A REVIEW OF NATURAL CO_2 OCCURRENCES AND RELEASES AND THEIR RELEVANCE TO CO_2 STORAGE

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Background to the Study

The security of storage of CO_2 in geological reservoirs is a key issue that has been, and will be increasingly, discussed as the technology moves closer to wide scale deployment. There are a number of ways through which the security of storage can be demonstrated. These include:

- Development of standards and best practise guidelines that ensure that storage reservoirs are carefully selected and the environmental risks are minimised,
- Development of risk assessment procedures that demonstrate long term safe storage is a realistic prospect,
- Monitoring of injection projects to confirm the containment of injected CO_2.

All these activities are now underway in a number of countries worldwide. However it may be several more years before a credible data base is established that will allow the issue of security of storage to be resolved to everybody's satisfaction. In the intervening period, this issue will represent a potential barrier to the introduction of CO_2 storage technology. In that interim period, groups not necessarily supportive of geological storage of CO_2, may emphasise the issue of storage security, through reference to natural geological events. In particular, natural events such as Lake Nyos in Cameroon that have resulted in deaths due to an uncontrolled CO_2 release may well be those that are focused upon in any debate. Unless these natural events are properly understood, and put in context, they could adversely affect public sentiment towards geological storage of CO_2.

The aim of this study was to evaluate natural occurrences of CO_2 leakage and compare and contrast them with engineered storage of CO_2 in geological formations. The objective of the study was to provide a reference manual for IEA Greenhouse Gas R&D Programme members and others interested in the subject, to provide a factual and balanced review of natural CO_2 releases and their relevance to geological CO_2 storage.

The study has been carried out by the British Geological Survey, UK and CREIPI, Japan.

Results and Discussion

The following aspects are discussed in this report:

- Natural releases of CO_2 occur and how they occur,
- Regions that are being considered for the geological storage of CO_2
- Notable natural incidents of CO_2 release in volcanic regions,
- Natural CO_2 emissions in sedimentary basins,
- Engineered CO_2 storage sites

Natural releases of CO_2 and how they happen.

There are a number of processes by which naturally occurring CO_2 can be emitted into the atmosphere, however, the most important is through the degassing of magma (molten rock[1]). Magma degasses due to the pressure reduction that occurs when it rises to the earth's surface. The degassing of magma is commonly associated with volcanic activity. Water vapour is the major gas species emitted from volcanoes representing typically 60% of the total gas content, whilst CO_2 represents only 10-40% of the total released gas[2]. Volcanic emissions of CO_2 are estimated to be about 300 Mt CO_2 per year. In contrast, global anthropogenic emissions of CO_2 are about 24Gt per year. Mt Etna is considered to be the most actively degassing volcano emitting about 25 Mt CO_2 per year. Non eruptive diffuse degassing can also be significant around some volcanoes, for instance around the Yellowstone hydrothermal area in the USA, diffuse degassing has been measured at 16 Mt CO_2 per year.

Volcanic regions by their very nature are prone to eruptions, ground movement, earth tremors and explosions that can fracture the surrounding rocks. They may also contain magma chambers or voids that are capable of holding large volumes of gas that can be suddenly released at high pressure as a result of the eruptions, ground tremors or fracturing.

Dormant or extinct volcanoes can also contain crater lakes although they are not common, worldwide there are less than 20 such examples in North and South America, Europe, Africa, Indonesia, Australasia and Japan[3]. A few like those at Lake Nyos and Lake Monoun in Cameroon have become saturated with CO_2. In tropical regions[4] like Cameroon such lakes are not seasonally overturning[5] hence if CO_2 accumulates in the waters of these tropical crater lakes, and its release is triggered by some natural event, then it can be released in large quantities with potentially serious consequences. In contrast, the lakes commonly found in temperate regions (like Europe, North America, Japan, Australia etc.,) are seasonally overturning and therefore pose much less potential danger

Regions that are being considered for the geological storage of CO_2.

Sedimentary basins are the regions of the world that are being considered as most suitable for CO_2 storage. They are large areas of the Earth's crust which are actively subsiding, or have subsided at some time in the past, allowing thick successions of sediments, and thus eventually sedimentary rocks, to accumulate. They are widely spread around the world and many occur in tectonically stable regions, where there is little or no volcanic/hydrothermal activity.

Sedimentary basins commonly contain both porous and permeable reservoir rocks and impermeable or very low permeability cap rocks that can act as natural seals that prevent gases and other buoyant fluids reaching the ground surface or sea bed. The existence of such natural barriers is proved by the presence of oil and natural gas fields in sedimentary basins. In a similar manner, naturally occurring CO_2 may be confined in the pore spaces of sedimentary rocks folded into domes or other structures that do not contain any pathways to the ground surface or seabed. In such cases, many naturally occurring underground CO_2 fields are formed, some of which have existed for millions of year. For example the Pisgah Anticline in Mississippi, USA holds some 215 Mt CO_2, which is a similar order of magnitude to that considered for an engineered CO_2 storage site. The CO_2 migrated into the field some 65 million years ago and has been contained there ever since.

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[1] The melting of carbonate rocks (limestone's, dolomites, chalks) will lead to the production of gaseous CO_2

[2] Other gaseous species released can include: SO_2, HCL, H_2S, CO and COS

[3] See Volcanic Lakes of the World at: http://www.wesleyan.edu/ees/JCV/volclakes.html

[4] Regions of the world lying between the tropics of cancer and Capricorn

[5] In tropical regions the lake temperatures vary less than those in colder or temperate climates. It is the seasonal changes in temperature that cause lakes even deep ones to mix or turn over. Deep lakes usually mix or turn over during the winter when water temperatures cool to near 4^{o}C and the lake becomes more susceptible to convective and wind-driven mixing. Shallow lakes usually mix more than deep lakes. In warm lakes, like those in tropics it has been demonstrated that increased warming results in more stability and, hence, less opportunity for turnover.

Natural CO_2 fields can, therefore, give assurance that in suitable locations CO_2 can be stored in the subsurface for millions of years. The widespread distribution of these fields in sedimentary basins indicates that these circumstances are relatively commonplace. The intensive search for, and development of, oil and gas resources that has taken place over the last century has resulted in a huge body of information about the world's major sedimentary basins, the rocks they contain and the oil and gas fields (including natural CO_2 fields) within them. There is every reason to suppose that this knowledge and the accompanying technology that has been developed to find and exploit these resources will enable the safe long term storage of carbon dioxide in the subsurface.

Notable natural incidents of CO_2 release in volcanic regions

There are a small number of incidents of natural releases of CO_2 that have lead to loss of life and hence these have been often referred to incorrectly as analogues for geological storage of CO_2. One of these incidents occurred at the Dieng volcano complex in Indonesia, whilst the two most notable and well referenced incidents of natural CO_2 release are Lake Nyos and Lake Monoun both of which are in Cameroon in West Africa. In the first case, CO_2 release occurred before a volcanic eruption, whilst both the latter incidents involved sudden emissions of CO_2 from volcanic crater lakes.

At the Dieng complex diffusive CO_2 emissions occurred prior to a major eruption. About 0.2 Mt of pure CO_2 was released and flowed from the volcano to the plain below as a dense sheet resulting in 142 deaths in 1979. The incident provides an example of the danger presented by the sudden release of CO_2 emissions from volcanoes following a build-up of gas within them. This incident was associated with a phreatic explosion[6] that resulted in the formation of a new crater and the reactivation of a pre-existing fracture. Phreatic explosions normally release large volumes of superheated water with only small amounts of CO_2. It is considered that the pure gaseous CO_2 released must have accumulated in a shallow reservoir as a high density fluid before the explosion and has then been released through fractures as they opened up due to the pressure build-up in the volcano prior to the explosion. This combination of large volumes of CO_2 gas in shallow reservoirs coupled with fracture development prior to an explosion could not occur in a sedimentary basin.

The sudden, large emissions of CO_2 from the crater lakes Monoun and Nyos in Cameroon, in 1984 and 1986 respectively, are also examples of the danger presented by sudden CO_2 emissions from volcanoes, in this case following a build-up of CO_2 within the crater lakes. These releases involved a set of specific geographical features and geological processes that contributed to each event and the loss of life that followed.

Crater lakes are located at the top of volcanoes and are commonly surrounded (almost totally) by high (several hundred metres) crater walls. The lakes overflow down a spillway leading to a valley system. In tropical areas such lakes may be deep and still and the water column within them can become stratified as there is little seasonal mixing of the lake waters. CO_2 percolating up highly permeable fissures and fractures into the crater lake floors can dissolve into the lower levels of the lake waters (increasing their density) until they become saturated with respect to CO_2. Once saturated, any disturbance that causes part of the lower lake waters to rise could cause CO_2 to come out of solution.

In 1984, a large release of volcanic CO_2 occurred when Lake Monoun over turned. The released CO_2 moved out of the crater and hung in a depression along a nearby river course where it asphyxiated 37 people. A similar, but worse, incident occurred at nearby Lake Nyos in 1986. Following sudden overturn of the lake waters, the cold CO_2 was confined by the crater walls and migrated down the lake spillway into a valley. It travelled along the valley, hugging the ground, asphyxiating 1700 people in a thinly populated area and extinguishing all animal life for more than 14 km along its course.

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[6] Phreatic eruptions are steam-driven explosions that occur when water beneath the ground or on the surface is heated by magma, lava, hot rocks, or new volcanic deposits (for example, tephra and pyroclastic-flow deposits). The intense heat of such material (as high as 1,170° C for basaltic lava) may cause water to boil and flash to steam, thereby generating an explosion of steam, water, ash, blocks, and bombs.

The CO_2 releases at Lakes Nyos and Monoun were again the result of exceptional circumstances unlikely to be found at or near purpose designed CO_2 storage sites; the presence of stratified lakes at considerable elevation compared to much of the surrounding local topography, the presence of a slow CO_2 leak into the bottom of the stratified lakes, the unobserved CO_2 saturation of the lower layer of the lake waters. Any deep lakes that could potentially become stratified in the vicinity of an engineered CO_2 storage site could be easily monitored to prevent such incidents and a "benign gas release" remediation programme, similar to that in place today at Lake Nyos, could be implemented.

In addition, to these major incidents there have also been numerous incidents in volcanic and hydrothermal areas in which the asphyxiation of animals can be attributed to CO_2 emissions. Deleterious effects on plants are also well documented in volcanic and hydrothermal areas, particularly at Mammoth Mountain, California, where large tree kills have occurred, caused by CO_2 seeping upwards from the geosphere into the soil.

Natural CO_2 emissions in sedimentary basins

To provide a balanced view point it must be noted that some emissions of naturally occurring CO_2 have been observed in sedimentary basins. However, the hazards posed by recorded natural CO_2 emissions in sedimentary basins are not on the same scale as those posed by the large sudden releases that have been recorded in volcanic and hydrothermal regions. For example in some areas of the Paradox Basin, USA CO_2 seepage along faults[7] results in CO_2 charged groundwater in several springs and through old well bores[8]. The Crystal Geyser is dramatic example of leakage along a well bore, which has erupted every 4-12 hours since the well was drilled in 1935 close to the fault line. The Crystal Geyser has since become a tourist attraction.

Other examples include the French carbogaseous area where carbonated springs are also common. The CO_2 occurrences all appear along a major fault line. Many of these springs are exploited by sparkling mineral water companies like Perrier and Vichy. There are also many other examples of such emissions, in Germany, Hungary and the USA, all of which appear to pose, at worst, only very local hazards.

Developing CO_2 storage sites.

As discussed earlier sites for the purpose designed storage of CO_2 are most likely to be situated in stable sedimentary basins because storage sites need:

- a reasonable storage capacity will be provided by the sedimentary reservoir rocks,
- a cap rock or rocks that will prevent leakage, provided by a sequence of overlying low-permeability seals.

Purpose designed CO_2 storage sites can be considered as closely analogous to those natural CO_2 fields that occur in sedimentary basins. They would be sited at carefully selected locations to take advantage of the geological factors that prevent the upwards or lateral migration of CO_2 from the intended storage reservoir towards the ground surface or sea bed.

It is expected that purpose designed CO_2 storage sites will be subject to a regulatory process that, prior to injection of any CO_2, is likely to include:

- detailed characterisation of the storage site and surrounding area,
- the construction of geological models of the site and surrounding area,

[7] There is some conjecture that the faults themselves may not be acting as conduits but instead fractured shale’s around the faults in certain areas are providing the pathway, this is because in other areas around the fault there is no evidence of surface seepage.
[8] The well bores concerned are old oil exploration wells and water wells.

- the simulation of CO_2 injection into the storage reservoir,
- a risk assessment based on the site characterisation, models and simulation.

If potential for leakage is identified a remediation plan may be required.

In addition, during CO_2 injection, monitoring of the subsurface, ground surface or sea bed and history matching of the monitoring results with the models, will be required to provide feedback to improve the understanding of the site. Agreement between the modelled and observed results, allowing reliable extrapolation of CO_2 behaviour into the future, will likely be required before the site is closed.

It is considered that once injection has ended, the stability of stored CO_2 in engineered storage sites is likely to increase rather than decrease through time. This is because reservoir pore fluid pressure is likely to be greatest during the injection period and gradually fall off after injection has ended. Enhanced pore fluid pressure is an important factor driving the migration of both free and dissolved CO_2. Geomechanical stresses will also decrease as pore fluid pressure decreases. Moreover, forward modelling of certain sites, including Sleipner, suggests that as time progresses, more and more CO_2 will dissolve into the surrounding pore fluid. The resulting CO_2-saturated pore fluid is slightly denser than the native pore fluid and will tend to sink through the pore system of the reservoir rock, migrating downwards rather than upwards, greatly decreasing the chances of it reaching the biosphere.

There are currently a number of purpose designed CO_2 storage sites that are operating, and many more are planned. The degree of seepage to the biosphere that might be expected from purpose designed CO_2 storage sites is difficult to determine from first principles. It is felt that seepage can only be considered on a case-by-case basis. This is, because the subsurface is considered to be an extremely variable natural system and each site will therefore be geologically unique. In the future, when we have considerable more data on geological storage sites it might be possible to generalise on potential seepage rates.

Detailed monitoring of the surface and subsurface is underway at a number of geological storage sites. Examples of such projects that have been monitored include: the Sleipner project in the North Sea and the CO2-EOR projects at Weyburn in Saskatchewan, Canada and Rangely, in Colorado, USA. The Sleipner project started storing CO_2 in 1996 and stores approximately 1 million tonnes of CO_2 per year. It has been closely monitored and no leakage from the storage reservoir has been detected. No surface seepage has been detected from the Weyburn field, where injection started in 2000. At Rangely, where CO_2 injection started in 1986, it is considered that up to 170 tonnes/year of CO_2 (out of approximately 23 million tonnes stored) may have seeped from the reservoir to the surface. However it is uncertain whether this is injected CO_2 or CO_2 formed by the microbial oxidation of methane in the surface soil. Arboreal sampling has not shown any areas of vegetative stress on the field which indicates that seepage of CO_2 (if it is occurring) is not affecting plant ecosystems on the field. Overall, the results imply that there is little data available that indicates that CO_2 seepage is occurring from those purpose designed CO_2 storage sites currently underway.

Expert Group Comments

The draft report on the study was sent to a panel of expert reviewers and to a number of IEA GHG's members who had expressed interest in reviewing it. The study was generally well regarded by the reviewers and was considered to present an unbiased review of the topic. A number of specific questions were raised by the reviewers on the report contents which have been addressed by the authors in the final draft of the report. The original title of the study: Public Perception: natural CO_2 occurrences and their relevance to CO_2 storage raised a number of comments from the reviewers in that it mislead them to expect a different report. The Programme has taken these comments into account and has revised the title of the report accordingly to avoid further misunderstandings about its content and purpose. It was always the Programmes intention to develop a detailed technical; report on these natural incidents as the main reference work and follow this with a glossy report for general dissemination to cover the public perception issue.

Major Conclusions

The main conclusions that can be drawn are that the most notable CO_2 emissions that are commonly referred to like Lake Nyos and the Dieng release all arise in volcanically active regions of the world. These volcanically active regions are not being actively considered for CO_2 storage in geological formations. Rather it is the volcanically inactive sedimentary basins around the world that contain extensive hydrocarbon accumulations and some natural CO_2 accumulations that are being actively considered for geological storage.

The major natural CO_2 emissions that have occurred and lead to significant loss of life, like Lake Nyos and the Dieng volcano can be regarded as representing fairly unique geological situations. These are either tropical craters lakes that do not overturn and are filling with CO_2 due to volcanic activity, or are the result of shallow CO_2 accumulations again resulting volcanic activity that are released as a precursor to a volcanic eruption as fractures in the strata open up prior to an explosion occurring. Such geological situations have nothing in common with the stable sedimentary formations, where it is proposed to store CO_2.

