only in the pool and keeping their face about 1.5 m above the water surface. This continued for some years until an accident showed the danger of CO_2 asphyxiation. A man tried to swim in the pool. The CO_2 which was concentrated close to the surface of the water caused his suffocation and death. At this point, the local authorities realized the real danger to human health and prohibited the use of this pool.

In 2000, during field work by G. Hatziyannis and A. Metaxas (IGME) it was observed that the water and CO_2 were still flowing from the pool. The flowing water had caused a red-brown staining on the banks of small streams created by the flowing water, an evidence of high iron content of the water. During field work for the NASCENT project in 2003, we observed that the pool and the well were dry, no water or gas was flowing, suggesting that after 12 years of continuous CO_2 flow its pressure was lowered and the borehole collapsed and closed.

5.4.4. Mátraderecske

The village of Mátraderecske (population 2500) is situated in the picturesque, forested Matra Mountains of northern Hungary. High CO_2 and radon concentrations have been known for a long time in this area; Plinius in ancient Rome mentioned the use and effect of CO_2. In 1992, high radon concentrations were discovered in cellars, homes and in the CO_2 springs (called “mofetta”) in Mátraderecske. This area is formed from the remains of the volcanoes of northern Hungary, and lies close to a major NNE-SSW fault zone (the Darnó Zone). Geologically, the area is simple with basement rock from the Eocene era consisting of andesite (a volcanic rock) and andesitic tuff (i.e. material that was emitted by volcanic eruption) in the shallow subsurface, and at depth along step-faulted blocks. Eocene and Oligocene clays and sands overlie the basement rock.

The deep gas arising in this region is about 95% CO_2, 4-5% methane, with less than 1% SO_2. The gas also contains high Radon levels (^{222}Rn=125 kBq/m^3). The CO_2 is thought to be a by-product of nearby deep polymetallic copper-zinc mineralisation. Methane is derived from nearby small hydrocarbon occurrences. SO_2 is derived both from the ores and the hydrocarbons, while Rn is derived from shallow (<10 m deep) weathered volcanic rocks. The gases (apart from the radon - derived from the shallow rock) migrate upwards, along faults and fractures from a deep-seated water reservoir at a depth of about 1000 m. In the overlying weathered andesite the gas disperses. The gas migrates laterally against local seals and can escape along faults opening to the surface; where the seal is missing, the gas escapes directly. The average gas flux is about 5-10 l/hour/m^2 but, along faults, it can be as much as 400 l/hour. The gas seeps are observed as bubbling in wells and in the Almáskút stream, that flows through the village of Mátraderecske, as well as in the form of strongly carbonated springs.

Early in 1992, CO_2 entered two houses in Mátraderecske where residents suffered headaches. Within twelve months, the two houses had been demolished and rebuilt elsewhere. Cheap and simple control systems were also installed in other houses by the not-for-profit RAD Lauder Laboratory (see below).

Initially, control was achieved by the installation in residential basements of long, horizontal, perforated tubes that allowed the CO_2 to be flushed out using a small (7 watt) high-efficiency pump (Figure 5.10). In addition, a small local museum helps to inform the village residents, patients visiting the spa (see below) and tourists of the nature of the gas hazard and the villagers' solutions.

5.5. HOW COULD WE MONITOR STORAGE PERFORMANCE?

5.5.1. URS Automatic Monitoring Stations

An automated monitoring station was installed at the San Vittorino study site (central Italy) at a location defined by soil gas and geophysical surveys conducted during this project and another project funded by the Region of Latium. Data from these surveys indicated some areas which may form sinkholes in the future, and so a system was designed which might give some warning prior to such an event. One of these sites in a small town was chosen and geochemical sampling equipment was installed in a 25 m deep piezometer to provide information on a number of parameters which may influence the formation of a sinkhole, such as the concentration of acidic gases (CO_2 and H_2S) dissolved in the groundwater. The dissolved gases were extracted from the water via gas permeable tubing (as shown in the experimental results given in Figure 5.8), pumped to the surface and analysed using an infrared detector.

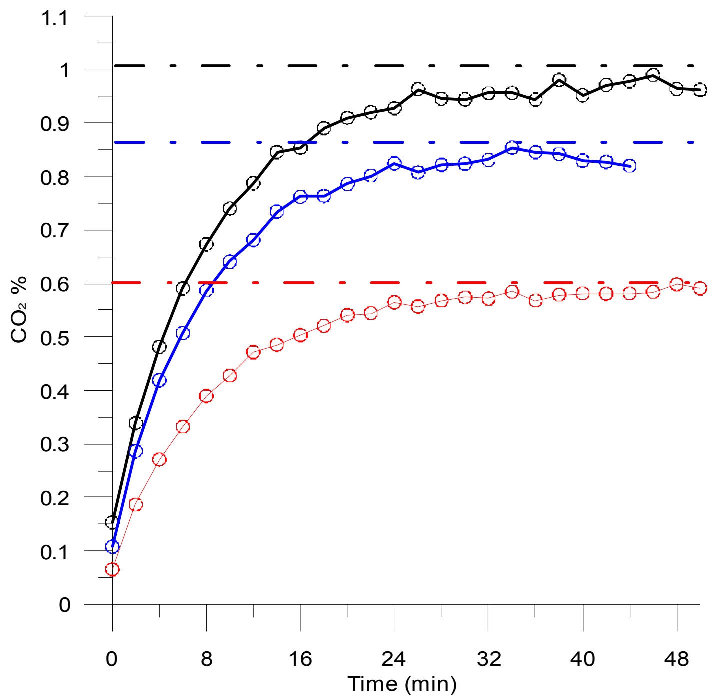

Figure 5.8: Plot showing the rates at which gas within a gas-permeable tube equilibrates with air having a known CO_2 concentration (dashed lines).

These data were stored on a computer, which was capable of automatically transmitting the data via modem to the laboratory. After installation, the unit was programmed to collect data between 8 and 20 times per day, and was left running for approximately 4 months during which it collected more than 2,500 dissolved CO_2 values. The values, measured from gas-permeable tubing in equilibrium with the surrounding groundwater, varied from a minimum of 0.3% to a maximum of about 1.8%. Numerous peaks and valleys occurred over the course of the test, with periods of high or low concentrations generally lasting on the order of 3 to 6 days. These data were compared with seismic data for the region, with some peaks appearing to coincide with small magnitude earthquakes on the order of 3 on the Richter scale. This correlation implies that ground motion may have resulted in the temporary opening of permeable pathways and the subsequent release of gas from depth, either as bubbles or dissolved in ascending deep waters. Other concentration variations, however, could not be correlated with seismic events, indicating that there are other processes which influence the dissolved CO_2 concentrations. In any case, the system has been tested and proven to be sensitive to relatively small concentration variations, indicating that it could be installed for the monitoring of injected CO_2 at a geological storage site. Although the station developed during the present project was designed to monitor for possible dissolved gas precursors related to CO_2-induced sinkhole formation, it can easily be modified to directly monitor soil gas concentrations above a CO_2 storage site to give an early warning should a leak to surface occur.