It must be noted that natural CO_2 emissions do occur in sedimentary basins. There are numerous natural CO_2 fields within sedimentary basins around the world. Some of these fields have held CO_2 for millions of years without evidence of leakage. Others, however, do leak along faults and as a result of wells drilled within the fault zones. Leakage generally manifests itself as carbonated springs or dry seeps (called moffettes) and can result in localized ecosystem damage. In general terms the environmental impact resulting of these leaks are significantly smaller than those occurring in volcanic regions

The study of natural CO_2 releases and accumulations has provided reference information that can be drawn upon in the selection of sites for geological CO_2 storage. Sites need to be in regions that are volcanically inactive, they require a thick overlying succession of impermeable rocks to prevent upward migration and they must be sited away from areas that are faulted. Wells provide a potential transmissive pathway for leakage from storage reservoirs. The frequency and abandonment status of all wells must be a critical analysis that is undertaken when selecting a potential CO_2 storage reservoir. Old wells may need to re-cemented to maintain their integrity and inadvertent drilling into these storage sites need to be controlled in the future to prevent accidental release of the stored CO_2.

Recommendations

The main recommendation that can be drawn from this study is that the selection of sites for geological storage of CO_2 needs to be rigorously controlled through a regulatory process to ensure that each potential storage site is carefully assessed to ensure that leakage from the reservoir and resultant surface seepage does not occur. Storage sites need to be in stable sedimentary basins with an effective impermeable seal, which is not faulted. The regulatory process should also ensure that careful attention is also required to the number, location and status of all wells with in the storage site to ensure they do not act as leakage pathways either during of after CO_2 injection has ceased.

A Review of Natural CO_2 Occurrences and their Relevance to CO_2 Storage

Sustainable Energy and Geophysics Programme

External Report CR/05/104

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SUSTAINABLE ENERGY AND GEOPHYSICS PROGRAMME

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A Review of Natural CO_2 Occurrences and their Relevance to CO_2 Storage

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Front cover

A CO_2 well blow-out in Florina, northern Greece. Courtesy of Dr. G. Hatziyannis, IGME, Athens.

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Foreword

In order to address the global warming threat posed by the emission of anthropogenic greenhouse gases to the atmosphere, many countries have committed themselves, through the recently-ratified Kyoto Protocol, to a 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 to be 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 energy from renewable sources can lead to significant reductions in carbon dioxide (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 at 550 ppmv (twice pre-industrial levels). Such a strategy requires several parallel approaches, including more efficient energy use, reduction of reliance on fossil fuels, removal of CO_2 from the atmosphere (e.g. through cultivating biomass), 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 captured CO_2. The capture and underground storage of industrial quantities of CO_2 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, 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.

Concerns have been expressed that if CO_2 capture and storage becomes a large-scale, widely deployed technology, future emissions of CO_2 from man-made underground storage sites could have a deleterious effect on the natural environment and/or be potentially hazardous to man. Concern has arisen largely because pure CO_2 is an asphyxiant and, over the last twenty years, a few natural events involving the rapid emission of large masses of CO_2 in volcanic areas have resulted in serious incidents involving many deaths and/or significant damage to the local environment.

This report addresses these concerns by reviewing examples of the major types of natural CO_2 emissions that occur from the geosphere (the part of the planet beneath the atmosphere and oceans) and some of the current man-made CO_2 storage projects under way around the world. It then compares and contrasts natural CO_2 emissions with putative unintentional leakages from man-made geological CO_2 storage sites.

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Summary

The examples of natural carbon dioxide (CO_2) emissions and man-made CO_2 storage sites presented in this report were all selected because they illustrate particular aspects of the accumulation, transport or emission of CO_2 in the geosphere. Some of the most important points are:

- The Pisgah Anticline natural CO_2 field demonstrates that large masses of CO_2, in this case over 200 million tonnes, can be trapped underground for tens of millions of years.
- The French carbogaseous area and the Paradox Basin on the Colorado Plateau are examples of sedimentary basins in which natural CO_2 emissions present, at most, only very local hazards to man or the natural environment.
- There is no evidence of leakage from the CO_2 storage sites at Sleipner and In Salah. The Sleipner project has been injecting CO_2 for nearly nine years.
- There is no evidence of leakage at the Weyburn enhanced oil recovery project, which has injected about 5000 tonnes CO_2 per day since 2000.
- There is a deep-sourced flux of 170-3800 tonnes/yr CO_2 from the Rangely oil field where an enhanced oil recovery project is in progress. It is likely that at least part, if not all, of this flux is due to the oxidation of deep-sourced methane from the oil reservoir, but part of it could be due to the migration of injected CO_2 from the oil reservoir. Approximately 23 million tonnes CO_2 have been injected into the field since 1986.
- Modelling of the long term fate of CO_2 at the Sleipner injection site suggests that over the long term much of the CO_2 may dissolve in the native pore fluid. As it does so, it will increase the density of the CO_2-saturated pore fluid, which will cause this to migrate downwards through the pore system in the reservoir rock and accumulate at the base of the formation.
- Both the previous point and the fact that reservoir pressure is likely to be highest during the injection phase of storage site development, suggest that many CO_2 storage sites may become more, rather than less, stable through time.
- The Colorado plateau and the Florina well case studies indicate that wells may provide leakage pathways to the ground surface from natural CO_2 fields or engineered CO_2 storage sites.
- Natural CO_2 emissions in an area of 15 km^2 in the offshore Tyrrhenian Basin have a minimum flux of 25,000 tonnes per year, most of which dissolves into the sea water.
- The incident involving asphyxiation of 142 people by CO_2 at the Dieng volcano in Indonesia in 1979 provides an example of the danger presented by sudden CO_2 emissions from volcanoes following a build-up of gas within them. This incident was associated with a phreatic (superheated water and steam) explosion that resulted in the formation of a new crater and the reactivation of a pre-existing fracture. This could not occur in a sedimentary basin because the necessary heat is not present at shallow depths.
- The sudden, large emissions of CO_2 from the crater lakes Monoun and Nyos in Cameroon, in 1984 and 1986 respectively, are also examples of the danger presented by sudden CO_2 emissions from volcanoes, in this case following a build-up of CO_2 within the crater lakes. The lake Monoun incident resulted in 37 deaths and the lake Nyos incident in approximately 1700 deaths. They were the result of exceptional circumstances very unlikely to be found at or near engineered CO_2 storage sites; the presence of

stratified lakes at considerable elevation compared to much of the surrounding local topography, the presence of a slow CO_2 leak into the bottom of the stratified lakes, the unobserved CO_2 saturation of the lower layer of the lake waters. Any deep lakes that could potentially become stratified in the vicinity of an engineered CO_2 storage site could be easily monitored to prevent such incidents and a "benign gas release" remediation programme, similar to that in place today at Lake Nyos (Halbwachs, 2001), could be implemented.

- Diffuse degassing through the soil on the flanks of volcanoes such as Mount Etna and Mammoth Mountain does not appear to present a hazard to man unless the mixing of the CO_2 with the ambient air is restricted, for example in buildings or hollows in the ground, or very close to the ground surface.
- In hydrothermal areas diffuse degassing of CO_2 is commonplace. There can be significant variations in emissions from vents in such areas at different times. For example, a sudden emission of an (inferred large) mass of CO_2 associated with seismicity recorded in the Cava dei Sielci region of the Alban Hills, Italy, resulted in the deaths of more than 30 animals.
- There is only very sparse CO_2 flux data recorded from sedimentary basins. No records of sudden large emissions of CO_2 from sedimentary basins were found during this study.

Origin of CO_2 in the geosphere

Much of the naturally occurring CO_2 emitted from the geosphere originates from the degassing of magma (molten rock). When magma rises towards the Earth's surface, the pressure on it is lowered. This enables dissolved CO_2 and other gases to come out of solution in the molten rock and accumulate as free gas. Most of the CO_2 originating from magma degassing is emitted through volcanoes and associated fissures, or hydrothermal sites such as the one in Yellowstone National Park in the USA. However, a proportion may travel up deep-seated faults rooted in the lower crust and make its way into sedimentary basins.

The heating and metamorphism of carbonate rocks, such as limestones, most commonly by magmatic intrusions, also produces CO_2. Some high purity carbon dioxide fields found in sedimentary basins are thought to have formed in this way.

CO_2 may also form in the geosphere by the thermal maturation of coal and other organic material. Most of this CO_2 is thought to dissolve in water and eventually precipitate as carbonate cements in the pore spaces of nearby reservoir rocks. CO_2 may also originate from the biodegradation of oil and gas. Under favourable circumstances, microbes living in the pore spaces of sedimentary rocks can feed on oil and gas and their respiration produces CO_2. Some fields of CO_2-rich hydrocarbons are thought to have formed in this way. CO_2 in the geosphere may also originate from the dissolution of limestone and other carbonate rocks.

The ratios of the stable isotopes of carbon (^{12}C, ^{13}C) in CO_2 and the ratios of other gases, such as ^{3}He, to CO_2, can help distinguish the origin of natural CO_2 occurrences. The unstable isotope ^{14}C can be used to distinguish CO_2 of relatively recent origin (up to approximately 50,000 years old) from that formed in the more distant geological past.

The distinction between natural CO_2 emissions and accumulations in volcanic areas and those in sedimentary basins

A distinction can be made between natural CO_2 emissions that occur in volcanic areas and those that occur in sedimentary basins. Volcanic regions and associated hydrothermal areas where natural emissions of CO_2 occur are commonly tectonically unstable, and may be liable to ground heave and fracturing. Moreover, because heat and steam are commonly present they can contain gas under great pressure, commonly in voids. The occasional large sudden emissions of CO_2 that have occurred in volcanic and hydrothermal areas have resulted from the accumulation of CO_2 in underground voids or stratified crater lakes. Active volcanic and hydrothermal areas are therefore unlikely to be selected as sites for engineered CO_2 storage.

By contrast, sedimentary basins are large areas of the Earth's crust which are actively subsiding, or have subsided at some time in the past, allowing thick successions of sediments, and thus eventually sedimentary rocks, to accumulate. They are widely spread around the world and many occur in tectonically stable regions. They commonly contain both porous and permeable reservoir rocks and impermeable or very low permeability cap rocks that can act as natural seals that prevent gases and other buoyant fluids reaching the ground surface or sea bed - this is proved by the presence of oil and natural gas fields in sedimentary basins. In a similar manner, naturally occurring CO_2 may be confined in the pore spaces of sedimentary rocks folded into domes or other structures that do not contain any pathways to the ground surface or seabed (for example the McElmo Dome, Figure 1). In such cases naturally occurring underground CO_2 fields are formed, some of which have existed for millions of years. One example is the natural CO_2 field in the Pisgah Anticline in Mississippi, USA, which is thought to be around 65 million years old. The Pisgah anticline holds over 200 million tonnes of CO_2 and is of comparable size to a putative large engineered CO_2 storage site.

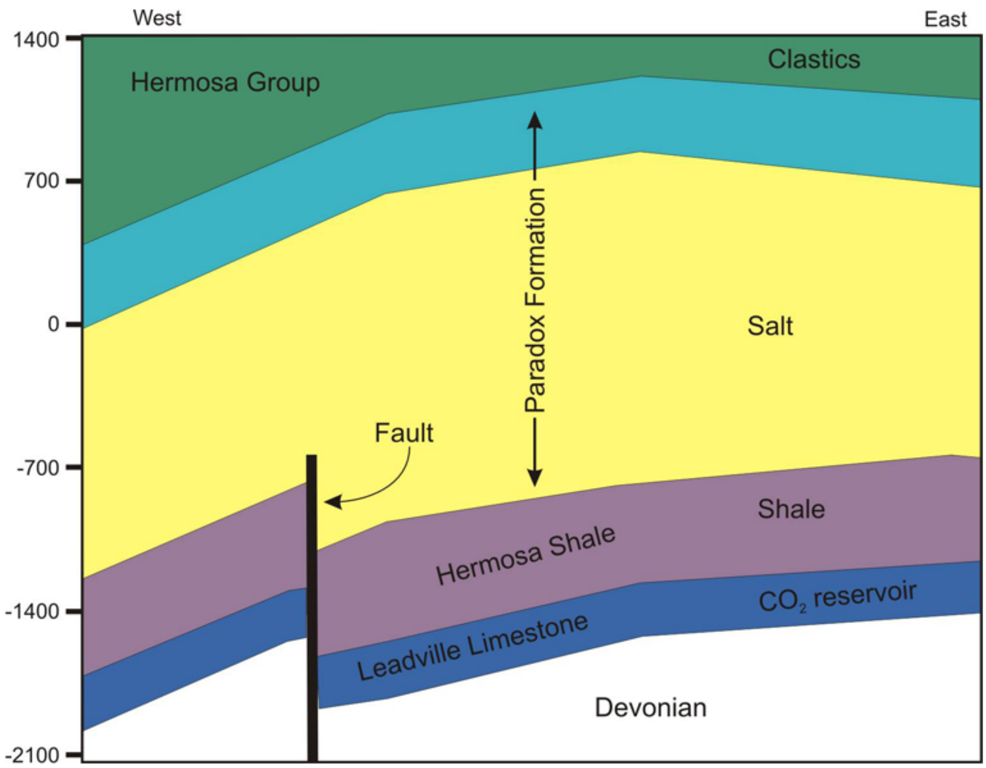

Figure 1. Simplified cross-section from (Stevens et al., 2004) through the McElmo Dome field, showing the CO_2 reservoir (the Leadville limestone) and overlying caprocks. Note that the normal fault has a throw of 100m in the reservoir but that thin overlying shales within the Paradox Fm salt are not displaced, indicating the fault does not penetrate through the salt.

Engineered CO_2 storage sites

Sites for the engineered storage of CO_2 are most likely to be situated in stable sedimentary basins because storage sites will need:

- a reasonable storage capacity provided by sedimentary reservoir rocks

- a cap rock or rocks that will prevent leakage, provided by a sequence of overlying low-permeability seals

The presence of oil and gas fields in many basins indicate that these criteria exist and are commonplace.

Engineered CO_2 storage sites are closely analogous to those natural CO_2 fields that occur in sedimentary basins. They would be sited at carefully selected locations to take advantage of the geological factors that prevent the upwards or lateral migration of CO_2 from the intended storage reservoir towards the ground surface or sea bed.

There are now three man-made CO_2 storage operations designed specifically to prevent CO_2 entering the atmosphere; the Sleipner project in the North Sea, offshore Norway, the In Salah project, central Algeria and the K12-B injection project offshore Netherlands. The Sleipner project started storing CO_2 in 1996 and stores approximately 1 million tonnes of CO_2 per year. It has been closely monitored and no leakage from the storage reservoir has been detected. The In Salah gas fields project in Algeria, began injecting approximately 1.3 million tonnes CO_2 per year in late 2004. This is most unlikely to leak because the CO_2 is injected just below a natural gas field, which by its very presence demonstrates the existence of low-permeability, high quality caprocks. The K12-B project is injecting approximately 30,000 tonnes per year of CO_2 into a compartment of a largely depleted gas field. As this compartment of the field formerly held natural gas it is very unlikely to leak.

Two enhanced oil recovery operations, at Weyburn in Saskatchewan and Rangely, in Colorado, that use CO_2 as an injectant and serendipitously store CO_2 underground, have also been monitored. No leakage has been detected from the Weyburn field, where injection started in 2000. At Rangely, where CO_2 injection started in 1986, there is a deep-sourced flux of up to 3800 tonnes/yr CO_2 into the soil. It is likely that at least part, if not all, of this flux is due to the oxidation of deep-sourced methane originating from the oil reservoir or overlying strata, but part of it could be due to the migration of injected CO_2 from the oil reservoir. Approximately 23 million tonnes CO_2 have been injected into the field since 1986.

Migration of CO_2 in the geosphere

CO_2 is buoyant compared to both rock and the water that is found in the pore spaces of sedimentary rocks. Consequently naturally occurring CO_2 originating at depth in the geosphere tends to migrate upwards towards the Earth's surface. Much of the CO_2 generated in natural systems does not encounter suitable subsurface structures that could trap it and so it is able to migrate both laterally and vertically as a result of its buoyancy compared to the native pore fluids found in sedimentary rock reservoirs. As it migrates, it travels along permeable pathways within the rock succession moving most freely along the most permeable pathways. These pathways may be beds of porous and permeable sedimentary rock, such as sandstone, in which the CO_2 moves predominantly through the connected pore spaces in the rock, and/or fractures and fissures that cut through both permeable and otherwise impermeable or less permeable rocks. Its migration is in many ways analogous to that of natural gas[1] - an example of the migration pathways followed by natural gas is shown in Figure 2.

[1] Natural gas is a term used to describe naturally occurring petroleum gas. This has a variable composition. It usually consists predominantly of methane and lesser amounts of other hydrocarbon gases, but it commonly also contains small amounts of other gases including CO_2. It is sometimes found in fields where it is mixed with CO_2 of, for example, mantle origin. In such cases the proportion of CO_2 may range up to >70%.

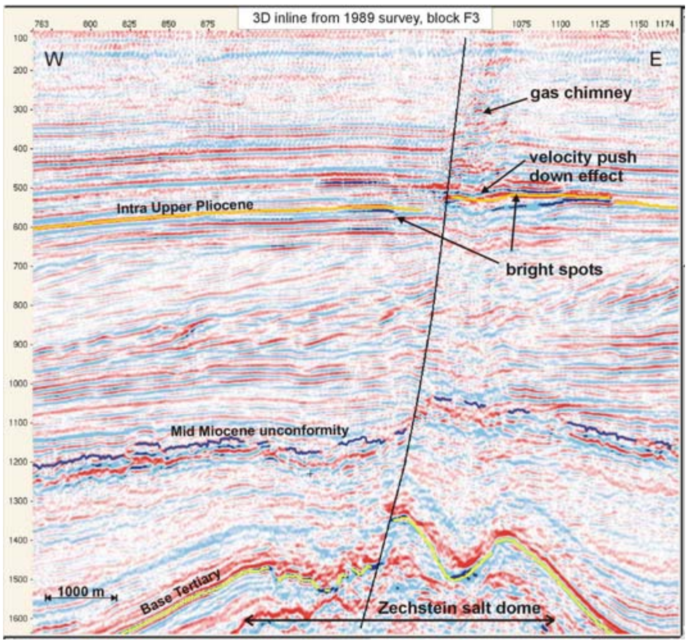

Figure 2. Seismic profile showing reflections indicating that gas is migrating along both permeable layers of sedimentary rock and along faults beneath the southern North sea. The bright spots indicate the likely locations of gas accumulations that have migrated from below the Zechstein salt dome up the fault and then laterally along more permeable beds. The gas chimney is thought to comprise sediment with high gas content through which gas is at least intermittently migrating to the sea bed (from Schroot & Schuttenhelm, 2003, reproduced by kind permission of TNO)

When it permeates through the rocks gas flow tends to be concentrated along any faults or fissures that may be present, or along the outcrop of porous and permeable sedimentary rocks. Most rocks at shallow depths of a few tens of metres or less contain fractures such as joints and faults that are open and highly permeable. Consequently in most natural CO_2 emission sites the CO_2 tends to flow along these fractures, though it does not necessarily escape along the entire length of a fracture or fault; it will tend to emerge at one or more discrete points along it. This is because the permeability of the fault will vary along its length and once ‘breakthrough’ occurs at one point, a channelling effect will occur. At some sites the migrating gas is able to move more easily through the damaged zone of rock immediately adjacent to a fault plane rather than along the fault plane itself, which may often be less permeable if, for example, it is smeared with clay or sealed with mineral precipitates.

In offshore areas the migration of gases through the seabed commonly produces pits called pockmarks (Figure 3) or, where gases emerge along with mud or muddy water, a mound on the sea floor called a mud volcano. Mud volcanoes may also occur onshore.

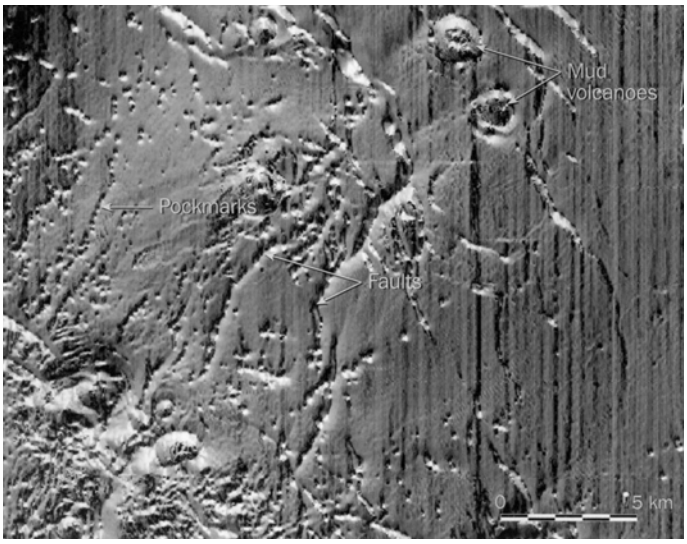

Figure 3. Seismic image showing pock marks and mud volcanoes lined up along faults in the sea bed in the Niger delta, off the coast of Nigeria. The pock marks and mud volcanoes indicate the points where gas and other fluids have emerged at the sea bed. (Reproduced by kind permission of Statoil and Roar Heggland).

CO_2 may emerge at the seabed dissolved in water or as a free gas. If in a free gas phase it may form a train of bubbles that will rise through the water column. Such bubble trains can be detected using sidescan sonar or other high frequency echo-sounding techniques (Figure 4). However, CO_2 bubbles are much more soluble than the commonly detected natural gas bubbles (which usually consist predominantly of methane) and are more likely to dissolve in the water column, unless the emission rate was very high.

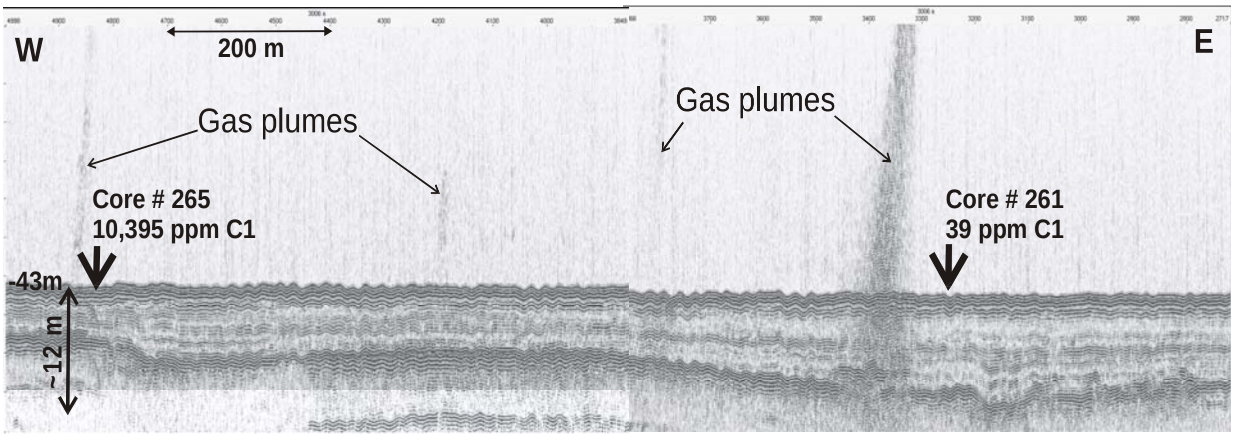

Figure 4. High frequency acoustic profile showing plumes of natural gas bubbles emerging from the sea bed. (Image reproduced by kind permission of TNO).

The dissolution of CO_2 into seawater lowers its pH (increases its acidity). The impact of lowered seawater pH on the marine environment would depend on the flux and the duration of any emissions. It is likely that different ecosystems and water masses will respond differently. Also it is known that some marine organisms are more sensitive to low pH at different stages in their life cycle. Further research and modelling is required to establish potential impacts on marine biota. Examples of natural emissions of CO_2 from the sea bed are found in the Tyrrhenian Sea offshore from the Aeolian Islands in Italy.

In onshore sedimentary basins, migrating CO_2 will pass through two hydrogeological zones on its way to the surface. Most of its passage will be through the lower zone, which encompasses everything beneath the water table. In this zone, the pore spaces, and any fractures found within the rocks, are fully saturated with fluids - in most cases water but, more rarely, oil or gas. This zone is known as the saturated (or phreatic) zone. The upper zone is above the water table and is largely filled with soil gas (air modified by soil processes) and lesser amounts of water. Water percolates through this zone, which is known as the unsaturated (or vadose) zone and commonly comprises the soil and subsoil. Once CO_2 emerges through the saturated zone it will tend to disperse within the vadose zone. It may pool on top of the water table and disperse laterally before emerging at the ground surface, because it is less dense than water but more dense than soil gas. CO_2 saturations can thus become very high in the vadose zone above leak points. This can impact on soil organisms and burrow-dwelling animals, as well as plants. Once the CO_2 reaches the atmosphere, wind or rising air currents eventually disperse and mix it with the ambient air. Typically, CO_2 emerging at the ground surface may be already dispersed in the vadose zone, so that it emerges over a larger area than that of the point of emission from the saturated zone (Figure 5, Figure 6). In many of the examples described in this report such CO_2 anomalies at the ground surface are thought to overlie faults or other fractures in the bedrock.

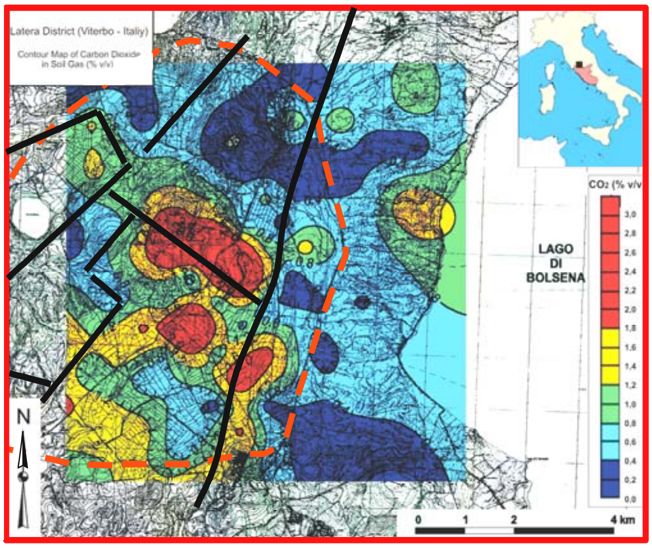

Figure 5. Contoured soil gas data in the western Latera caldera area, Italy. Elevated CO_2 values occur in the areas transected by known faults and where gas vents and mineralised springs occur. (Reproduced by kind permission of the University of Rome).

The other way in which naturally occurring CO_2 typically emerges from the geosphere in onshore sedimentary basins (and also volcanic and hydrothermal areas) is in carbonated springs. These occur when CO_2 has dissolved in the groundwater in the saturated zone. There are many examples of naturally carbonated water springs in France (Perrier, Badoit, Vichy) and elsewhere. These have been used as sources of drinking water for centuries.

CO_2 could also be accidentally emitted from natural or man-made CO_2 storage sites via boreholes. If improperly sealed or poorly cemented to the surrounding strata, these could form man-made pathways directly from the reservoir to the ground surface or sea bed, see Figure 7.

Impacts of natural emissions of CO_2

The impacts of natural CO_2 emissions from underground on the biosphere are highly variable. They depend ultimately on the concentration of CO_2 that builds up in the soil and subsoil, atmosphere, sea bed or sea water. In many cases emissions at the ground surface are not a significant hazard to man because they are dispersed by the wind. However, CO_2 is heavier than air and, if not dispersed, it can be a significant hazard because it is an asphyxiant. Thus the main threat to man from CO_2 emissions from underground is where CO_2 is emitted in situations where it can build up to high concentrations, for example in buildings or in hollows in the ground.

There are examples of natural disasters in volcanic areas caused by sudden emissions of large volumes of CO_2. However, the two worst recorded disasters were both associated with sudden emissions of CO_2 from volcanic crater lakes and are linked to a specific set of geographical features and geological processes that are highly unlikely to occur at or near engineered CO_2 storage sites. Crater lakes are perched at the top of volcanoes and are commonly almost surrounded by high crater walls. The lakes overflow down a spillway leading to a valley system. In tropical areas such lakes may be deep and still and the water column within them can become stratified as there is little seasonal mixing of the lake waters. CO_2 percolating through crater lake floors can dissolve into the lower levels of the lake waters (increasing their density) until they become saturated with respect to CO_2. Once saturated, any disturbance that causes part of the lower lake waters to rise could cause CO_2 to come out of solution. In 1984, a large release of volcanic CO_2 thought to have accumulated in this way was caused by the sudden overturn of Lake Monoun (a volcanic crater lake in Cameroon, West Africa). The released CO_2 moved out of the crater and hung in a depression along a nearby river course where it asphyxiated 37 people. A similar but worse incident occurred at nearby Lake Nyos in 1986. Following sudden overturn of the lake waters, the cold CO_2 was confined by the crater walls and migrated down the lake spillway into a valley. It travelled along the valley, hugging the ground, asphyxiating 1700 people in a thinly populated area and extinguishing all animal life for more than 14 km along its course. It should be emphasised that this kind of disaster can only occur where there are deep lakes that could become stratified; seasonally overturning lakes such as those commonly found in temperate regions pose much less danger. Moreover, the disasters were exacerbated by the fact that the lakes are perched at the top of valleys, which naturally confined the CO_2. If deep lakes that could potentially become stratified were found to be present at or near an engineered CO_2 storage site, this type of incident could be avoided by monitoring such lakes for the build-up of CO_2, as is now done at Lake Nyos. If a build-up is detected the lake can be remediated by installing simple gas-lift equipment. This has been successfully undertaken at Lake Nyos, to prevent a repeat of the 1986 disaster. However, it is worth noting that any CO_2 emerging at a lake surface may pool immediately above the water and pose a threat to swimmers.

There have also been numerous incidents in volcanic and hydrothermal areas in which the asphyxiation of animals can be attributed to CO_2 emissions. Deleterious effects on plants are also well documented in volcanic and hydrothermal areas, particularly at Mammoth Mountain, California, where large tree kills have occurred, caused by CO_2 migrating upwards from the geosphere into the soil.

Figure 6. Tree kill on the shore of Horseshoe Lake, Mammoth Mountain, California, caused by CO_2 emerging through the ground. (Photo John Rogie).

Figure 7. Small lake created as a result of the upwards migration of naturally occurring CO_2 outside the casing of a mineral water exploration well drilled in the Florina area of Greece. (Photo reproduced by kind permission of IGME).

The hazards posed by recorded natural CO_2 emissions in sedimentary basins are not on the same scale as those posed by the large sudden releases that have been recorded in volcanic and hydrothermal regions. In some areas, e.g. the Paradox Basin of the USA, the French carbogaseous area, and the Eifel region of Germany, such emissions appear to pose, at most, only very local hazards.

Putative emissions from engineered CO_2 storage sites

Fluxes to the biosphere that might be expected from man-made CO_2 storage sites can only be considered on a case-by-case basis, because the subsurface is an extremely variable natural system and each site will be geologically unique. For this reason, engineered CO_2 storage sites will be subject to a regulatory process that, prior to injection of any CO_2, is likely to include: detailed characterisation of the storage site and surrounding area, the construction of geological models of the site and surrounding area, the simulation of CO_2 injection into the storage reservoir, and risk assessment based on the site characterisation, models and simulation. If potential for leakage is identified a remediation plan may be required. During CO_2 injection, monitoring of the subsurface and ground surface or sea bed and history matching of the monitoring results with the models, to provide feedback to improve the understanding of the site, will take place. Agreement between the modelled and observed results, allowing reliable extrapolation of CO_2 behaviour into the future, will likely be required before the site is closed.

Emissions at monitored man-made CO_2 storage sites and enhanced oil recovery projects to date are either non-existent or very low (Figure 8). However, it should be borne in mind that the oldest monitored site (Rangely) has been injecting CO_2 for less than 20 years. It is considered that once injection has ended, the stability of storage of CO_2 in engineered storage sites is likely to increase rather than decrease through time. This is because reservoir pore fluid pressure is likely to be greatest during the injection period and gradually fall off after injection has ended. Enhanced pore fluid pressure is an important factor driving the migration of both free and dissolved CO_2. Geomechanical stress will also decrease as pore fluid pressure decreases. Moreover, forward modelling of certain sites, including Sleipner, suggests that as time progresses, more and more CO_2 will dissolve into the surrounding pore fluid. The resulting CO_2-saturated pore fluid is slightly denser than the native pore fluid and will tend to sink through the pore system of the reservoir rock, migrating downwards rather than upwards, greatly decreasing the chances of it reaching the biosphere.

Natural CO_2 fields and oil and gas fields give assurance that in suitable locations CO_2 can be stored in the subsurface for millions of years - far longer than CO_2 is likely to be stored in soils or trees. The widespread distribution of these fields indicates that these circumstances are relatively commonplace. The intensive search for, and development of, oil and gas resources that has taken place over the last century has resulted in a huge body of information about the world's major sedimentary basins, the rocks they contain and the oil and gas fields (including natural CO_2 fields) within them. There is every reason to suppose that this knowledge and the accompanying technology that has been developed to find and exploit these resources will enable the safe long term storage of carbon dioxide in the subsurface.