Development and "proof of concept" of the automated geochemical monitoring station during the present research is seen as an important step forward in providing tools which will help in assuring the public at large as to the safety of geological CO_2 storage. The recent advances in microchip technology, portable analytical instrumentation and decreasing prices means that, once fully developed, a significant number of these relatively low cost stations might be deployed above an injection site in order to monitor for CO_2 leaks. In particular, these might be particularly useful if placed around any deep wells that penetrate the reservoir or deep aquifer in which the CO_2 is being injected. This is because results from the gas injection test performed during this research project showed how gas breakthrough was first observed in the vicinity of the injection borehole, implying that fracturing during drilling provided preferential flow pathways. In addition, if a depleted oil reservoir is used for storage there will be many decommissioned, sealed wells that penetrate the reservoir. Acidification of water by the addition of CO_2 may result in the degradation of these seals, and eventual leakage to surface via the abandoned wells themselves. Preliminary data provided by the development and installation of a prototype automated geochemical-geophysical monitoring station in the San Vittorino area (Figure 5.9) has shown that this technology exists and that it can provide, together with other techniques, a useful tool for the safety assessment and monitoring of geological storage sites.

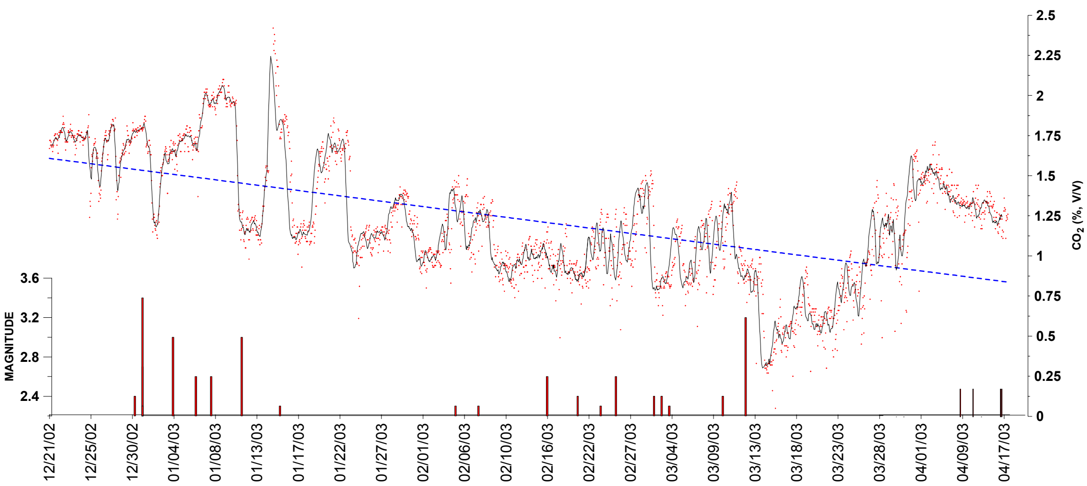

Figure 5.9: Dissolved CO_2 results from the geochemical monitoring station. The figure represents 5 months worth of monitoring, with individual values in red and the running average as a black line. The vertical bars represent earthquakes in the area of the station which were registered by the Istituto Nazionale di Geofisica e Vulcanologia in Italy.

5.5.2. BGR Automatic monitoring system

To monitor storage sites for possible CO_2 leakages, an automatic protocol has to be applied. A problem not yet finally solved is the question of selecting the suitable monitoring sites. They can be identified in advance by soil gas surveys using a dense grid, but due to the inhomogeneities of the soil, gas emanations will vary strongly within short distances and will also vary over time due to meteorological effects (rain, snow etc.). Instead of monitoring selected points, it would be more helpful to monitor continuously an entire area, but such systems are not commercially available at this moment.

For monitoring, an automatic and continuously operated system is to be preferred. Discontinuous measurements may be influenced by many temporal effects, which will prevent geogenic and biogenic signals being distinguished. Prior to storage, it may be necessary to have information on background CO_2 concentrations. For this investigation, over one year of continuous monitoring will be required.

To accurately determine the CO_2 concentration in the shallow subsurface, reliable monitoring tools are required for continuous operation. The Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) developed a new type of monitoring system which was operated at potential point sources for geogenic CO_2 (e.g. in boreholes, fractures in rocks and salt beds). It was operated automatically and controlled remotely. The test site was the Oechsen CO_2 deposit in Thuringia, Vorderrhön. Monitoring of gas emanations from the shallow subsurface for periods of months and years gave no indications for contributions from the underlying CO_2 reservoir. Details of the selection of monitoring sites, the instrumental setup and monitoring results are given in detail in Pearce (Ed.) (2003) and Kemp et al. (2003).

5.6. CAN WE PREDICT RISK?

5.6.1. GIS Risk Assessment of the Latera Study Site

The release of large fluxes of gases from the subsurface pose a great human health risk in geologically active areas, such as central Italy where high heat fluxes produce these gases and then faults provide a transport pathway for their migration to the ground surface. However as production, migration, release and accumulation of gases is dependent on many factors it is often difficult to assess the risk faced by the local population. The development of Geographic Information System (GIS) software packages have greatly aided in combining these disparate data sets in order to semi-quantitatively assess the influence of each on the overall risk. In general a GIS program is used to store, organise, manipulate, analyse and display all forms of geographically referenced information by combining and cross-referencing different datasets contained within unique "themes" or "layers". The general approach is to sum the various layers to produce a graphical representation of the inferred risk, however this technique does not take into account the fact that each layer may contribute different amounts to the final risk. Work partially performed within the Nascent project has attempted to address this problem by applying a covariance matrix (i.e. kriging) to calculate the layer weights and using inter-layer correlations defined with a statistical matrix. This technique reduces researcher subjectivity, defines redundant variables and presents data as an interactive vector model instead of the typically-used raster model. The method has been applied to data from the Latera study site, using the GIS program "ArcView", in order to search for a spatial link between geology and gas potential risk.

A number of geological factors (themes) were studied which relate to the production, migration and accumulation of hazardous gases in the near-surface environment, including faults, depressions, geothermal gradient, spring and gas vent locations, depth to carbonate substratum, radon emanation, radium (Ra) content and distribution of soil gas concentrations. These data were transformed into spatial numerical data and then joined with a grid having 500x500 m coded cells to produce vector “grid layers” (Figure 5.10). If the layer contained point data each cell in the grid would have a unique score but if the layer consisted of a range of values an area-weighted value was assigned to the cell. As each layer has a different number of total classes, however, the cell score for each layer was normalised in order to obtain the cell index. Finally in order to combine the data of the various themes and calculate the total risk map each layer had to be assigned a weighting factor which assesses the contribution of each factor. In this work a geostatistical method (kriging) was applied and a statistical matrix was used to objectively calculate some of the needed parameters.

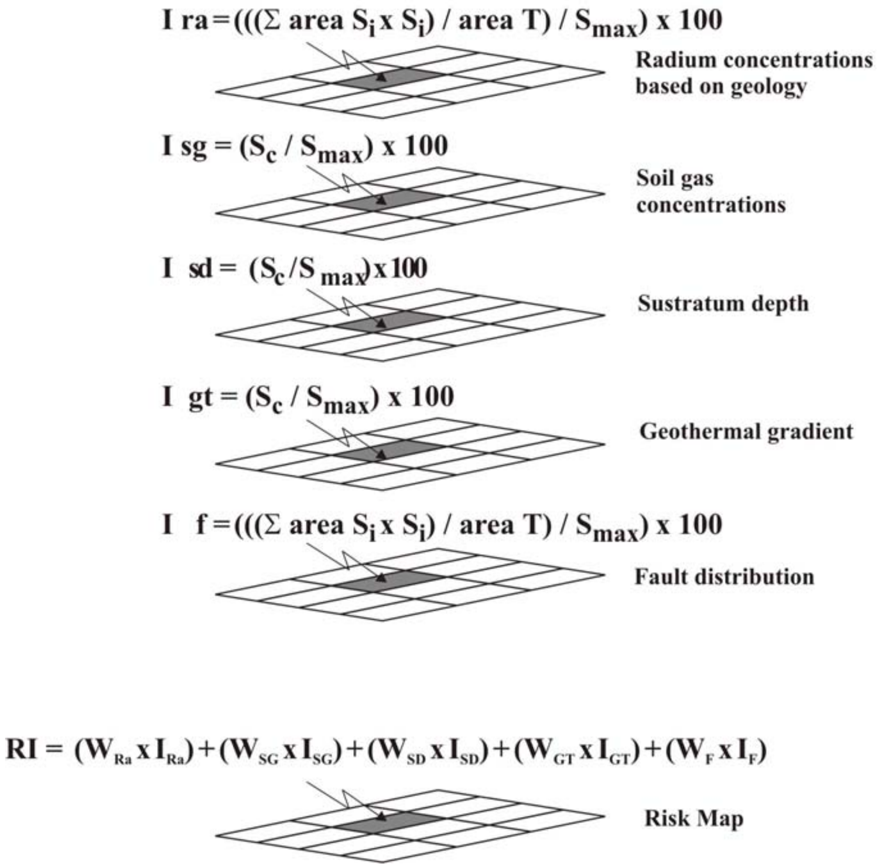

Figure 5.10: Diagram showing the approach and formulas used to produce the risk map, where I represents the cell index, S_C the cell score, S_i the score value of polygon i, S_{max} the maximum score value for that theme, $area_T$ the total area of the cell, W the variable weight and RI the Risk Index.

A preliminary analysis was conducted using all of the geological parameters mentioned above, with the low weights calculated for some parameters results indicating that they provided a small or redundant contribution to the risk. These were removed, thus leaving a final covariance matrix with only six variables, as shown schematically in Figure 5.10 along with the mathematical formulas used to calculate the final risk factor. The procedure was then repeated with the smaller number of themes, and the resulting risk matrix data was examined statistically to define 4 classes: no, low, medium and high risk. These four classes were then assigned a unique colour and then the gridded data were plotted to define a gas risk map, as shown in Figure 5.11.

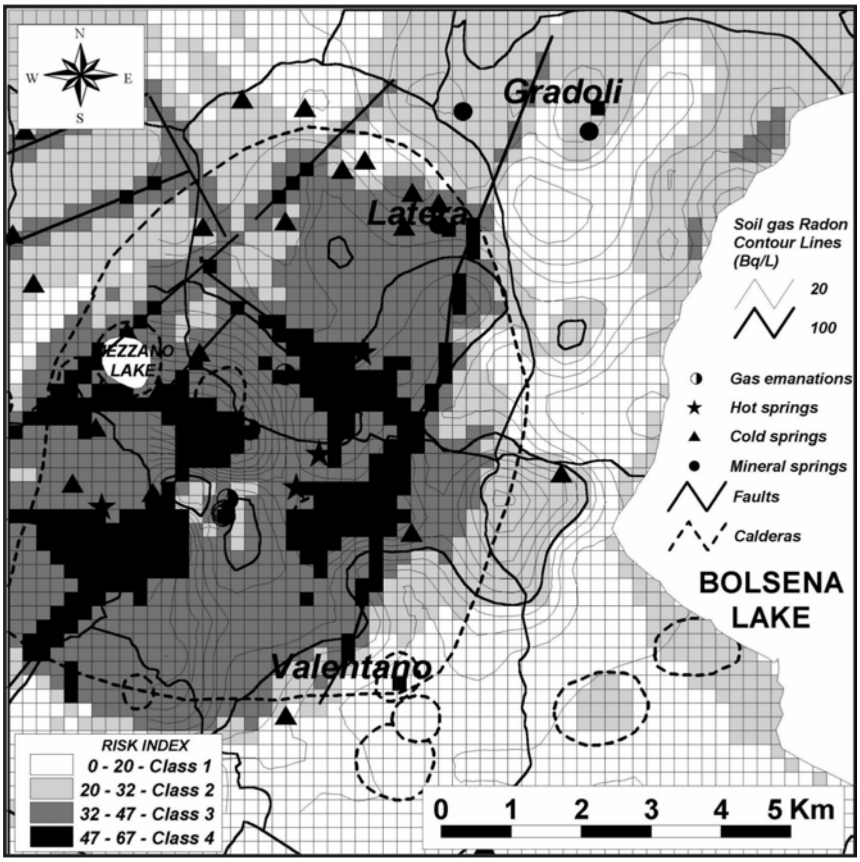

Figure 5.11: Gas risk map of the Latera area, with Class 4 representing the areas of highest risk.

The risk map shows that the unit cells with medium to high risk index fall in the central caldera rim where the major faults (which caused the collapse of the volcano) and the thinnest sedimentary cover occur. As a comparison with the soil gas results, the radon concentration contour lines are also shown, which were calculated using the parameters obtained by modelling the experimental isotropic variogram of the data. As Rn has a relatively short half-life (c. 3.8 days) if it is present at the surface in concentrations that cannot be explained by in situ production it is most likely that it has been transported from depth within an advecting gas like CO_2. The contour line of 100 Bq/L (100 kBqm^{-3}) is highlighted (bold line) in the map because it represents a graphically-calculated anomaly threshold; all radon values above this threshold are located in correspondence with the GIS-defined high-risk areas (i.e. class 4), except for two zones on the eastern side of the caldera. It is probable that there is incomplete data for this area, or that other important factors were not considered, and thus this is an example of how soil gas surveys can be used to improve and focus GIS risk-map development.

In summary, this work provides an objective GIS and geostatistical technique for the integration of geological factors responsible for hazardous gas emission. The proposed method permits the elaboration of risk models based on existing geological data, without the need for survey data. However, in order to truly calculate an area's risk, the model needs to be validated using field geochemical data, such as soil gas distributions which are the direct result of the contributions of the various production, migration and consumption mechanisms.

5.7. FURTHE READING

PEARCE, J.M. (Editor), 2003. *Natural Analogues for the Storage of CO_2 in the Geological Environment: Report on Field Characterisation* including Soil Gas Surveys, Characterisation of Offshore Shallow Gas Seeps, Hydrogeochemistry and Diagenetic Studies. British Geological Survey External Report CR/03/147, 333 pages.

KEMP, S.J. (Editor), 2003. *Natural Analogues for the Storage of CO_2 in the Geological Environment*: *CO_2 leakage mechanisms and migration in the near-surface.* British Geological Survey External Report CR/03/196, 55 pages.

Chapter 6. Future implementation

This chapter summarises some of the potential future applications to which the outputs of the Nascent project can be put and summarises the plans, where possible, of future development and continued implementation of these outputs.