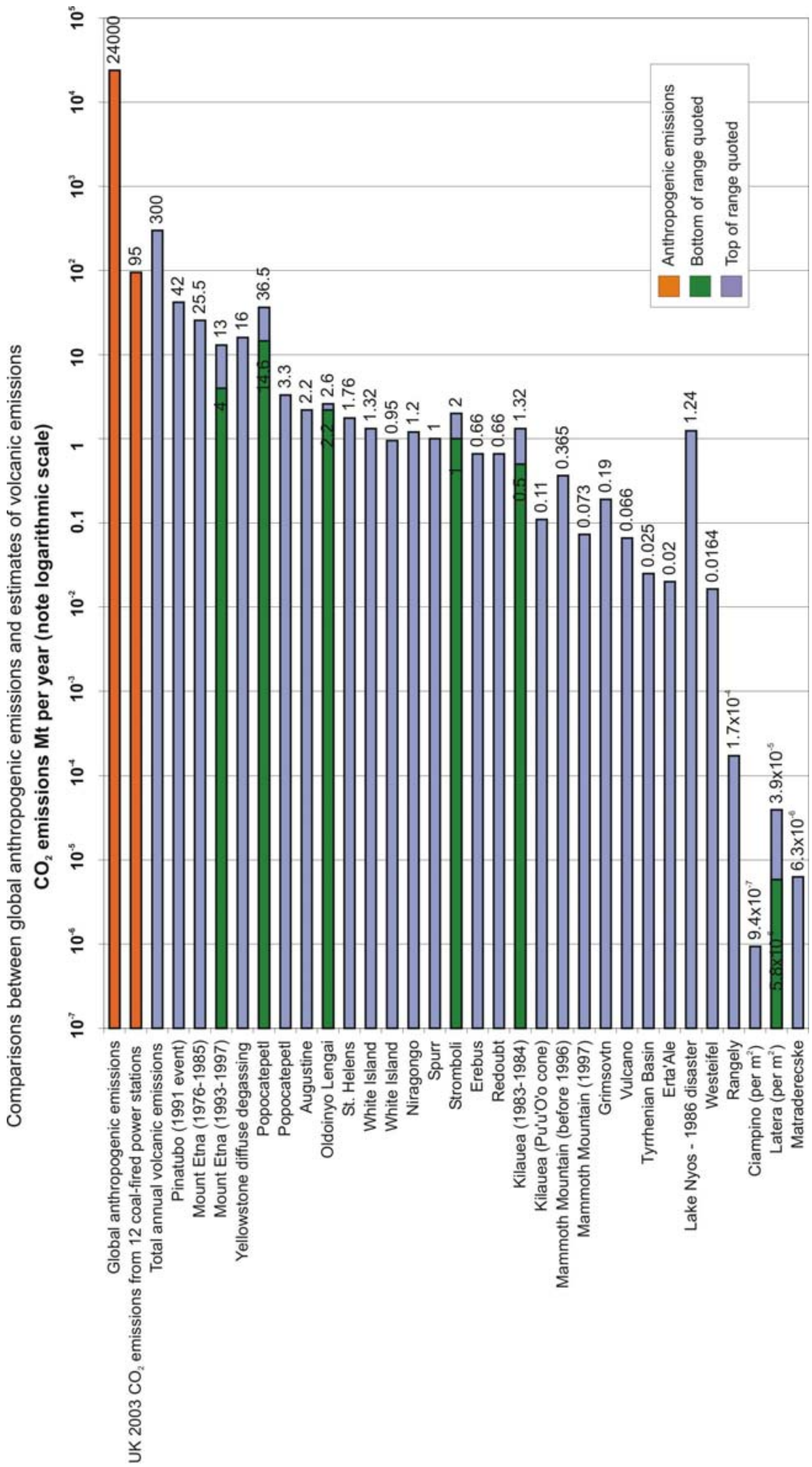

Figure 8. Comparison of CO_2 emissions from volcanoes, moffettes and other natural sources compared with anthropogenic emissions.

1 Introduction

If carbon dioxide capture and storage becomes a large-scale, widely deployed technology, concerns that emissions of CO_2 from man-made underground storage sites could have a deleterious effect on the natural environment and/or be harmful to man must be addressed.

This report addresses these concerns by describing the following:

- The origin of CO_2 emitted from underground
- The major types of natural CO_2 emissions that occur from the geosphere (the solid part of the planet beneath the atmosphere and oceans) by means of detailed case-studies
- Some of the man-made CO_2 storage projects under way around the world.

In the final chapter we assess the relevance of natural CO_2 emissions to man-made storage sites by comparing natural CO_2 emissions with putative emissions from engineered geological CO_2 storage sites.

1.1 ORIGIN OF CARBON DIOXIDE EMITTED FROM UNDERGROUND

There are many processes that can generate significant quantities of CO_2 in the geosphere (Imbus et al., 1998; Wycherley et al., 1999). The most important are:

1. Degassing of magma
2. Contact metamorphism of carbonate rocks
3. Thermal maturation of type III (coaly) kerogen and coals
4. Biogenic breakdown of oil and gas
5. Regional metamorphism of carbonate rocks
6. Dissolution of carbonate rocks

Of these, the degassing of magma and contact metamorphism of carbonate rocks appear to be by far the most important in creating natural emissions of CO_2 from underground.

1.1.1 Degassing of Magma

The degassing of magma (molten rock) commonly releases large volumes of CO_2. Magma degasses because of the pressure reduction that occurs when it rises towards the Earth's surface. The degassing of magma is commonly associated with volcanic activity or intrusion of molten rock into the crust. Volcanic activity (volcanism) can occur at any point on Earth where pressure/temperature conditions are such as to allow at least partial melting of the upper mantle or crust (Figure 9). However, most volcanism occurs at constructive and destructive plate margins.

Constructive plate margins are places where the Earth's tectonic plates are being pulled apart and new mantle material passively upwells to fill the void thus created. They are also described as spreading centres and usually correspond to the mid-ocean ridges.

Destructive plate margins are places where one tectonic plate is being subducted (dragged or pushed down) beneath another. The surface expression is termed a "subduction zone". It is commonly characterised by a deep ocean trench and a chain of volcanoes that may occur some 250 km into the over-riding plate. The volcanoes either form island chains in oceanic settings (e.g. the lesser Antilles) or mountain ranges (e.g. the Andes) on the continents. Subduction results in the destruction of the leading edge of the under-riding plate as it is re-absorbed into the mantle (Figure 9).

Volcanism also occurs at apparently random locations, sometimes at great distance from plate margins. This is referred to as *intraplate* or *hotspot* volcanism. Hot spots are generally accepted to be the surface manifestation of plumes of up-welling hot, buoyant material from the core-mantle boundary (Figure 9).

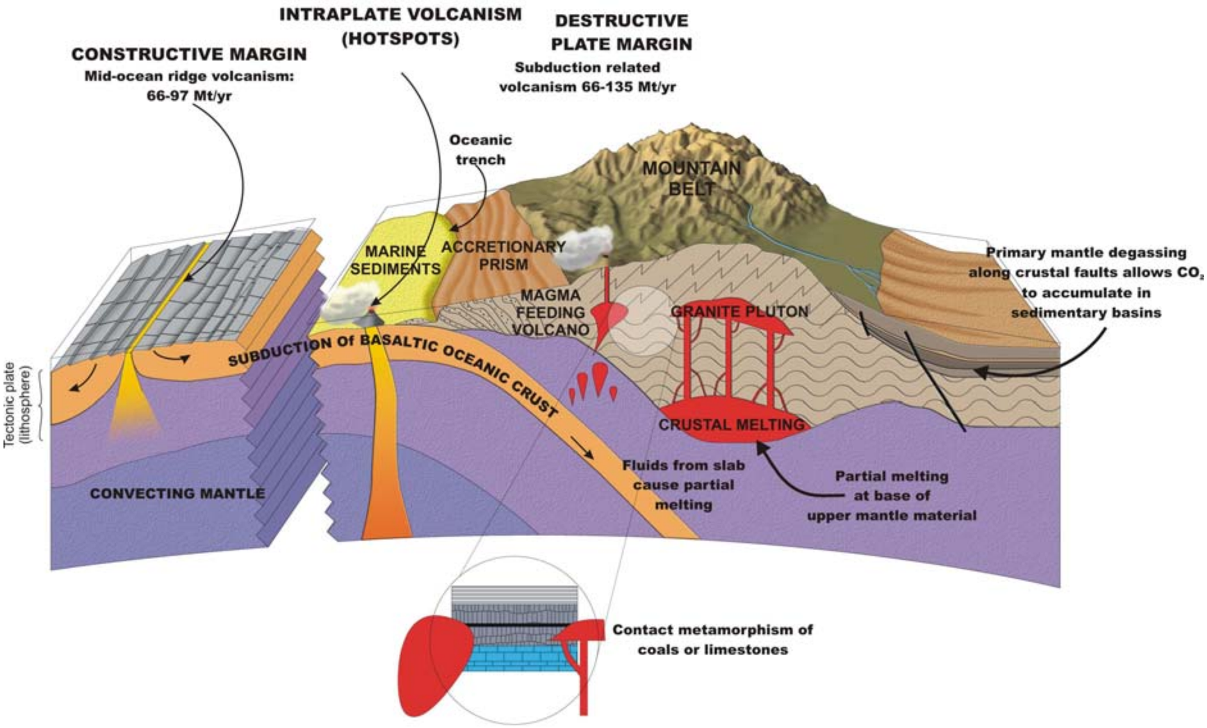

Figure 9. Diagram illustrating the relationship between plate tectonics, volcanism and the generation of carbon dioxide by contact metamorphism of carbonate rocks and coals. Fluxes of carbon dioxide from the different types of volcanism are shown.

1.1.1.1 COMPOSITION OF GASEOUS EMISSIONS FROM VOLCANOES

H_2O (in the form of water vapour) is the dominant gas emitted by volcanoes. It normally makes up more than 60% of the total gas content. CO_2 is the second most abundant gas, typically making up 10-40% of the total gas content. Other typical components are SO_2, H_2S, HCl, CO and COS. The actual gas composition at a given volcanic site is highly variable depending on tectonic setting and magma type.

1.1.1.2 MID-OCEAN RIDGE VOLCANISM

At the mid-ocean ridges the ductile mantle material upwells passively into the void created as the tectonic plates part (Figure 9). As it rises, the mantle material undergoes partial melting in response to decompression, and most volatile phases (including CO_2) enter into the molten rock. This then degasses as it rises, erupts at the surface, and solidifies to form new oceanic crust. Thus the CO_2 given off at mid-ocean ridges is derived from almost pure mantle material.

CO_2 emitted from a mid-ocean ridge has no relevance to man-made CO_2 storage sites, which will be sited in sedimentary basins. The mid-ocean ridges are dramatically different geological environments from such sedimentary basins.

1.1.1.3 VOLCANISM AT CONVERGENT PLATE MARGINS

At convergent plate margins, volcanism results from melting of the mantle due to its hydration by volatiles (H_2O, CO_2, etc.) released from the subducted tectonic plate - the melting point of the overlying mantle material is reduced by the increased volatile content. The pressure/ temperature-dependent breakdown of hydrous minerals in the subducted lithospheric material as it descends is commonly invoked to explain the release of volatiles. The subducted lithospheric slab may contain large amounts of carbon in the form of limestones or other sedimentary rocks and seabed sediments. In fact, the current consensus is that most of the total CO_2 flux from the geosphere results from recycling of crustal carbon into the mantle at convergent plate margins and then back to the surface via volcanoes.

Much greater variation is seen in the composition of volcanic emissions at convergent plate margins compared to those at mid-ocean ridges, indicating that the CO_2 is produced from variable mixtures of crustal rocks - probably sourced from the subducted slab. Subduction zone emissions show very high CO_2:He ratios (3-15 times those at divergent plate or hotspot settings) and the excess CO_2 is attributed to input from the subducted slab. Carbon isotope data indicate that, on average, more than 80% of arc volcanic CO_2 is recycled from the lithosphere (Varekamp et al., 1992) although this can reach more than 90% where two arcs collide (Jaffe et al., 2004). The remainder is derived from the mantle (Sano and Marty, 1995).

1.1.1.4 Estimates of the carbon flux from volcanoes

Volcanoes do not emit substantial amounts of CO_2 into the seabed or atmosphere. On average about 300 Mt CO_2 are emitted to the atmosphere annually (Morner & Etiope, 2002). For comparison, global anthropogenic CO_2 emissions are about 24,000 Mt CO_2 each year or more than 80 times volcanic emissions.

Mt Etna is usually considered to be the most actively degassing volcano. It emits about 25 Mt of CO_2 per year (Allard et al., 1991). Its large emissions have been attributed to the calcination of limestones and dolomite from the carbonate platform on which Etna lies, and the alkaline nature of the magma (Gerlach, 1991). However, recent estimates suggest Popocatepetl (Mexico) may emit up to 36.5 Mt per year CO_2 (Morner & Etiope, 2002). More typically, active volcanoes emit about 0.1 to 2.0 Mt CO_2 per year.

Recently it has been recognised that non-eruptive diffuse degassing, rather than gas release during major eruptions, may be the principle mode of gas release from volcanoes. Diffuse emissions of CO_2 are known to be large around some volcanoes and associated hydrothermal areas (Evans et al., 2001). For example, surface measurements suggest that 16 ± 0.6 Mt per year CO_2 are released from the Yellowstone hydrothermal area by diffuse degassing (Werner and Brantley, 2003).

1.1.1.5 CO_2 thought to be derived from the mantle but not associated with volcanic activity or magmatic intrusions

CO_2 thought to be derived from the mantle also occurs where there is apparently no volcanic activity (Wycherley, et al., 1999). This is thought to penetrate into sedimentary basins via deep seated faults that cut through the base of the crust. Though known examples are relatively rare, such accumulations may be more widespread.

1.1.2 Contact Metamorphism of Carbonate Rocks

Not all the magma, formed by partial melting of the crust or upper mantle, emerges at the surface. Some penetrates to higher levels in the continental crust where it intrudes into sedimentary rocks and crystallises as plutons (large masses of igneous rock), or dykes and sills - relatively thin sheets of igneous rock that respectively cross-cut, or lie parallel to, the bedding of sedimentary rocks (Figure 9). The intrusion heats up and metamorphoses a zone of the surrounding sedimentary rocks, a process called contact metamorphism because it results from contact between the igneous body and the surrounding rocks. If carbonate rocks, such as limestone, undergo contact metamorphism, they may metamorphose into oxides or hydroxides and give off CO_2, a process directly analogous to the calcination of limestone in cement manufacture. However, isotopic analysis of the carbon in some CO2 accumulations formerly thought to have originated by contact metamorphism now suggests that they may have originated fro CO_2 the degassing of the intruded magma itself (see Section 2.2). Some of the largest pure accumulations of CO_2 in sedimentary basins are thought to have originated in this way.

1.1.3 Regional Metamorphism of Carbonate Rocks

Regional metamorphism affects broad areas of the crust, such as places where plates once collided and mountain belts formed (Figure 9). It results from the burial of rocks to sufficient depths within the Earth for the temperature and pressure to change their mineral composition. It has been suggested that regional metamorphism of limestones could result in the generation of CO_2 in a similar manner to contact metamorphism. Natural occurrences of CO_2 in the Békès Basin, a sub-basin of the Pannonian Basin in Hungary, may have originated in this way (Clayton et al., 1990).

1.1.4 Maturation of Type III (Coaly) kerogen

Kerogens are organic chemical compounds generated from the plant and animal organic matter that becomes incorporated in sediments. They can be divided into types depending on the source from which the majority of the kerogen was derived:

- Type I algal kerogen - mostly derived from algae
- Type II liptinitic kerogen - mostly derived from plankton, some derived from algae
- Type III humic kerogen - mostly derived from higher (land) plants

Rocks with high concentrations of kerogen are known as petroleum source rocks. Most source rocks are mudstones and shales that contain a few percent of finely dispersed kerogen. However some source rocks, known as oil shales, may contain significantly more kerogen. As kerogen-rich rocks become more deeply buried beneath other strata in actively subsiding sedimentary basins, they are converted into other compounds by the increasing heat and pressure, a process known as maturation. During this process they give off volatiles such as water, methane, CO_2 and the compounds that make up crude oil. Type III kerogens are gas-prone, meaning that they give off predominantly methane rather than the higher hydrocarbons that make up crude oil.

As maturation progresses, the carbon content of the kerogen increases because there is a proportionally greater loss of hydrogen and oxygen than carbon. Most of the hydrogen is lost by demethylation - loss of methane. The oxygen is lost by a combination of dehydroxylation (loss of water) and decarboxylation (loss of carbon dioxide). The mass of carbon dioxide generated from maturation of large volumes of gas-prone source rock can be considerable. However, this does not mean it is typically significant as a component of natural gas. This is because it is more soluble than methane and much of it probably dissolves in the water expelled from the rocks during maturation and is fixed within nearby reservoir rocks as carbonate cement.