These outputs include, *inter alia*:

- Knowledge and case histories on long term processes of CO_2 interactions within reservoir rocks,
- knowledge on caprock sealing capacities in natural systems
- the effects of CO_2 accumulations on the geomechanical integrity of a natural accumulation
- knowledge and case histories of shallow gas migration offshore and onshore
- development and testing of monitoring methods for CO_2 leakage onshore and offshore
- development and testing of GIS-based methodologies to identify areas of high risk from a CO_2 leak
- databases of
  - petrophysical properties of CO_2 reservoirs and caprocks
  - gas diffusions coefficients
  - CO_2 permeabilities in caprocks
  - Geomechanical strength data on reservoir and caprocks
  - Groundwaters and porewaters in and above CO_2 accumulations
  - Flux rates and CO_2 soil gas concentrations in naturally leaking sites

1. Study on mitigation and exploitation options in areas of high CO_2 leakage

Some of the sites studied in the NASCENT project provided case studies of areas where CO_2 is actively leaking in populated areas. These case studies provide examples of how risks are identified and in some cases how these risks were mitigated. The potentially harmful effects can be reduced through various mitigation options including increased ventilation in basements and housing and building regulations in the local planning process. These case studies provide examples of potentially suitable safeguards that may be required during and following anthropogenic geological CO_2 storage to manage some of the risks associated with large-scale leaks from a storage site.

2. Indicators of CO_2 leakage mechanisms and effects in the near surface

Demonstration of soil gas measurement techniques at sites of natural CO_2 accumulations provides validated methodologies and protocols that could be used at a storage site, to establish baseline conditions before injection and subsequently to monitor for leakage during and after injection.

The results from soil gas measurements and continuous CO_2 concentration monitoring provided information on how CO_2 migrates through the near-surface environment.

Specifically these results identified the migration pathways for CO_2. The most likely pathways are faults that allow CO_2 to migrate from depth.

The data, knowledge and experience gathered by URS during the NASCENT project is already being used in "real-world" applications in order to understand and minimise any risks related to natural CO_2 leakages throughout Italy, and plans and projects are in place to use this know-how for risk assessment and safety monitoring for possible geological CO_2 storage sites in the future. What follows below is a brief overview of these present and planned uses for near-surface geochemistry, laboratory / field experiments and data management / processing as applied to CO_2 storage as well as the plans of URS for the dissemination and publication of this data to both the scientific community and the public at large.

One of the principle methods used by URS during the Nascent project was soil gas chemistry as a tool for understanding the mass transfer processes of deep CO_2 migrating to the atmosphere. During the project it became clear that this tool could be very powerful for addressing a number of issues related to this topic, including mapping and assessing the risk of toxic gas emissions to local inhabitants, correlating gas emission points with altered groundwater compositions and the formation of collapse structures, and for research into the processes controlling gas migration in the shallow subsurface and the capacity of this interval to attenuate the upward migration of leaking CO2 and other gases.

A particularly clear example of how the soil gas data collected during this and other related, Italian-funded, projects can be applied is the use of soil-gas CO_2 and Rn contour maps produced for the cities of Ciampino-Marino. Local authorities are already using these results to aid them in zoning high-risk areas for non-residential uses and to educate the public who already live in areas of elevated toxic-gas concentrations on how they can minimise any risk. Similarly the soil gas data collected in the San Vittorino Plain is being examined by local authorities, together with geophysical and geological data, in order to predict the formation of other sinkholes in the area. In fact a new collapse structure did form in the Plain in 2003, not surprisingly within the area defined by anomalous soil-gas and groundwater concentrations. Together with local agencies there are plans for further, more detailed soil gas sampling in these areas to better understand the processes involved and to better assess the risks to the local inhabitants.

In addition to health and safety issues soil gas is an important research tool which can help in understanding many of the processes controlling a gas leak in the near surface as well as the effects of such a leak on the surrounding environment. In particular highly detailed surveys in the Latera area have shown that different gases are being transported in the CO_2 stream and that the different chemical – physical characteristics of these gases, once in the shallow environment, control their lateral distribution and mass-transfer rates to the atmosphere. This type of data will be very important for computer modellers attempting to predict the eventual fate of leaking CO_2, as the attenuating capability of the unsaturated zone has only recently been recognised in the literature (e.g. Davis et al., 1997 and Etiope and Martinelli, 2002) while the issue of CO_2 acting as a carrier gas for other trace, toxic gases has received very little attention. In addition to CO_2 storage issues, this data will also be of great use for climate modellers who need natural greenhouse-gas input values in order to predict the effect of anthropogenic gases.

Other areas of research that the soil-gas and gas flux results of this study has defined, and which URS intends to pursue in collaboration with other research institutes, include:

- Processes controlling near-surface migration / attenuation (e.g. unsaturated zone thickness, gas chemical characteristics, mineralogy, climate etc.),
- The effect of CO_2-induced acidification of groundwater and the associated water-gas-rock reaction pathways,
- The link between gas flux rates and vadose zone attenuation,
- The link between gas vents and faults, and the link between soil-gas and indoor gas concentrations,
- The effects of various gas mixtures (pure CO_2 as well as $CO_2/H_2S/H_2/CH_4$ mixtures) on local flora and fauna (plants, microbial communities etc.).

Data on these topics from Nascent and from future works will greatly aid regulators, politicians and the public at large to assess the risks of a possible CO_2 leakage to surface, to aid in the selection of the most appropriate sites for deep geological storage, to establish background gas concentrations and then to assess storage performance above any eventual geological storage site (e.g. as is being done at the Enhanced Oil Recovery (EOR) project at Weyburn, Canada (e.g. Moberg et al., 2002)).

Related to the soil gas work, the gas injection test performed at Latera also showed the importance of gas chemistry in terms of controlling arrival times and locations of upwardly migrating gas, in this case injected CO_2, He and Ar. These results can be used by computer modellers who are trying to predict gas flow rates from depth, particularly in terms of the fact that the non-reactive He arrived immediately after injection in the vicinity of the injection well as compared to the much later arrival of the highly soluble CO_2 in a more diffuse area. Plans are underway to repeat the test at the same site (i.e. same injection well and monitoring grid) in order to verify the results and to compare migration processes under different climatic conditions (i.e. spring vs. fall).

Groundwater chemistry studies also formed an integral part of the URS contribution to Nascent, primarily through the collection of spring water samples throughout the San Vittorino Plain. As mentioned above, a very clear correlation was found between the occurrence of elevated gas concentration and anomalous aqueous geochemistry in the local groundwater. This data is being used by the local authorities to help in the management of the local groundwater resource and to assist residences in understanding issues related to water quality. As discussed elsewhere in the report, none of the anomalous groundwaters would be considered un-potable, however the results do raise the question of whether the same flux of gas through a different geological environment (i.e. different rock chemistry) would result in the waters becoming undrinkable. Future work on gas vents - water springs located in other valleys having different lithologies - are planned to address this issue. Together with planned laboratory experiments and geochemical modelling (alone or with other Institutes) this information will give a much broader view of the possible effects of CO_2-induced acidification of groundwater. Finally, monitoring of the chemistry of these affected waters may give information about the processes controlling the system, its evolution and any eventual significant change which the local authorities should be aware of.

At the Florina site, the relationship between changes in CO_2 flux rates and seismic activity has been determined. In the seismically inactive Vorderrhön and San Vittorino fields, the continuous CO_2 monitoring provided information on the CO_2 flux rates in other, different geological settings.

The potential effects of CO_2 on groundwaters and drinking water supplies, if it leaked from a storage reservoir were determined by examining waters above natural systems. This information is useful to establish the levels and the timescales at which CO_2 leakage might be tolerated from a reservoir. Once the effects of CO_2 on groundwaters have been established this information could also be used to further constrain the choice of storage site in areas of groundwater extraction.

The automatic monitoring equipment installed and further optimised during this project by BGR's gas-geochemistry group will stay in continuous operation at the same monitoring sites to gain more information on yearly variations in external parameters. Similar equipment will be used to monitor CO_2 and other gases in early warning projects for earthquake research. It is known from the literature that in several cases changes in gas concentrations have been good proxies for an increase of seismic activity.