Thus, whilst significant quantities of CO_2 are generated from normal maturation of Type III kerogen, the resulting CO_2 either reacts with porewaters and minerals to produce carbonate cements or is trapped as a small component of natural gas. Therefore, it is of limited interest as an analogue for potential CO_2 emissions from man-made CO_2 storage sites, which would store relatively pure CO_2.

1.1.5 Biodegradation of hydrocarbons

CO_2 may also be formed by the biodegradation of oil and gas. For example, oil that is leaking from a salt diapir in the Central North Sea is biodegrading as it migrates upwards and converted to CO_2 (Cody et al., 1999; Clayton et al., 1997). CO_2 concentrations can reach 100% at certain intervals above the hydrocarbon source. $\delta^{13}C_{CO_2}$ values (see Section 1.2 below) vary between –

43.9 to –34‰, which is indicative of biodegradation processes. Pallasser (2000) also identifies this process as being responsible for the production of CO_2 ($\delta^{13}C_{CO_2}$ values up to +19‰) in natural gases from the North West Shelf, and the Gippsland and Otway Basins, in Australia.

1.1.6 Maturation and Metamorphism of Coals

Coal is an almost entirely organic material. It is derived from peat, by a process known as coalification or maturation. As the peat is buried it undergoes a very similar process to the maturation of Type III kerogen, and becomes converted first into lignite, then with increasing temperature and pressure into bituminous coal and then anthracite.

An example of elevated CO_2 concentrations resulting form decarboxylation of coal has been described in the Taranaki Basin, New Zealand (Killops et al., 1996). CO_2 concentrations can reach 40% in the onshore Kapuni field, compared with less than 14% in the offshore Maui field (McBeath, 1977). Isotopic evidence (See Section 1.2 below for an explanation) suggests that the source of CO_2 is crustal rather than mantle (Giggenbach, 1993). In addition, the hydrogen and carbon isotopic compositions for CH_4 and CO_2 also point to the thermogenic breakdown of organic matter: for the Kapuni field $\delta^{13}C_{CO_2}$ = -14.5‰ and for the McvKee field $\delta^{13}C_{CO_2}$ = -16.2‰ (Hulston et al., 2001; Lyon, 1989). However, high $^3He/^4He$ ratios in an offshore seep may also suggest that some mantle gases are reaching the surface (Giggenbach, 1993). The $\delta^{13}C_{CO_2}$ values for the Maui field (–10.7‰) may also be indicative of a mantle origin. The highest CO_2 levels occur in Eocene sandstone reservoirs and are associated with the main coal units. During coal evolution, from lignite through to early high-volatile bituminous coal stages, the main volatiles are CO_2 and H_2O (Boudou et al., 1984). Relatively high heat flow in the Taranaki Basin (Armstrong et al., 1996) may account for the large amounts of CO_2 being generated from the vertically adjacent coals. This may have implications for similar Tertiary basins with relatively high heat flows throughout southeast Asia.

1.2 IDENTIFYING THE SOURCE OF NATURALLY OCCURRING CO_2 IN THE GEOSPHERE USING CARBON ISOTOPES

A CO_2 molecule comprises one carbon atom and two oxygen atoms, and can have different molecular weights as a result of the presence of one of the two stable carbon isotopes and/or one of the three stable isotopes of oxygen. The most common configurations of CO_2 are:

$^{12}C^{16}O^{16}O$ - this is by far the most common molecule and has a molecular weight of approximately 44
$^{13}C^{16}O^{16}O$ - this has a molecular weight of approximately 45
$^{12}C^{18}O^{16}O$ - this has a molecular weight of approximately 46

Further combinations of carbon and oxygen isotopes are possible, but extremely rare in nature. Carbon isotope data from CO_2 are usually expressed relative to the PDB standard which has been chosen as a standard for historical reasons. The PDB standard is the ratio of ^{12}C to ^{13}C in parts per thousand compared to those found in carbon in the belemnite *Belemnitella americana* from the Late Cretaceous PeeDee Formation in South Carolina (hence PeeDee Belemnite - PDB). The unit used to express this is $\delta^{13}C_{CO_2}$ PDB, values are quoted in ‰ ('per mil'). Negative values contain less than the standard and positive values contain more. The range of $\delta^{13}C_{CO_2}$ PDB values found in a sample of CO_2 can help distinguish its origin (Figure 10).

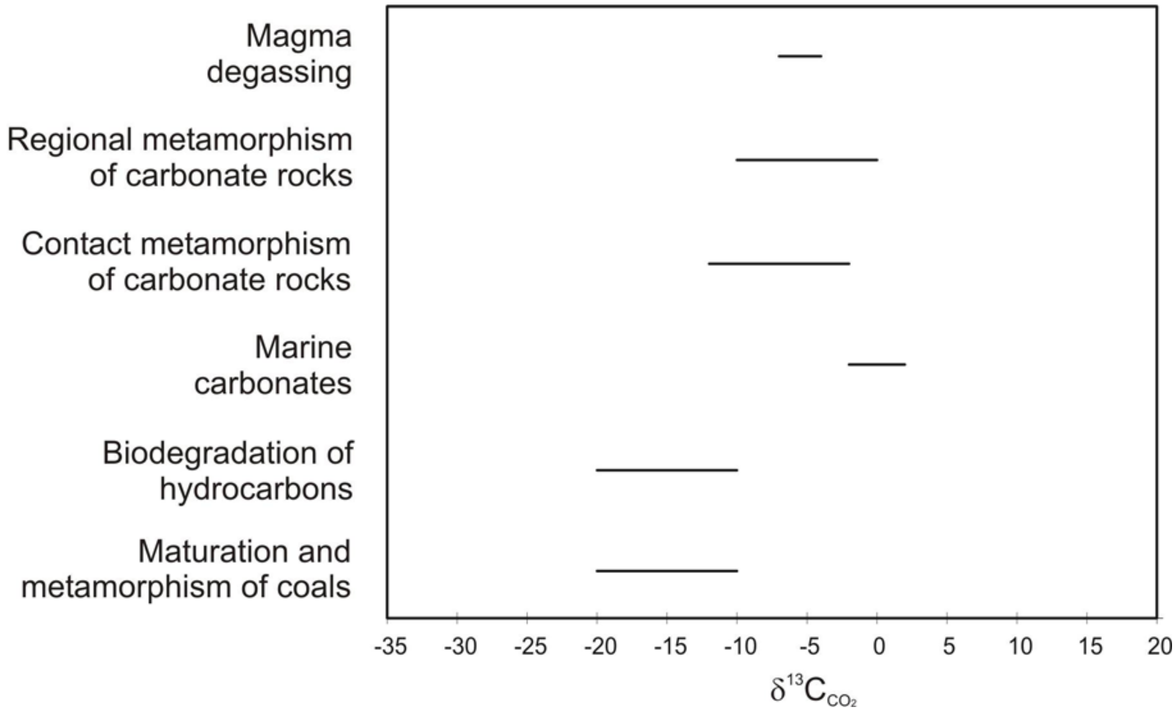

Figure 10. The range of $\delta^{13}C_{CO_2}$ values expected in CO_2 derived from different geological processes. Note that there is little overlap between the $\delta^{13}C_{CO_2}$ values for CO_2 with a biogenic origin (that derived from coal, kerogen and biogenic decay) and CO_2 with a thermal or magmatic origin (derived from magma degassing, or metamorphism of limestones).

As well as stable carbon isotopes, the unstable radiaoactive isotope of carbon, ^{14}C, can help identify the source of CO_2. It is continually being created in the Earth's atmosphere at what is thought to be a constant rate and is incorporated into carbon compounds in living organisms. It has a half-life of 5730 years and can be used to date material less than 50,000 - 100,000 years old. The presence of significant amounts of ^{14}C in CO_2 would indicate that it has a relatively recent origin. This could be useful in monitoring man-made CO_2 storage sites because it can help distinguish ‘old’ CO_2 generated from fossil fuels and stored by man at depth, from biogenic ‘young’ CO_2 generated within the soil.

2 CO_2 Emissions and CO_2 Fields in Sedimentary Basins

2.1 INTRODUCTION

Sedimentary basins are the favoured sites for man-made CO_2 storage projects. They are (large) areas of the Earth's crust which are actively subsiding, or have at some time in the past subsided, allowing considerable thicknesses of sediments, and thus eventually sedimentary rocks, to accumulate in them. These rocks are typically fine-grained types such as mudstones and siltstones, coarse-grained types such as sandstones and conglomerates, carbonate rocks such as limestones and dolomites, evaporitic rocks such as halite (rock salt) and anhydrite (calcium sulphate) and biogenic rocks such as coal. Other types of rocks, in particular igneous intrusions, may also occur in sedimentary basins.

Both natural CO_2 accumulations and CO_2 emissions to the ground surface are found in sedimentary basins; some of the former have been preserved underground for millions of years. These natural emissions of CO_2 in sedimentary basins probably provide the closest analogy to putative emissions of CO_2 from man-made CO_2 storage sites because they occur in similar geological settings.

Four examples are described below. The Colorado Plateau is particularly interesting because it contains both major CO_2 fields and areas where CO_2 is leaking from underground to the ground surface. The French carbogaseous region is a good example of an area characterized by many carbonated springs and minor CO_2 fields. The Pisgah Anticline is an example of a very long-lived CO_2 field. The Florina field provides an example where there was a CO_2 leak around the outside of the well casing.

A recurring theme is that CO_2 emissions to surface are associated with faults, carbonated springs and abandoned boreholes.

2.2 THE COLORADO PLATEAU, USA

2.2.1 The Region

The present day Colorado Plateau covers an area of approximately 360,000 km^2. It extends over large parts of Utah and Arizona, and the western parts of New Mexico and Colorado. It is an area of relatively undeformed rocks surrounded by the highly deformed Rocky Mountain and Basin and Range provinces.

For about the last 5 million years (since Pliocene times), the mid-continent region has been rising, with more than 1600 m of vertical crustal uplift of the entire southern Rocky Mountains and Colorado Plateau regions. Rivers have incised deep canyons, and massive erosion of the landscape has taken place. Soft sedimentary strata were washed away leaving more resistant rocks to form the plateaus, buttes, peaks and ridges of the modern landscape.

2.2.2 The Paradox Basin

The Paradox Basin is one of the Late Carboniferous-Permian sedimentary basins found on the Colorado Plateau. It is located in southern Colorado and Utah (Figure 11), and contains examples both of places where natural CO_2 has been trapped for geological timescales and also locations where natural CO_2 is actively leaking to the land surface.

The Paradox Basin covers approximately 190 × 265 km and is confined on all sides by various uplifted structural highs that developed during Pennsylvanian (Late Carboniferous) to Permian times. To the northeast, the basin is bounded by the Uncompahgre Plateau, composed of granitic rocks and metamorphic pre-Cambrian basement, and to the east by the San Juan Dome, which is partially covered by Tertiary volcanics. The basin is defined by the extent of salt in the (Middle Pennsylvanian) Paradox Formation (Nuccio and Condon, 1996).

It has been structurally deformed (folded and faulted) at various times, with the most recent and significant deformation occurring during the Late Cretaceous to Early Tertiary Laramide orogeny.

The northern part of the basin consists of roughly parallel, northwest-trending faults and folds (Nuccio and Condon, 1996). The northernmost area, where the Crystal Geyser and associated CO_2-rich springs occur, is more complexly folded with some anticlines pierced by underlying salt. Dissolution of this salt has caused downfaulting and graben development along the anticlinal crests. In the south the Blanding sub-basin contains the McElmo Dome natural CO_2 field. This is an undeformed area, with Jurassic and Cretaceous rocks cropping out at the surface. The Paradox Basin is separated from the San Juan Basin by the Four Corners platform, which also has Cretaceous rocks cropping out at the surface (Figure 11).

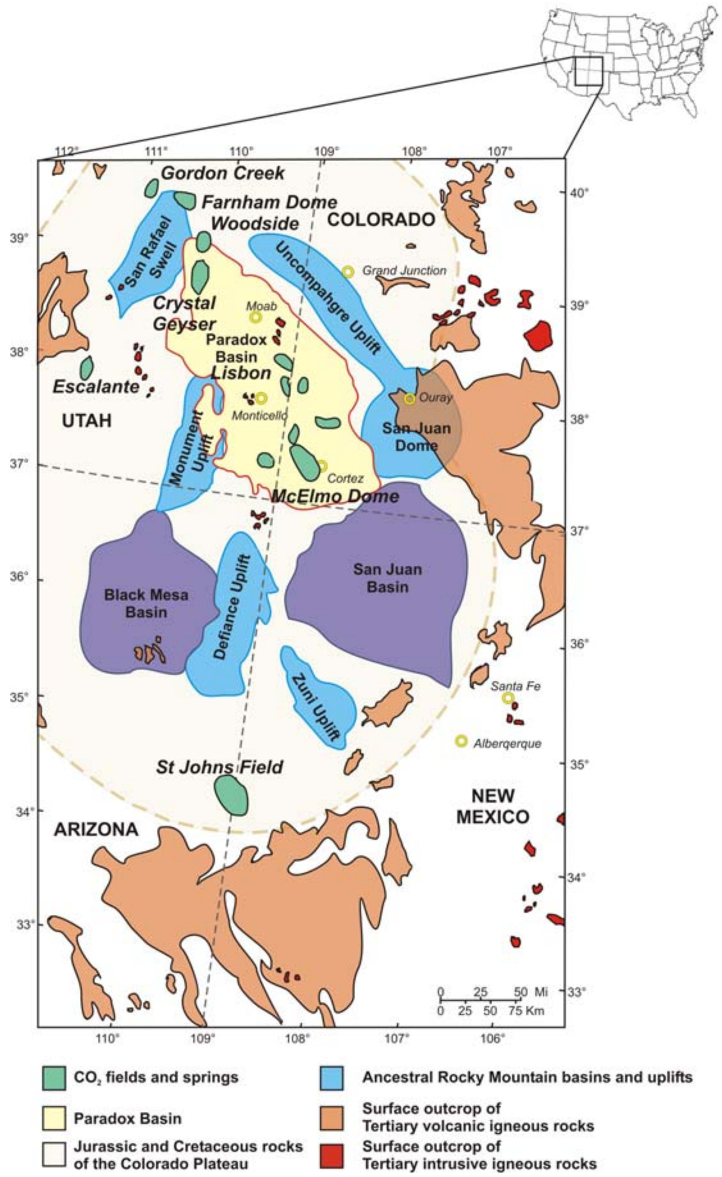

Figure 11. Simplified geology of Colorado Plateau and adjacent areas showing locations of major CO_2 accumulations and areas of leaking CO_2. Based on (Allis et al., 2001); USGS 1:2500000 US Geology (1974) and (Baars, 1972).

2.2.2.1 Distribution of CO_2 occurrences in the Paradox Basin

CO_2 occurrences are common in the Colorado Plateau (Table 2.1) and in particular in the Paradox Basin and adjacent areas. The Mississippian (Early Carboniferous) Leadville Limestone (Figure 12) is the main reservoir rock for the CO_2 fields found in the basin. Commercially exploited fields contain from 28 to 2800 billion m^3 (2.8×10^{10} to 2.8×10^{12} m^3) of CO_2 (Allis et al., 2001). These occurrences have been studied in recent years both for their economic potential, as a relatively cheap source of CO_2 for enhanced oil recovery and industrial applications, (e.g. Cappa and Rice, 1995), and as analogues for both CO_2 storage (Allis et al., 2001; Stevens et al., 2004) and leakage (Dockrill et al., in press; Shipton et al., 2005).

Table 2.1. Summary of data in (Allis et al., 2001) and references therein for various CO_2 accumulations in the Colorado Plateau province.