Gas geochemical investigations will also be applied to monitor emanations from active volcanic fumaroles. Gas-geochemical data with high time resolution (intervals of seconds) will then be co-interpreted with seismic data to judge on the activity stages of volcanoes. For this application, some technical modifications have been required in the gas-sampling device to allow operation in gas streams at elevated temperatures (higher than 80 °C), but for gas detection, measurement, data storage and data transfer identical instrumentation is in use. Results of these investigations have recently been published and have been presented at international symposia.

The results obtained so far suggest that there will be a commercial market for automatic gas monitoring devices. Therefore, some vital parts of BGR's system are presently in the process of being patented. Contacts to potential manufacturers for the monitoring equipment have also been established.

3. Increased confidence in predicting the behaviour of CO_2 following storage.

Modelling the geochemical interactions between the CO_2, reservoir water and reservoir lithology at Montmiral and Florina has advanced our understanding of how CO_2 storage could alter reservoir properties. The kinetics of these reactions will mean that some, faster reactions could have an effect during the storage process itself. Slower reactions will determine how much of the CO_2 is ultimately trapped as mineral precipitates on geological timescales.

Further, by demonstrating that natural systems can be successfully modelled, greater confidence can be obtained in the ability and limitations of these models to predict how CO_2 will interact during a storage process, both on shorter and longer timescales.

In addition, geomechanical models allow the effects of CO_2 injection on reservoir stability, in terms of fault reactivation, subsidence or absidence to be more clearly identified. Again, by demonstrating successful modelling of natural accumulations such as at Montmiral, Sleipner and Florina, greater confidence can be achieved in the ability and limitations of these models to predict similar effects during and after storage.

4. Increased understanding of CO_2 effects on reservoir properties

The need for the development of long-term geochemical models for current CO_2-storage projects makes the geochemical modelling of natural analogues indispensable in order to have confidence in our long-term extrapolations. Over both shorter and longer timescales, CO_2 could react with reservoir lithologies and change their properties. The most important in the short term, i.e. during CO_2 injection, are reactions that increase or decrease the reservoir porosity and hence permeability. An understanding of these processes will be important during site selection and field operation. Determining the types of changes that have occurred in natural systems, such as the likely amount of CO_2 that could be permanently trapped through mineral precipitation or the increase in porosity as a result of mineral dissolution, increases our understanding of the longer term processes that can not be easily determined during laboratory-based experiments. These processes have been identified at the Montmiral and Florina sites, leading to a better understanding of the likely changes in reservoir quality (permeability and porosity) that could occur in similar reservoirs during and following CO_2 storage. This will improve predictions of storage capacity and long-term CO_2 behaviour following injection. In each case, the chemical composition of the produced water will be affected by the presence of the CO_2-H_2O mixture. The methodology based on isotope composition and requiring only the calculation of the fractionation factors between (a) H_2O and CO_2 or between H_2O and SO_4 and (b) brine and gaseous H_2O, at the measured temperature, will be of great help to determine the chemical composition of the deep brine.

The experience gained from the geochemical modelling of the reservoirs at Montmiral and Florina will be used within WP2 of the 5th Framework CO2-STORE project to increase our confidence in the long term modelling results of the geochemical reactions within the Sleipner Reservoir in the North Sea, where CO_2-injection is currently taking place. Furthermore, the modelling of the natural analogues will enhance the geochemical modelling of future CO_2-storage sites (such as sites identified within the Framework 6 Integrated project CASTOR).

5. Development, installation and testing of automatic monitoring stations

Automatic CO_2 monitoring stations developed to monitor CO_2 gas emissions at volcanoes have been adapted and installed above some of the natural CO_2 accumulations. These stations will observe changes in CO_2 concentrations at fixed points over several months to determine any temporal changes in CO_2 leakage. At Vorderrhön, monitoring has already indicated that the evaporite and clay lithologies provide an effective seal, preventing CO_2 leakage on geological timescales. Faults in the area, however, may act as very limited pathways for variable leakage.

The development and application of a prototype geochemical monitoring station in the San Vittorino area during the project showed the viability of using low-cost electronics and sensors for monitoring the migration of deep gases in the near-surface environment. Combined with an innovative sampling technique involving gas-permeable tubing the instrument has proven itself to be robust and stable, and thus work is underway for the improvement of this prototype through the integration of environmental sensors (to help in data interpretation), modular sensors (to help in station maintenance and longevity) and improved data transfer and remote software control. The laboratory experiments begun during Nascent, which studied diffusion rates through the gas-permeable sampling tubes, will be continued in order to calibrate the system, to better understand environmental factors which can affect analytical responses and to choose the best tubing material which maximises response time while minimising memory effects. Plans are underway for the possible deployment of the new prototype in the area of Ciampino for the analysis of soil gas and groundwater chemistry for health and safety monitoring within the city limits, likely within one of the new housing developments which were found, during the Nascent project, to have been built on ground having very high soil gas CO_2 concentrations. The eventual goal of this work would be to produce, possibly commercially, a robust and reliable unit, which could be used for monitoring above CO_2 storage sites, such as around abandoned wells at an EOR project. By keeping costs low it will be possible to deploy numerous monitoring stations. This has been shown to be necessary because of the spatially restricted nature of the natural CO_2 vents observed during the Nascent project. The use of such stations will aid industrial partners in ensuring the safety of their projects, will help regulators develop and monitor storage performance criteria and will provide an early warning system for the public living near a CO_2 storage site.

The demonstration of this technology at sites of natural CO_2 accumulation and leakage will enable methodologies and protocols to be established that could be subsequently used at storage sites. Such automatic, continuous monitoring may be deemed necessary to serve as a check and safeguard for site performance.

6. Empirical and experimentally-derived data on the sealing capacity of caprocks

Public acceptance of CO_2 storage in geological formations will depend strongly on convincing evidence concerning the long-term stability of the reservoir/seal system. This requires comprehensive screening and analysis of mechanisms that might resul in formation damage and/or seal leakage. Natural CO_2 systems exhibit various degrees of integrity or leakiness, depending on the geological and geochemical conditions. Rapid or gradual changes in a geological system's chemical regime e.g. by CO_2 injection, may result in substantial changes in the fluid transport properties.

Determining the properties of seals from natural systems that have successfully trapped CO_2 for geological timescales provides evidence that similar seals could successfully act as barriers during CO_2 storage. This information could be used to further constrain future site selection by identifying potential seals where it can be proven through laboratory-based experiment, that at reservoir conditions, CO_2 is unlikely to migrate through the seal, or, at least, the rate of migration is acceptable.

The experimental equipment developed in the project to test seals from natural accumulations can be used to test seals in potential storage sites.

7. Improved awareness among policy makers and regulators of the potential for geological CO_2 storage through dissemination.

An important aim of the Nascent project is to inform policymakers and regulators of the potential for geological CO_2 storage through the use of natural analogues as both proof of the concept and as a means of understanding the potential hazards. This improved awareness has been achieved through dissemination of the main outputs. Activities include articles in scientific journals, presentations at conferences, workshops and network meetings, publications in appropriate trade journals, development of undergraduate course material and development of the Nascent websites (see bibliography in Chapter 7).