Name	Depth	Reservoir	Seal	Gas composition					Porosity	Permeability	Reference
	m			CO_2	N_2	O_2	HC	others	%	mD	
Farnham Dome, Utah	900	Jurassic Navajo Sandstone	Moenkopi interbedded shale & siltstone	98.9	0.9	0.2	0		12	> 100	(Morgan and Chidsey, 1991)
Gordon Creek, Utah	3900	Permian White Rim Sandstone	Permian Black Box Dolomite	98.82	1.03	0.01	0.14		8-12	?	(Allis et al., 2001) and references therein.
	3340	Sinbad limestone of Triassic Moenkopi Fm.	Torrey Member of the Moenkopi Fm.	99.5		0.01	CH_4 0.1 C_2H_6 0.1 C_nH_n 0.1	Trace He Trace Ar		?	
Escalante, Utah	960	Permian Cedar Mesa Sandstone	Permian Organ Rock Fm. shale	96.1-93.1	2-5.5	0-0.2	CH_4 0.4 -0.7 C_2H_6 0.2 C_nH_n 0.1	Ar 0.1 He 0.1-0.3 H_2 0-0.4	12-16	?	(Allis et al., 2001) and references therein.
	787	Dolomite & interbedded sandstone and shale, Permian Toroweap Fm.	Shale & carbonates, Permian Toroweap Fm	As above					6-8		
	787	Permian White Rim Sandstone	Permian Kaibab Limestone (dolomite)	As above					6-8		
	720	Limestone and dolomite of Timpoweap member of Moenkopi Formation	Permian Kaibab Limestone	As above					6-8		
	691	Limestone & dolomite of Timoweap Member of Triassic Moenkopi Fm.	Shale of upper Moenkopi Fm.	As above					4-5		
	418	Coarse sandstone of Shinarump Member of Triassic Chinle Fm.	Shale of upper Chinle Fm.	As above					4-8		
McElmo Dome, Colorado	2100	Mississippian Leadville Limestone	Paradox Salt	98.2	1.6		CH_4 0.2		3-20	23-200	Allis, et al., 2001; Stevens & Tye, 2004

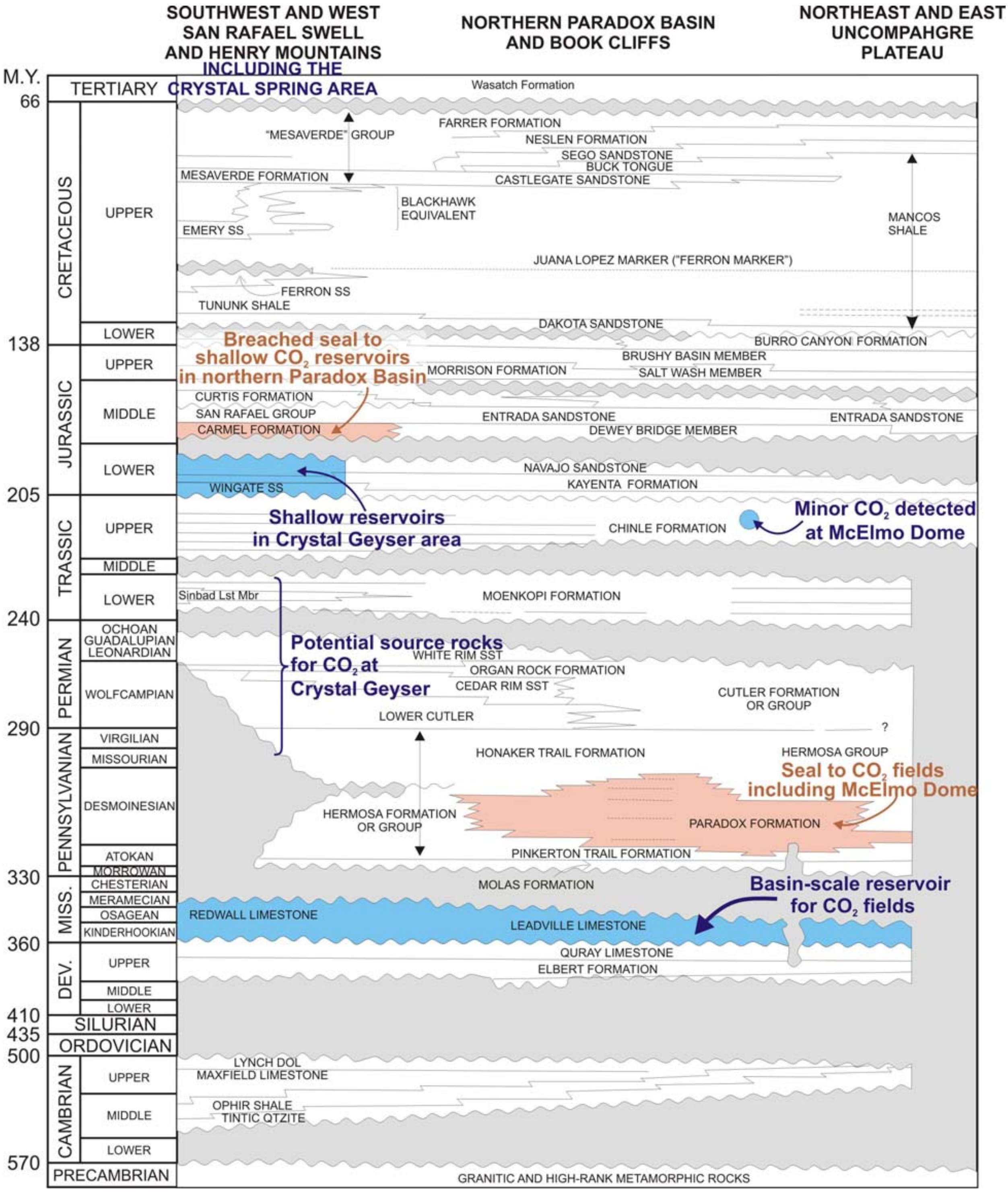

Figure 12. Simplified correlation chart from Nuccio and Condon (1996), showing both reservoirs and seals for CO_2 accumulations in the Paradox Basin.

2.2.3 McElmo Dome natural CO_2 field in the Paradox Basin

The McElmo Dome and nearby Doe Canyon natural CO_2 fields are located in the southeastern Paradox Basin in southwest Colorado (Figure 11). These fields have been studied in detail by Stevens et al. (2004) and the following description is a summary largely based on their work. McElmo Dome supplies ~14 Mt of CO_2 per year to enhanced oil recovery projects in the Permian Basin, Texas, accounting for approximately 70% of CO_2 supplied to the province. CO_2 was discovered in 1948 with further exploration and production expanding in the mid 1970s to early 1980s, when Shell and Mobil wanted to secure CO_2 supplies for EOR projects in Texas.

The main reservoir at McElmo Dome is the Leadville Limestone, a sequence of carbonate rocks that were deposited in shallow water, resting on igneous and metamorphic basement rocks (Figure 12). Structural interpretation by Stevens et al. (2004) indicates that the reservoir is filled to the spill point. Formation waters within the Leadville Limestone reservoir are saline NaCl-dominated waters. A small amount of CO_2 has been detected in the Triassic Chinle Formation in one well. Massive evaporite deposits of the Pennsylvanian Paradox Formation (Figure 12) form the seal. Oil and natural gas shows occur throughout the overlying sequence.

The Leadville Limestone crops out in the San Juan Mountains ~80 km east, which act as a hydrogeological recharge zone. A slight (0.5°) dip in the CO_2-water contact is thought to reflect the hydrogeological gradient from recharge in the east and discharge in the Grand Canyon.

The Ute Mountain igneous intrusion, a potential cause of the CO_2 in some fields (see Section 2.2.5), was intruded between approximately 40 and 72 million years ago, approximately 8 km to the south. The La Plata Mountain intrusion lies to the east of the field. The temperature gradient in the McElmo Dome is consistent with the regional gradient and no residual thermal effect from these intrusions is observed.

It is worth noting that the evaporite seal makes seismic imaging of the CO_2 in the reservoir difficult and prevented early use of seismic imaging to detect the CO_2 distribution at McElmo Dome. Gravity and magnetic data did, however, provide additional information on the large-scale tectonic features.

2.2.3.1 Reservoir Geology

The Leadville Limestone is a regional marine carbonate, 75 to 90 m thick, composed of interbedded dolomite and limestone, topped by a significant erosional unconformity (Figure 12). Almost all of the Mississippian oil and natural gas reservoirs in the Paradox Basin also occur in the Leadville Limestone (Cappa and Rice, 1995). Lithofacies (rocks deposited in specific environments) vary from crinoidal biomicrites, which subsequently developed the best reservoir qualities, to oolitic pelsparites and micrites (very fine grained carbonate muds).

Reservoir quality developed through dolomite replacement of specific lithofacies. Only the micritic facies were dolomitised, as the coarser oolitic limestones were calcite-cemented soon after deposition, which prevented subsequent replacement by the dolomitizing fluids, as they could not penetrate the low permeability, cemented limestones. Several episodes of dolomitisation have been recognised (Miller, 1985) which resulted in the replacement of the micritic matrix with coarser and more porous dolomite, and dissolution of crinoids, to leave vuggy porosity. The dolomites are therefore the most porous and consequently best reservoir rocks. Pay quality in the central area of the reservoir ranges from 3.5-25.0% porosity (average 11%) and 0.1 to >500mD permeability (average 23mD). This is reflected throughout the Paradox Basin, where original facies distribution controlled subsequent diagenesis, which in turn controls the distribution of reservoir quality. It is not known what effects, if any, CO_2 emplacement has had on the reservoir quality.

Stevens et al (2004) performed a detailed structural and stratigraphic analysis of the Leadville Limestone reservoir and Paradox Formation seal. They concluded that the field is a combination structural-stratigraphic trap. Faults present in the southern portion of the field do not appear to be sealing within the Leadville reservoir, as no evidence was found for pressure differences across them based on production well pressure responses. Seven normal faults with northeast/southwest trends were identified but none appeared to affect transmissivity, especially those with smaller throws of less than 10 m. However, larger faults, with throws up to 100 m, may have lower transmissivities.

2.2.3.2 Caprock Geology

The Leadville Limestone reservoir is overlain by a series of excellent caprocks; directly above is the 60 m thick Hermosa Shale plus 400 m of Paradox Formation halite. Above this is a further 300 m of shale. Note that the faulting that cuts the Leadville dies out in the overlying Paradox halite (Figure 13).

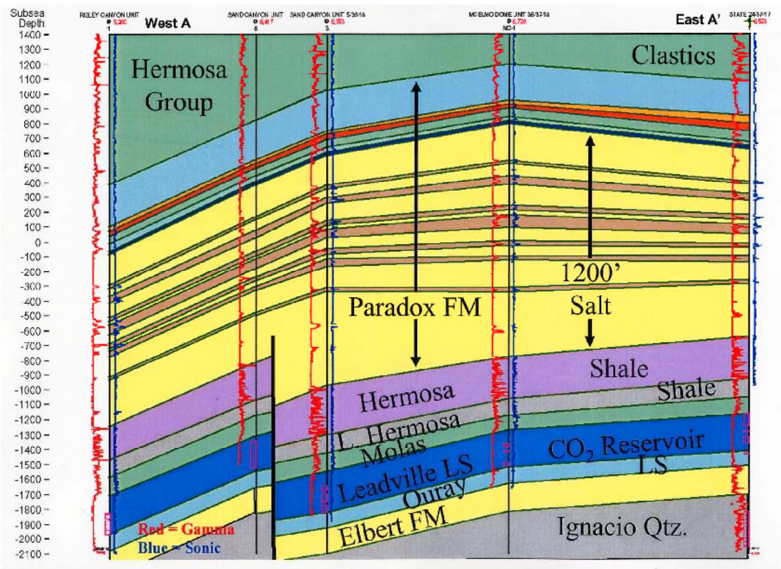

Figure 13. Detailed cross-section from (Stevens et al., 2004) through the McElmo Dome field, showing the CO_2 reservoir and overlying caprocks. Note that the normal fault has a throw of 100m in the reservoir but that thin overlying shales within the Paradox Fm salt are not displaced, indicating the fault does not penetrate through the salt.

No surveys aimed at detecting leakage from the McElmo Dome field have been carried out but, equally, there is no evidence of leakage at surface.

2.2.4 Natural, leaking CO_2 systems in the Paradox Basin

The following account of this area is based entirely on the work of Shipton et al. (2005). In the north of the Paradox Basin (Figure 11) CO_2 actively leaks along faults. The area consists of a north-plunging anticline cut by two fault complexes, the Little Grand and Salt Wash faults. The 61 km-long Little Grand fault is a complex zone of anastomosing normal faults with a throw of 180-210 m. The Salt Wash fault forms a graben over 15 km long.

CO_2-charged groundwaters effuse from several springs and leaky well bores along the Little Grand fault. The well bores are mainly abandoned oil exploration wells but include a few water wells. The Crystal Geyser is a dramatic example of leakage along a well bore, and has erupted at 4 to12-hourly intervals since the well was drilled (to the base of the Triassic), 70 years ago in 1935. At the surface, the well was drilled through a pre-existing travertine deposit (calcite formed at the surface through natural degassing of CO_2-rich springs), indicating that the spring system existed before the well was drilled. Where the Little Grand fault is intersected by the Green River, small bubbles can be seen, and dry gas seeps, known as "moffettes", indicate other sites of gas escape along the fault.

Five CO_2 springs, small geysers and oil seeps occur along the northern Salt Wash fault, including the Three Sisters spring, which flows continuously but with limited travertine formation. The Tenmile Geyser, located over an abandoned well, erupts episodically with 1-1.5 m high geysers. Similarly, Torrey's Spring, also associated with an abandoned well, flows continuously and emits CO_2 bubbles. Pseudo-Tenmile geyser, approximately 100 m north of the fault, also continuously emits CO_2 bubbles. Several other CO_2-charged springs, all associated with abandoned water wells, occur in the northern Paradox Basin. Palaeo-springs are indicated by ancient travertine deposits, which are now up to 30 m above the current CO_2 springs, reflecting progressive downcutting of the Green River.

Spring waters have *in situ* temperatures of less than 18°C, indicating a possible shallow source, which is further supported by stable isotopic values that indicate a meteoric origin (Heath et al., in press). Given local geothermal gradients, Shipton et al. (2005) estimated the waters come from the Jurassic Wingate and Navajo Sandstones at ~300-500 m depth (Figure 14). These waters are acidic (pH 6.07-6.55); with $\delta^{13}C_{CO_2}$ values from 0.0 to 1.2‰. All the waters have similar, NaCl-dominated chemistries. The travertines probably precipitate as the water degasses en route to, or at, the surface. At Crystal Geyser, Shipton et al. (2005) showed that the salinity of the water decreases during and after an eruption, indicating that fresh water drains into the wellbore. Gas comprises 95.66-99.41% CO_2 with trace amounts Ar, O_2 and N_2 that may be derived from an atmospheric component (Heath et al., in press). The $\delta^{13}C_{CO_2}$ values of the gas phase have a narrow range from –6.42 to –6.76, indicating one CO_2 source is likely for all the springs analysed in the northern Paradox Basin. Helium isotope ratios ($^3He/^4He$) expressed relative to the atmospheric ratio from two locations are 0.302 and 0.310 (Heath et al., in press), indicating a crustal origin.

In the Crystal Geyser area, the CO_2-bearing reservoir rocks that feed the CO_2-rich springs are postulated to be the Wingate and Navajo sandstones of the Lower Jurassic Glen Canyon Group (Figure 12 and Figure 14) (Nuccio and Condon, 1996). However, high dissolved CO_2 concentrations occur in many formations, from the Devonian Elbert Formation to the Jurassic Entrada Sandstone. This implies that a series of stacked reservoirs occur in the Paradox Basin, separated by partially breached local seals.

The lack of CO_2 springs to the south of the Little Grand and Salt Wash faults suggests that they are sealing and prevent CO_2 migration across the faults. However, CO_2 does leak upwards from the Jurassic reservoir rocks immediately to the north of both faults. These seals above the Jurassic reservoir rocks are shale units of the Middle Jurassic Carmel Formation (Figure 12 and Figure 14). Lithologically similar cap-rocks at other locations have successfully retained CO_2 for geological timescales and Shipton et al. (2005) suggest that whilst the actual fault planes themselves may have negligible permeability, damaged zones of fractured shales around the faults provide conduits for CO_2 escape.

Shipton et al.'s study of the ancient travertines suggests that fracture networks, up to 15 cm wide and often cemented by carbonate, provide the main migration pathways. $\delta^{13}C$ and $\delta^{18}O$ values of both active and ancient travertines are similar, suggesting that they formed from the same parental fluid that remained isotopically consistent over time.