The application of Geographical Information System (GIS) programs for the organisation and processing of various forms of data which are related to the escape, migration, attenuation, accumulation and release of CO_2 from a geological storage site to the atmosphere is critical for the objective assessment of risk for any given area chosen as a potential CO_2 storage site. The application of this method to the Latera area, and the comparison of these results with those of the soil gas surveys, showed the utility of this approach for outlining areas which should either be zoned for non-residential use or which should be monitored closely for increased risk caused by gas leakage. The promising results from this work has led to similar work being started on the San Vittorino and Ciampino sites. This tool will be extremely important for regulators and local civil protection agencies for risk assessment of a site chosen for possible CO_2 storage, and will aid in focussing resources in any eventual monitoring system established above the injection site.

Finally, dissemination of the URS results of this project, as well as the work planned in the future as a result of the data collected during Nascent, will be primarily through web pages, international peer-reviewed journals and public forums. The present university web page will be updated with the results of the project, and consideration is being given to the creation of a site dedicated to the occurrence and safety issues surrounding natural CO_2 emissions in Italy. Publications and conference proceedings are already in the preparation phase for the results of the water and soil gas data from San Vittorino, the detailed soil gas surveys and profiles at Latera, the injection test at Latera, the laboratory diffusion experiments, the application of GIS to the Ciampino site and the development of the geochemical monitoring station at San Vittorino. Finally short courses are being planned for the near future, within the Network of Excellence "CO2GeoNet", which will use the combined expertise of many large European research institutes involved in geological CO_2 storage to disseminate the results of the last 10 years of research to regulators, technicians and students.

6.1. REFERENCES

DAVIS, G.B., PATTERSON, B.M., BARBER, C. and JOHNSON, C.D. 1997. Evaluating in situ remediation using innovative monitoring technologies. 45-62 in *Proceedings of the International conference on groundwater quality protection: remedial technology and management policy for NAPL contamination*, Taipei, Taiwan.

ETIOPE, G. and MARTINELLI, G. 2002. Migration of carrier and trace gases in the geosphere: an overview. *Phys. Earth Planet. Inter.*,129, 185-204.

Moberg, R., Stewart, D.B. and Stachniak, D. 2002. The IEA Weyburn CO_2 Monitoring and Storage Project. In Gale, J. and Kaya, J., Proceeding of the 6th greenhouse Gas Control technologies Conference, Kyoto, Japan

Chapter 7. Further information

The following technical reports have been published by the Nascent project. A CDRom containing these reports together with this final report is available from J.M. Pearce, BGS, Keyworth, Nottingham, NG12 5GG, United Kingdom. Tel: +44 (0)115 9363 222, Fax: +44 (0)115 9363352 or email: jmpe@bgs.ac.uk.

Pearce, J.M. (Editor), 2003. *Natural Analogues for the Storage of CO_2 in the Geological Environment: Report on Field Characterisation* including Soil Gas Surveys, Characterisation of Offshore Shallow Gas Seeps, Hydrogeochemistry and Diagenetic Studies. British Geological Survey External Report CR/03/147, 333 pages.

Kemp, S.J. (Editor), 2003. *Natural Analogues for the Storage of CO_2 in the Geological Environment*: *CO_2 leakage mechanisms and migration in the near-surface.* British Geological Survey External Report CR/03/196, 55 pages.

Gaus, I. C. Le Guern, H. Serra. 2004. *Natural Analogues for the Storage of CO_2 in the Geological Environment: Modelling of CO_2/fluid/rock interactions*. BRGM External Technical Report BRGM/RP-52934-FR, 87 pages.

Orlic, B., Schroot, B.M. Hatziyannis, G…. 2004. *Natural Analogues for the Storage of CO_2 in the Geological Environment: Geohazard Assessment.* TNO External Technical Report NITG 04-049-B0309, 44 pages.

There are two Nascent websites:

www.bgs.ac.uk/nascent

http://www.rwth-aachen.de/lek/Ww/nascent/nascent_password/1seite.html

The following lists are a selected bibliography of published papers from the Nascent project.

Peer Reviewed Articles:

1. ANNUNZIATELLIS A., CIOTOLI G., LOMBARDI S. AND NOLASCO F. (in press) Short and long term gas hazard: the release of toxic gases in the Alban Hills volcanic area (central Italy). *Submitted to Journal Geochemical Exploration.*
2. BRUNE, S. AND FABER, E., 2001. Projekt NASCENT - *Natural Analogues to the Storage of CO_2 in the Geological Environment*. Jahrestagung der Gesellschaft für Geowissenschaften e.V. Berlin. Exkursionsführer und Veröffentlichungen der GGW, Schmalkalden, **10**, 97-98.
3. HILDENBRAND A., SCHLOEMER S. AND KROOSS B.M. (2002). *Gas breakthrough experiments on fine-grained sedimentary rocks.* Geofluids, **2**, 3-23.
4. HILDENBRAND A., SCHLOEMER S. AND KROOSS B.M. (2002). N_2 and CO_2 gas breakthrough experiments on fine-grained sediments. In: *Poromechanics*, Auriault et al. (eds). Swets & Zeitlinger, Lisse, 445-450.
5. HILDENBRAND A., SCHLOEMER S. AND KROOSS B.M. submitted to Geofluids. *Gas breakthrough experiments on pelitic rocks: Comparative study with N_2, CO_2 and CH_4.*
6. PHD THESIS: HILDENBRAND A., January 2003. Fluid Transport Processes in Mudstones. PhD Thesis, RWTH-Aachen.
7. F. MAY, ST. BRUNE, P. GERLING, P. KRULL (2003).Möglichkeiten zur untertägigen Speicherung von CO_2 in Deutschland – eine Bestandsaufnahme. Geotechnik, **26(3)**, 162-172.
8. F. MAY, ST. BRUNE, P. GERLING, P. KRULL (2003).Möglichkeiten zur untertägigen Speicherung von CO_2 in Deutschland – eine Bestandsaufnahme. Glückauf Forschungshefte, **(64,4)**, 138-146.

9. HEGGLAND, R., (in press), *Definition of geohazards in exploration 3D seismic data using attributes and neural network analysis*. AAPG Bulletin Geohazards Theme Special Issue, June 2004.

10. HEGGLAND, R., (in press), *Using gas chimneys in seal integrity analysis, A discussion based on case histories*. AAPG Hedberg Volume Evaluating the Hydrocarbon Sealing Potential of Faults and Caprocks.

11. HEGGLAND, R., 2004, Seismic Evidence of Vertical Fluid Migration Through Faults, Applications of Chimney and Fault Detection, article **to be submitted** to *AAPG Theme Volume Near-Surface Hydrocarbon Migration: Mechanisms and Seepage Rates*.

12. HEGGLAND, R., (in press), Hydrocarbon Migration and Accumulation Above Salt Domes - Risking of Prospects by the Use of Gas Chimneys. *24th Annual GCSSEPM Foundation Bob F. Perkins Research Conference, Salt-Sediment Interactions and Hydrocarbon Prospectivity: Concepts, Applications, and Case Studies for the 21st Century*, Houston, Dec. 5-8, 2004.

13. B.M. SCHROOT & R.T.E. SCHÜTTENHELM, 2003. *Expressions of shallow gas in the Netherlands North Sea*. Netherlands Journal of Geosciences, **82(1)**, 91-105.

14. B. M. SCHROOT & R.T.E. SCHÜTTENHELM, 2003. *Shallow gas and gas seepage: expressions on seismic and other acoustic data from the Netherlands North Sea*. Journal of Geochemical Exploration, **4061**, 1-5.

15. H. PAUWELS, I. GAUS , Y M LE NINDRE, J PEARCE, I CZERNICHOWSKI-LAURIOL. *Chemical and isotope composition of fluids from a natural CO_2 accumulation (Montmiral, France): estimation of reservoir water composition and evidence for water origin and water-CO_2-rock interactions*. submitted to Chemical Geology (special issue on CO_2 sequestration).

16. HILDENBRAND A. AND URAI J. L. (2003) *Investigation of the morphology of pore space in mudstones-first results*. Marine and Petroleum Geology, **20(10)**, 1185-1200

17. J. PEARCE, I. CZERNICHOWSKI, S. LOMBARDI, S. BRUNE, A. NADOR, J. BAKER, H. PAUWELS, G. HATZIYANNIS, S. BEAUBIEN, E. FABER *In press. A review of natural CO_2 accumulations in Europe as analogues for geological sequestration*. Special Publication of the Geological Society of London.

18. MELDAHL, P., HEGGLAND, R., BRIL, B. AND DE GROOT, P. (2001). *Identifying targets like faults and chimneys using multi-attributes and neural networks*, The Leading Edge*,* May 2001.

19. AMINZADEH, F., CONNOLLY, D., HEGGLAND, R., MELDAHL, P., AND DE GROOT, P, 2002. *Geohazard detection and other applications of chimney cubes*, The Leading Edge*,* July 2002, 681-685.

20. BEAUBIEN S.E., CIOTOLI G. AND LOMBARDI S. 2003. *Carbon dioxide and radon gas hazard in the Alban Hills area (central Italy)*. Journal of Volcanology and Geothermal Research, **123**, 63-80.

Non-refereed literature and other dissemination activities:

1. PEARCE, J. (Ed.), June 2001. Natural analogues for the storage of CO_2 in the Geological environment: WP1: Data collation, review and site selection.

2. GALE, J., March 2001. Nascent project launch Green-house Issues, vol. 53. *Trade magazine article*.

3. BRUNE. S., September 2001. CO_2 in the Vorderrhön area of Thuringia. Regionale und Angewandte Geologie in der Grenzregion der Süddeutschen und der Mitteldeutschen Scholle" (regional and applied geology in the region of the Süddeutsche and the Mitteldeutsche Schwelle) GGW, Schmalkalden, Thuringia (near the Vorderrhön area). *Conference proceedings*

4. GALE, J., 18-19 October 2001. CO_2 sequestration activities 1st Annual European Energy and Transport Summit Conference, 18-19 October 2001, Barcelona, Spain. *Conference proceeding*

5. PEARCE, J.M. 13th to 14th March, 2001. An overview of the NACSENT Project. Launch meeting of the CO2NET Thematic Network, Statoil R&D Centre, Trondheim, Norway. *Conference proceeding*

6. RILEY, N.J., 5-9 November 2001. Nascent & Weyburn project descriptions Carbon Capture Project workshop, Potsdam, Berlin *Conference proceeding*

7. SCHROOT, B.M. 27-28 August 2001. Surface and Subsurface Expressions of Shallow Gas Accumulations in the Southern North Sea. Natural hydrocarbon seeps, global tectonics and greenhouse gas emission, Delft *Conference proceeding*

8. SCHROOT, B.M. APRIL 7-10, 2002 (postponed from 16-19 September 2001). Near-Surface Hydrocarbon Migration Mechanisms and Seepage Rates The AAPG Hedberg Research Conference, Vancouver, BC Canada *Conference proceeding*

9. HEGGLAND, R. APRIL 7-10, 2002 (postponed from 16-19 September 2001). Seismic Evidence of Vertical Fluid Migration Through Faults, Applications of Chimney and Fault Detection. AAPG Hedberg Conference, "*Near-*

Surface Hydrocarbon Migration: Mechanisms and Seepage Rates", Vancouver, BC, Canada, *Conference proceeding*

10. PEARCE, J.M. 29-30 April 2002. An update on progress in the Nascent project, since the inaugural meeting in Trondheim in December 2000 CO_2NET meeting at Institute Français de Petrole, Paris, *Workshop briefing*
11. PEARCE, J.M. 28-29 May 2002. An overview of the Nascent project CCP Sponsored workshop on risk analysis, British Geological Survey, Nottingham, United Kingdom *Workshop briefing*
12. SCHROOT, B.M. 27-31 May 2002. North Sea shallow gas as a natural analogue in feasibility studies on CO2 sequestration. 64th EAGE Conference, Florence *Conference proceeding*
13. PEARCE ET AL 28 September to 5 October 2002. Natural Accumulations In Europe: Understanding Long Term Processes In Geological Storage Greenhouse Gas Control Technologies Conference (GHGT6) organised by the International Energy Agency Greenhouse Gas R&D Program, Kyoto, Japan. *Conference proceeding*s
14. CZERNICHOWSKI-LAURIOL, I., PAUWELS, H., VIGOUROUX, PH., LE NINDRE Y-M., 28 September to 5 October 2002. The France's Carbogaseous Province: An Illustration Of Natural Processes Of Co_2 Generation, Migration, Accumulation And Leakage Greenhouse Gas Control Technologies Conference (GHGT6) organised by the International Energy Agency Greenhouse Gas R&D Program, Kyoto, Japan. *Conference proceedings*
15. HILDENBRAND A., KROOSS B.M., SCHLÖMER S., August 26-28, 2002. N_2 and CO_2 gas breakthrough experiments on fine-grained sediments 2nd Biot Conference on Poromechanics, Grenoble. *Poster*
16. HILDENBRAND A. AND KROOSS B. M., 2002. Investigation of CO_2 migration processes in argillaceous rocks: implications for sealing efficiency and diagenesis. CSCOP-TSOP Conference: Emerging concepts in Organic Petrology and Geochemistry, Banff. *Oral presentation*
17. CZERNICHOWSKI-LAURIOL, I., PAUWELS, H., November 8th, 2002. Présentation des recherches sur la sequestration géologique du CO2 au BRGM Meeting, hosted by Institute de Physique du Globe, held in Paris on the "*Outline of French research in the domain of geological sequestration of CO_2*" attended by 31 delegates from 13 French industrial and research organisations. *National workshop*
18. HEGGLAND, R., Dec 2002. Using detection of seismic chimneys in seal integrity analysis "*Evaluating the Hydrocarbon Sealing Potential of Faults and Caprocks"* AAPG HEDBERG CONFERENCE, December 2-5, 2002, Barossa Valley, South Australia. *Conference proceeding*s
19. BRUNE, S. Kohlendioxidlagerstätten n der Vorderrhön – Analoga für eine möglich Kohlendioxidspeicherung in geologischen Strukturen (Thüringens). Erdöl und Erdgas in Thüringen, Tagung des TGV in Gotha, 2002. *Conference proceeding*s
20. DR. STEFAN BRUNE, DR. FRANZ MAY, DR. ECKHARD FABER, DR. J. PETER GERLING, DR. PAUL KRULL, DR. BERNHARD M. KROOß, FuE Initiativen zur CO_2- Speicherung. VDI Tagung Bochum 2002. *Conference proceeding*s
21. GERLING, P., MAY, F., BRUNE, S.: TV report about CO_2 sequestration and storage in the geological environment, title: CO_2 Speicher. Production of artavis TV, telecasted in 3Sat "nano", DW, MDR.
22. ANNUNZIATELLIS A., BEAUBIEN S.E., CIOTOLI G. AND LOMBARDI S. Submitted December 2003. Allaying public concern regarding CO_2 geological sequestration through the development of automated stations for the continuous geochemical monitoring of gases in the near surface environment. GHGT7 in Vancouver, September 2004. *Oral presentation*
23. ANNUNZIATELLIS A., CIOTOLI G., PETTINELLI E., BEAUBIEN S.E., LOMBARDI S. Submitted December 2003. Geochemical and geophysical characterisation of an active CO_2 gas vent near the village of Latera, central Italy. GHGT7 in Vancouver, September 2004. *Oral presentation*
24. S. LOMBARDI, S. BEAUBIEN, G. CIOTOLI, G. HATZIYANNIS, A. METAXAS, J. PEARCE Submitted December 2003. Potential hazards of CO_2 leakage - learning from nature. GHGT7 in Vancouver, September 2004. *Oral presentation*
25. ST. BRUNE, E. FABER, M. TESCHNER, J. POGGENBURG, J. HAGENDORF. September 2003. CO_2 deposits at Vorderrhön area (Thuringia) - gas migration from deep reservoir to surface? 7th International Conference on Gas Geochemistry, ICGG7, Freiberg 22.-26.September 2003 *Oral presentation*
26. HEGGLAND, R., December 2004. Hydrocarbon Migration and Accumulation Above Salt Domes - Risking of Prospects by the Use of Gas Chimneys, abstract submitted for the 24th Annual GCSSEPM Foundation Bob F. Perkins Research Conference, Salt-Sediment Interactions and Hydrocarbon Prospectivity: Concepts, Applications, and Case Studies for the 21st Century, Adams Mark Hotel, Houston, Dec. 5-8. *Oral presentation*
27. SCHROOT, B. M. AND HEGGLAND, R., September 2004. Natural gas migration to the near-surface environment as an analogue to potential leakage of CO_2 – detection and mechanisms, submitted for GHGT-7, 7th International Conference on Greenhouse Gas Control Technologies, Vancouver Convention Centre, Canada, Sep. 5-9. *Oral presentation*