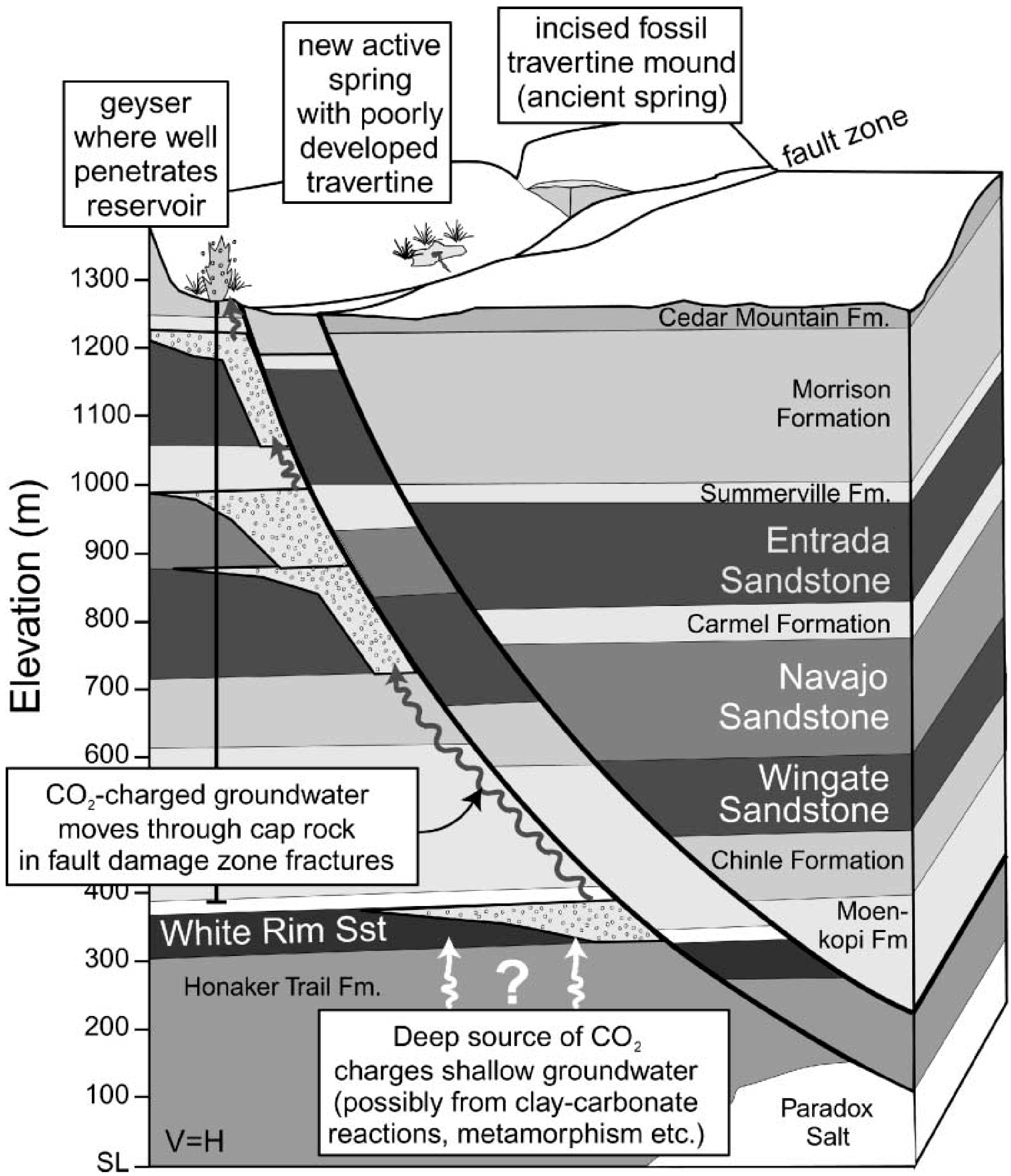

Figure 14. Schematic conceptual cross-section from Shipton et al., (2005) showing the production of CO_2 at depth, upwards migration to shallow Jurassic sandstone reservoirs and leakage to the surface.

2.2.5 Sources of CO_2 in the Paradox Basin

The potential source(s) of CO_2 in the Paradox Basin have been discussed by a number of authors, based largely on gas compositions and stable isotopic data (Cappa and Rice, 1995; Dockrill et al., in press; Garden et al., 2001; Heath et al., in press; Shipton et al., 2005; Stevens et al., 2004). Cappa and Rice (1995) carried out selected $\delta^{13}C_{CO_2}$ analyses on samples from both McElmo Dome and the Lisbon Field, which contains up to 35% CO_2. $\delta^{13}C_{CO_2}$ values (4 samples) at McElmo ranged from -11.80 to –3.77 ‰ and ranged from –11.09 to –9.50 ‰ (2 samples) at the Lisbon field. $\delta^{13}C_{calcite}$ from the Leadville Limestone ranged from –0.64 to 0.34 ‰ (2 samples) and $\delta^{13}C_{organic\ carbon}$ from the Lisbon field was –27.06 ‰. On the basis of the proximity of these fields to the Ute Mountain intrusion (McElmo Dome is ~8 km from it) and these $\delta^{13}C$ values, Cappa and Rice (1995) concluded that the CO_2 was primarily derived from thermal decomposition of the Leadville Limestone caused by the emplacement of the Ute Mountain Intrusion. Some mixing with an organic CO_2 source is indicated by the lighter $\delta^{13}C_{CO_2}$ values at McElmo and Lisbon. They also highlighted the potential for direct degassing of the Laramide and younger intrusive igneous rocks (such as Ute Mountain and those close to the Sheep Mountain CO_2 accumulation in Colorado). They discounted a primary mantle source since no correlation was observed between CO_2 concentration and depth, which would be expected to increase if mantle degassing was a significant source. This expected trend may not develop if CO_2 accumulated locally in sealed traps.

Heath et al. (in press) suggest that diagenetic reactions occurring during deep burial of clay-rich carbonate rocks may be responsible for CO_2 generation in the Crystal Geyser area, though they do not discount the possibility that CO_2 could also be derived from metamorphic thermal decomposition of limestones. This implies a deep source for the CO_2. They suggest that the lower part of the Moenkopi Formation, members of the Cutler Group and/or the Honaker Trail Formation (Figure 12) are potential sources, since they have the appropriate mixed clay and carbonate lithologies, and have been buried sufficiently to the required temperatures to initiate reactions. Shipton et al. (2005) suggest that the rapid uplift and erosion of the Colorado Plateau has brought these sources closer to the surface, allowing their accumulation in shallow reservoirs.

Stevens et al. (2004) found the CO_2 at McElmo Dome had a narrow range of $\delta^{13}C_{CO_2}$ values, between –4.3 to –4.5 ‰. These are similar to those found by Cappa and Rice (1995), except that no significantly lighter values, which may indicate mixing with organically derived CO_2, were obtained. Within this narrow range, a clear and statistically significant trend to lighter values with distance from the Ute Mountain intrusion was observed (see Section 2.2.3). These values by themselves, in the absence of trace gas concentrations, do not provide unambiguous evidence for the source of CO_2. More recently, Stevens and co-workers have confirmed that direct mantle degassing associated with the Ute Mountain intrusion is a more likely source for the CO_2 than thermal decomposition of the Leadville Limestone, as proposed by Cappa and Rice (1995), since further noble gas analyses confirm a mantle source for the CO_2 (Stevens, pers. comm., based on work by Gilfillan and Ballentine, University of Manchester).

2.2.6 St Johns Field

The following description of the St. Johns Field is largely based on the work of Scott Stevens and colleagues of Advanced Resources International (ARI).

St Johns Dome is a large asymmetric dome, located along the Arizona/New Mexico border (Figure 11 and Figure 15). The field is located along the southern edge of the Colorado Plateau in the Transition Zone with the Basin and Range and Rio Grande Rift tectonic provinces. The St Johns field comprises Precambrian basement, sedimentary rocks of Palaeozoic, Mesozoic and Cainozoic age, and Cainozoic volcanic rocks.

The first recorded report of naturally occurring CO_2 in the area was from the Mae Belcher 1 State well drilled approximately 12 miles east of Springerville in 1959 (Anon, 1999). The flow was estimated at 3.5 MMCFD (194.59 tonnes per day) and contained 87% CO_2 and 0.17% helium. Subsequent oil exploration drilling in the area by Ridgeway produced 640 MMCFD (35,582 tonnes per day). Due to the relatively shallow depths of the CO_2-bearing strata (200-700 m) the CO_2 occurs as a free gas rather than in the supercritical phase. The field is operated by Ridgeway who have estimated resources of 780 billion m^3 (1531 Mt or 14.8 Tcf) of which 730 billion m^3 (1433 Mt) is CO_2 and 1.8 billion m^3 is helium. Recent analyses by ARI indicate an average composition of 92% CO_2, 6.6% nitrogen and 0.6% helium along with minor methane and argon.

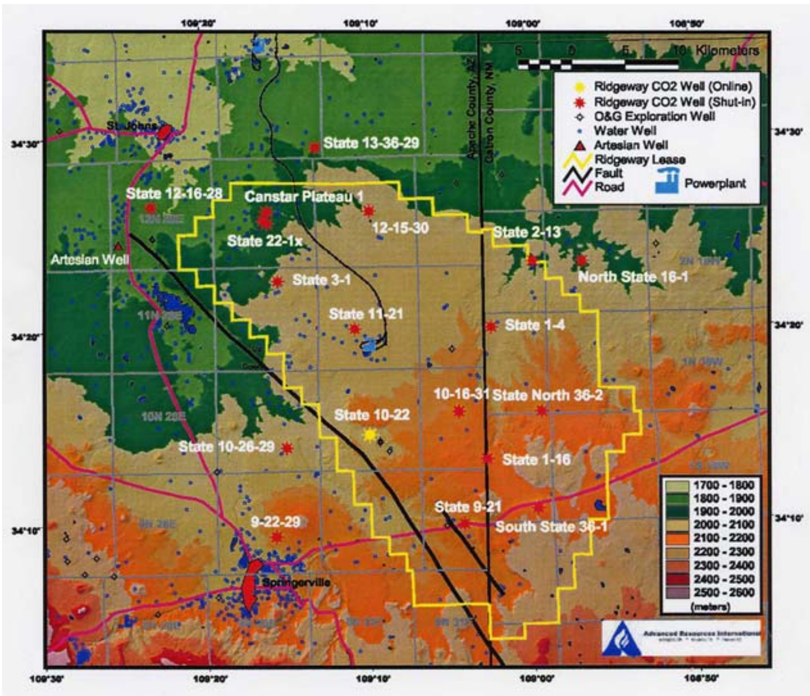

Figure 15. St Johns CO_2 Field showing locations of production wells and Ridgeway lease. Reproduced by kind permission of ARI Inc.

2.2.6.1 RESERVOIR ROCKS

The main CO_2 reservoir is the Permian Supai Formation (Figure 16), comprising mostly of a red to reddish-brown clay-rich siltstone and mudstone with significant evaporitic gypsum and anhydrite. Most of the high purity CO_2 comes from the Amos Wash and Big A Butte members. The Amos Wash Member comprises brown sand to gravel conglomerate, fine-grained sandstone and minor clay-rich siltstone with anhydrite nodules. Core analyses indicate a mean porosity of 6.6% and permeability of 1.4 mD. The Big A Butte Member is a reddish-brown siltstone and very fine-grained sandstone with minor dolomite and thin, but laterally persistent, anhydrite beds. Porosities range from 4.7 to 30.3% and permeabilities from <0.01 to 1,619 mD.

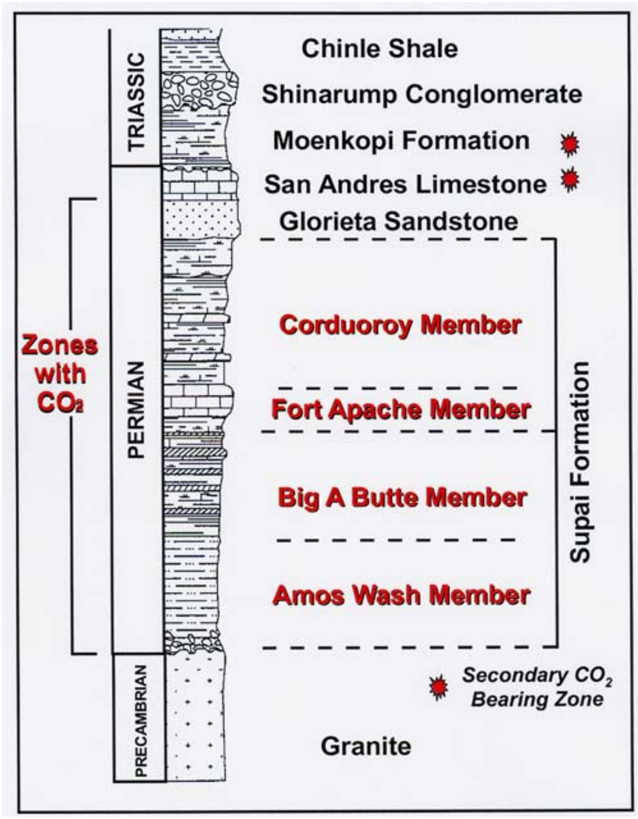

Figure 16. Stratigraphy of the CO_2-bearing reservoir rocks at St Johns Field. Reproduced by kind permission of ARI Inc.

2.2.6.2 CAP ROCKS

The cap rocks are evaporitic anhydrite and gypsum layers with minor halite within the Supai Formation. Estimated total caprock thicknesses have been calculated by ARI and vary between 250 m and 1000 m. The CO_2 is trapped in multiple reservoir strata below these impermeable evaporite and mudstone seals in the Big A Butte and Fort Apache members. Anhydrite recovered in cored sections of the reservoir had porosities of 0.4 to 10.6% and permeabilities of <0.01 to 0.02 mD.

It is worth noting that extensive karst has developed in many areas of the Colorado Plateau. Karst is a geographical term for topography that has developed through both limestone and salt dissolution involving the formation of sinkholes, caves and other large scale dissolution features. However, Stevens and co-workers observed only limited karst topography in the St Johns Dome area. Karst development could lead to loss of seal integrity, allowing CO_2 to leak out of the reservoir. The lack of karst at St Johns, possibly due to the lower proportion of halite and higher proportions of anhydrite and gypsum, which are less susceptible to dissolution by meteoric waters, would seem to explain the successful trapping of CO_2 in the St Johns area. For comparison, dissolution of halite and sylvite (a potassium chloride salt also produced by evaporation and sometimes associated with halite) has led to CO_2 leakage in the Vorderrhön area of Thuringia, central Germany (Jagsch and Rohleder, 2001; Kastner, 1994). Stevens et al. (2004) have estimated, based on current erosion rates, that the relatively shallow evaporitic caprock at St Johns could be exposed within 80,000 years.

Despite the significant CO_2 accumulations at St Johns, shallow water wells frequently contain high CO_2 concentrations. Stevens et al. (2004) suggest this is because the structural closure has been overfilled and CO_2 is migrating beyond the spill point or is migrating along major faults in the west of the field. No soil gas measurements have been made over the field.

2.2.6.3 Source of CO_2

The origin of the CO_2 at St Johns Dome has yet to be established. Stevens et al. obtained three $\delta^{13}C_{CO_2}$ measurements with a mean value of -3.8‰, which does not conclusively indicate the origin. They suggest two possible mechanisms:

- Migration of CO_2 from Laramide or younger intrusive rocks
- Migration of CO_2 directly from the mantle, since the Supai reservoir rocks rest directly on Precambrian granite.

Subsequent trace gas analyses performed at University of Manchester confirms a mantle origin for the CO_2 (Stevens and Tye, 2004; Zhou et al., 2003).

2.3 THE CARBOGASEOUS AREA OF FRANCE

2.3.1 Introduction

Several CO_2-rich gas fields and springs occur in the area of the Ardèche palaeomargin of the Southeast Basin of France (Figure 17, see also Arthaud et al., 1994; Pearce, 2003). The Southeast Basin is located to the southeast of the Massif Central, beneath the valley of the river Rhône and its tributary valleys, and extends offshore into the Golfe du Lion. It is bounded to the east by the Tertiary thrust belts of the western Alps and to the south by the Pyrenees. The CO_2 occurrences are located along major fault systems, which may be seen cropping out in the basement in the nearby Massif Central. These fault systems are related to the margins of, or deep extensional structures within, the Southeast Basin. Montmiral, the one field that is currently produced as a source of industrial CO_2 gas, is located in the northern part of this domain. Many of the naturally carbonated springs in the area are exploited by the sparkling mineral water industries centred around Vichy, Badoit and Vergèze (Perrier).

Oil exploration in the Southeast Basin has often been hampered by the discovery of CO_2 rather than hydrocarbons, eight accumulations having been discovered in total.

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. Among them, only the Montmiral accumulation is currently exploited as a source of CO_2 gas for industrial uses (Figure 17), production having started in 1990. Figure 17 indicates the location of several wells known for their CO_2 occurrences: Montmiral, and Montoison in the north within Miocene sub-basins; Villeneuve de Berg, downdip of the Cevennes-Ardeche passive margin; and Les Angles, near the centre of the Mesozoic basin. The Montmiral site has been studied by Pearce et al., (2003) as part of the EC-funded Natural Analogues for the Storage of CO_2 in the Geological Environment (the "Nascent" project). The following description is based largely on the work of BRGM (the French geological survey) and British Geological Survey as part of the Nascent programme.