28. BARTHOLD M. SCHROOT. May 2003. Seismic Anomalies Indicating Leakage: Examples From The Southern North Sea. AAPG 88th Annual meeting, 11-14 May 2003, Salt Lake City. *Oral presentation*

29. BARTHOLD M. SCHROOT AND RUUD T.E. SCHÜTTENHELM, May 2003. Shallow Gas And Gas Seepage: Expressions On Seismic And Other Acoustic Data From The Netherlands North Sea. GeoFluids IV Conference, 12-16 May 2003, Utrecht. *Oral presentation*

30. CZERNICHOWSKI-LAURIOL.I., AUDIBERT.N., FOUILLAC C., BONIJOLY D. September 2003. Combining hydrogen production and geological sequestration of CO2, a way toward a low GHG emission society 1st European Hydrogen Energy Conference, 2-5 September 2003 - Grenoble, France, 7 p. *Oral presentation*

31. GAUS, I., LE GUERN, C., PAUWELS, H., GIRARD J-P, PEARCE J., SHEPHERD, T., HATZIYANNIS G., AND METAXAS, A., September 2004. Comparison of long term geochemical interactions at two natural CO2-analogues: Montmiral (Southeast Basin, France) and Messokampos (Florina Basin, Greece) case studies. Abstract submitted to the GHGT7 conference. *Oral presentation*

32. LE.NINDRE.Y.M., PAUWELS.H., SHEPHERD.T., PEARCE.J.M. June 2004. 3D geological modelling of a CO_2-bearing natural analogue, matching the geohistory. EAGE 66th (European Association of Geoscientits and Engineers) Conference & Exhibition - 7-10 June 2004 - Paris, France. *Oral presentation*

33. AUDIGANE P., AZAROUAL M., CZERNICHOWSKI-LAURIOL I., DURST P., GAUS I., KERVEVAN C., LE NINDRE Y-M., SBAI A. 2004. Long term predictions of CO_2 migration and reactivity with the host rock during CO_2-sequestration Submitted 32nd International Geological Congress, Firenze. *Oral presentation*

34. PEARCE, J.M., SHEPHERD, T.J., GIRARD., J-P., LE NINDRE, Y-M., KEMP, S.J., PAUWELS, H., AND CZERNICHOWSKI, I., May 2003. CO_2–Pore Water-Rock Interactions From Natural CO_2 Gas Pools – *A Case History from the Southeast Basin of France*. AAPG annual conference in Utah, USA, May 2003. *Oral presentation*

35. HILDENBRAND, A., KROOSS, B.M., May 2003. CO_2 migration processes in argillaceous rocks: pressure-driven volume flow and diffusion. Geofluids IV, Utrecht, Netherlands, May 12-16, 2003. *Poster presentation*

36. HILDENBRAND, A., URAI, J.L., KROOSS, B.M., May 2003. Relationship between pore structure and fluid transport in argillaceous rocks. Symposium on the mechanics of physiochemical and electromechanical interactions in porous media (IUTAM-Symposium), Kerkrade, Nederlands, May 18-23, 2003. *Poster presentation*

37. HILDENBRAND, A., KROOSS, B.M., LITTKE R., September 2003. Dynamik leakage through fine-grained seal lithologies. EAGE Conference "Fault and Top Seals", Montpellier, France, September 8-11, 2003. *Poster presentation*

38. HILDENBRAND, A. October 2003. Gas breakthrough experiments and its application. SINTEF, Trondheim, Norway, 3. – 4. October 2003. *Oral presentation*

39. HILDENBRAND, A., KROOSS, B.M., SCHLOEMER, S. November 2003. Capillary gas breakthrough and muliphase gas/water transport in argillaceous rocks. Gas-Water-Rock Interactions, Induced by Reservoir Exploration, CO_2 Sequestration, and other Geological Storage, Rueil-Malmaison, France, November 18-20, 2003. *Oral presentation*

40. KROOSS, B.M., BUSCH, A., ALLES, S. HILDENBRAN A., November 2003. Experimental investigation of molecular diffusion of CO_2 in coals and shales. Gas-Water-Rock Interactions, Induced by Reservoir Exploration, CO_2 Sequestration, and other Geological Storage, Rueil-Malmaison, France, November 18-20, 2003. *Poster presentation*

41. HILDENBRAND A., KROOSS, B.M., SCHLÖMER, S., LITTKE, R.: (submitted) Dynamic gas leakage through fine-grained seal lithologies. EAGE Proceedings, 2004: Fault and Top Seals: What do we know and where do we go? *Proceedings*

42. HILDENBRAND A., KROOSS B.M., URAI J.L. (submitted). Relationship between pore structure and fluid transport in argillaceous rocks IUTAM Proceedings: On the mechanics of physicochemical and electromechanical interactions in porous media. *Proceedings*

43. J.M. PEARCE. March 2003 The NASCENT Project, natural CO_2 systems in the Geological Environment, analogues for CO_2 storage. Coping with Climate Change Conference, Geological Society of London, March 2003. *Oral presentation*

44. J.M. PEARCE. February 2004 What can we learn from natural analogues? IEAGHG/ CCP International Workshop on Risk Assessment in Geological Sequestration, DTI London, UK. *Oral presentation*

45. J.M. PEARCE, B.M. SCHROOT, I. CZERNICHOWSKI-LAURIOL, G. HATZIYANNIS. April 2004 The Nascent project – selected highlights CO2NET Annual seminar, Utrecht, Netherlands. *Oral presentation*s