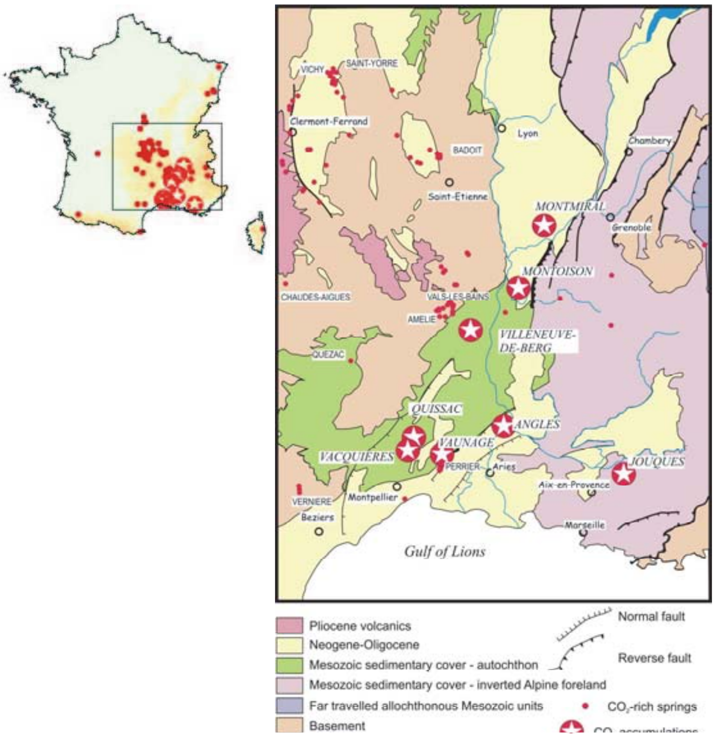

Figure 17. Simplified geological map showing locations of main CO_2-rich springs and accumulations across the Southeast Basin of France and part of the Massif Central. Reproduced by kind permission of BRGM.

2.3.2 Geological setting

The conceptual model of Blavoux and Dazy, (1990) displays several typical settings for springs and deep wells with CO_2 occurrences (Figure 18). The fault systems work as drains for surface water infiltration, and CO_2 exhalation from the mantle. A Montmiral-type setting can be found in this section where a Tertiary basin overlies and seals older, deep faults.

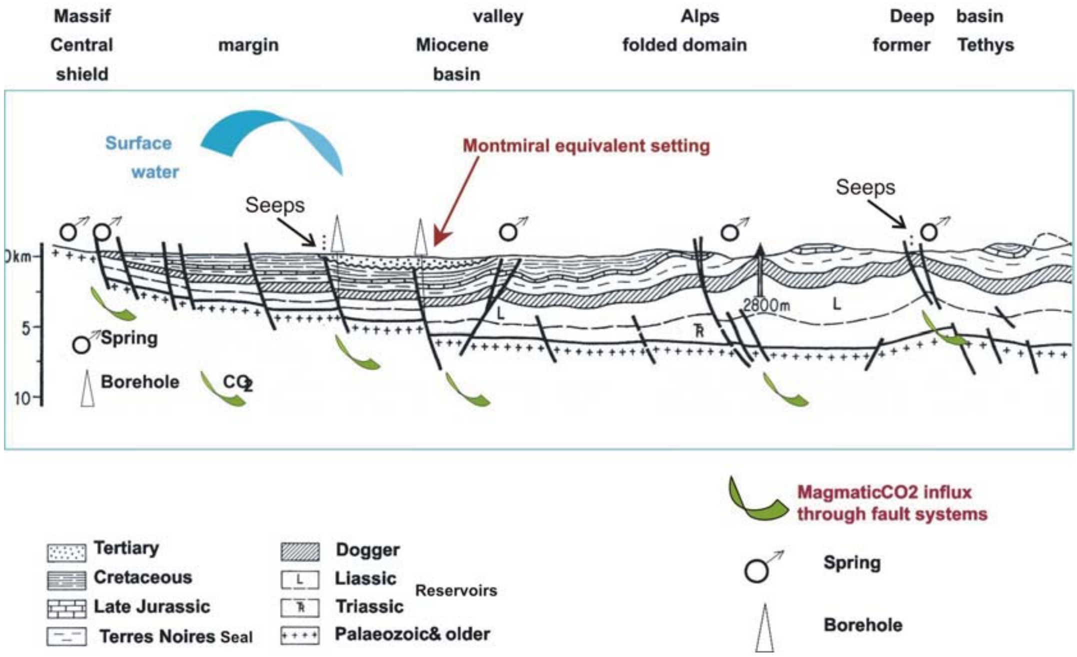

Figure 18. Conceptual model of Blavoux and Dazy (1990). Reproduced by permission of BRGM.

Montmiral itself is located in a Tertiary basin between the basement of the Massif Central and the Alpine foldbelt (Figure 19, from Chiron & Kerrien, 1979). Miocene sediments consisting mainly of shallow marine sand and clay, deposited by marine flooding of the Rhône valley, are found at outcrop.

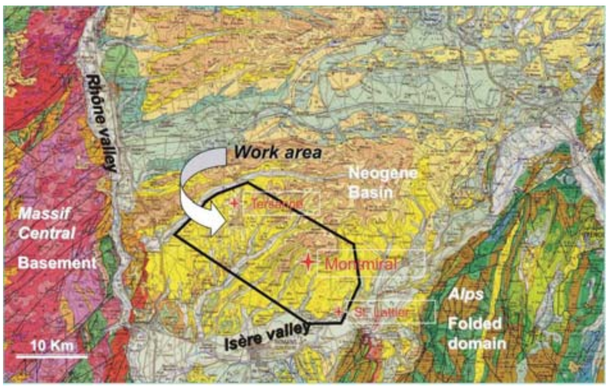

Figure 19. Montmiral geological setting (Lyon 1:250,000 Geological Map, BRGM)

The Montmiral 2 (VMo2) well was drilled in 1961 to explore the Mesozoic horizons that lie beneath the Tertiary basin. They had revealed promising oil shows in the Saint-Lattier 1 and 2 (SL.1, SL.2) wells several kilometres to the south. Some traces of hydrocarbons were found in the Dogger. The base of the Hettangian and the Rhaetian, which are fractured, and the Triassic sandstone which occur at depths between 2402 and 2480 m, were found to be gas reservoirs containing 97-99% CO_2 (Figure 20). This resource is currently exploited as an industrial source of CO_2. The seal of the reservoir, between 1840 and 2337 m, consists of clay and marl of the Terres Noires Formation of Early to Middle Jurassic age.

A detailed study of the reservoirs and seals was undertaken to find out as much as possible about the migration and retention of the CO_2.

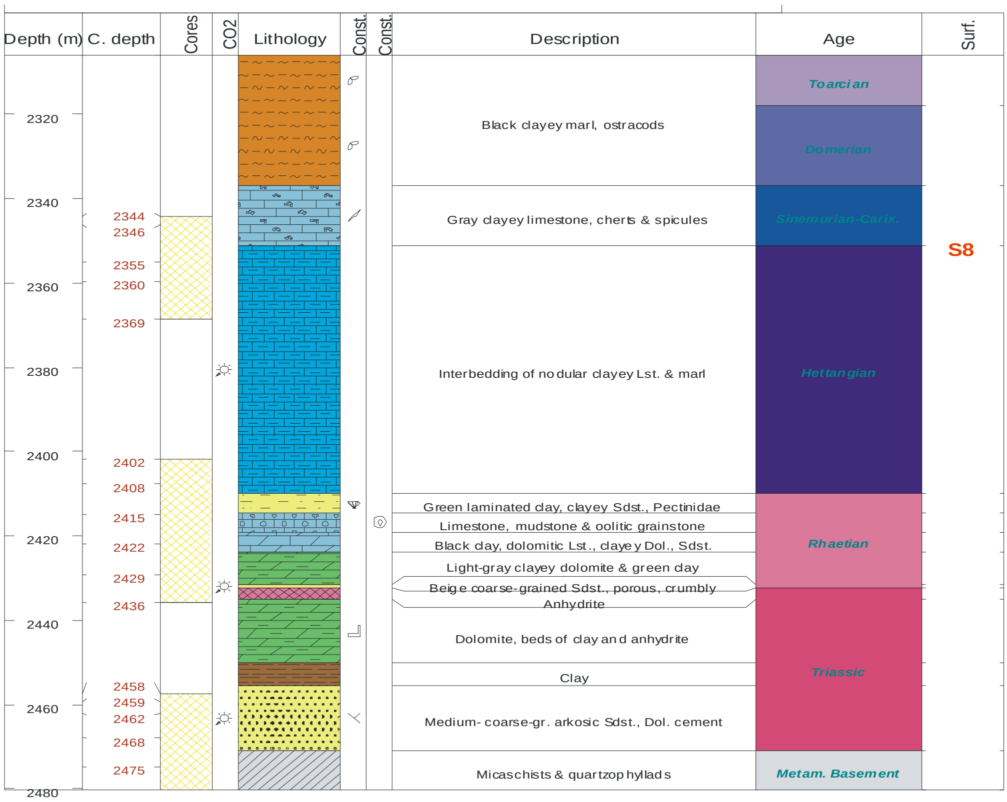

Figure 20. Lithostratigraphic section of the borehole VMo2 in the Liassic-Triassic interval. (Reproduced by permission of BRGM).

2.3.3 Facies distribution

Montmiral is located in the north of the Mediterranean portion of the Southeast Basin, a precursor of the later Subalpine basin. A WSW-ENE trending structural feature, the so called “Eperon Lyonnais”, forms the northern boundary of this domain. Triassic siliciclastic rocks form the main CO_2-bearing strata. During the Middle Triassic, the paleogeography was characterised by a NW-SE trend in lithology, with sandstone on the highs and transitional sandy claystone and evaporitic claystone in the lows (Figure 21), with total thicknesses of this unit varying from zero to about 200 m.

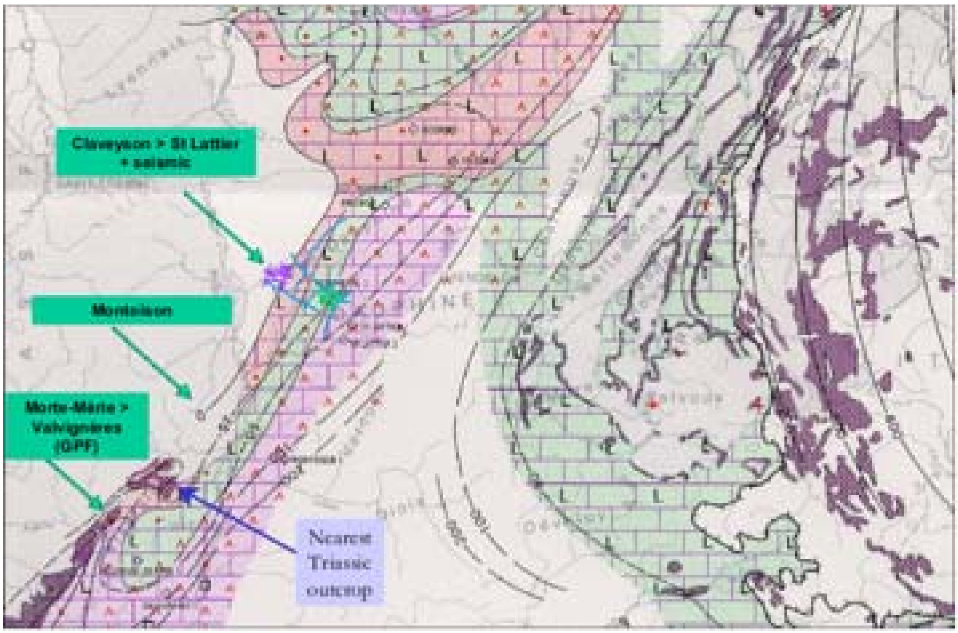

Figure 21. Paleogeography of the Triassic lower interval - Facies and thickness from bottom Triassic to top mid carbonate (from Debrand-Passard, Courbouleix & Lienhart, 1984).

During the late Triassic, the "Eperon Lyonnais" shows deposition of claystone and carbonate, with a lateral shift to local sandy claystone and more widespread claystone and evaporite.

From a petrographic point of view, it is important to point out that the Montmiral VMo2 well is located in the facies where sandy claystone or carbonate dominates, Saint-Lattier remaining downdip in the evaporitic claystone. This configuration explains why the comparison of the mineralogy in these two wells shows significant differences, namely the higher anhydrite content in Saint-Lattier (see Section 2.3.5.1).

2.3.4 Aquifer geochemistry

Pauwels et al. (in press) have analysed the fluid geochemistry of produced gases and waters from the VMo2 production well. As a result of degassing during fluid lift in the borehole, the chemistry of the waters sampled at the surface did not represent the *in situ* reservoir chemistry. A series of calculations based on modelled interactions during production enabled the *in situ* conditions to be estimated. 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 during, the CO_2 invasion (Pauwels et al., in press.).

Major-element (Na, K, Ca, Mg) concentrations are either higher or lower than would be expected from the degree of evaporation, which may indicate that dissolution and precipitation reactions have occurred, some of them being due to CO_2 invasion.

The reconstitution of the brine's chemical composition enabled an evaluation of the water-rock CO_2 interactions, based on comparison between mineral saturation indices and petrographic characterisation of the reservoir rock (see Section 2.3.6). 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 its observed removal.

2.3.5 Assessing CO_2 interactions with siliciclastic reservoir rocks at Montmiral

2.3.5.1 Evidence from the reservoir

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. For example, early diagenesis in the St. Lattier sandstones is marked by the presence of micritic calcite cement, which is either absent or only very poorly developed at Montmiral. As explained above, this is due to their differing palaeogeographic settings.

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 22). 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 tested by geochemical modelling (Section 2.3.6.2).

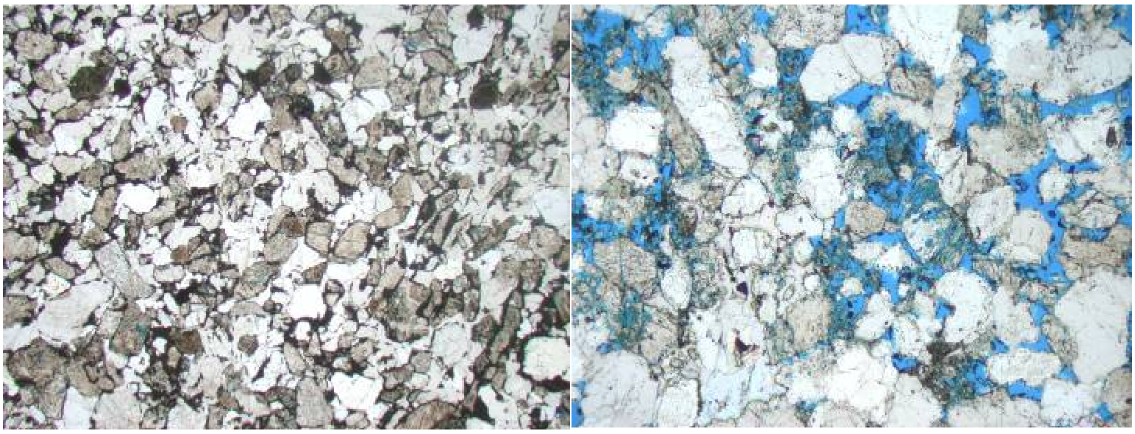

Figure 22. Comparison between broadly equivalent Triassic sandstones, showing differences in degree of porosity (indicated in both images by the blue colour): Left – From Saint Lattier, where no CO_2 is present; Right – from Montmiral – CO_2 production borehole. Field of view is 3.5 mm

2.3.5.2 Evidence from modelling

Geochemical modelling was applied at Montmiral to determine if the observed differences in degree of feldspar dissolution between Montmiral and St Lattier could be due to CO_2-related dissolution. The modelling of rock-fluid interactions in the reservoir at Montmiral suggests that K-feldspar dissolution induces the precipitation of kaolinite, some carbonates and chalcedony (although the latter was not confirmed in petrographical observations). This results in a significant increase in secondary porosity, although even after contact times of at least hundreds of thousands of years, feldspars are still present. This indicates that reaction kinetics used in forward geochemical modelling, which may be based on short-term kinetic data derived from the literature, are too fast to correctly reproduce reactions seen at Montmiral. 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 the research at Montmiral indicate that, following geological storage, it would take hundreds of thousands of years for the feldspar in a reservoir to fully react with CO_2. This timescale should therefore be considered if mineral trapping is to be utilised. The reservoir temperature was 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.

Dawsonite is often referred to as an important CO_2-trapping mineral (Johnson and Nitao, 2002; Baker et al, 1995). However, dawsonite was not identified during the petrographical analysis at Montmiral. The modelling confirmed that under the observed conditions it was unlikely to precipitate. This does not imply however that under different reservoir conditions (e.g. high pressure reservoirs containing evaporites) mineral trapping via dawsonite could not have a significant impact.

2.3.6 Identifying past CO_2 migration along fractures at Montmiral

The following account is taken from the Nascent final report (Pearce, 2004).

Evidence was obtained of CO_2 migration along fractures in Rhaetian limestones overlying the Triassic reservoir at Montmiral. These limestones have been subjected to a prolonged and episodic history of fracturing, 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. In this study they revealed that some of the fractures have enabled CO_2 to migrate out of 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, a property exploited in the oil industry during enhanced oil production.

Limestones overlying the Triassic reservoir, and sub-reservoir basement lithologies, provide exceptionally good evidence for the microfracture-controlled migration of supercritical CO_2 fluids (Figure 23). 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 operations. 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 reservoir integrity. 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.

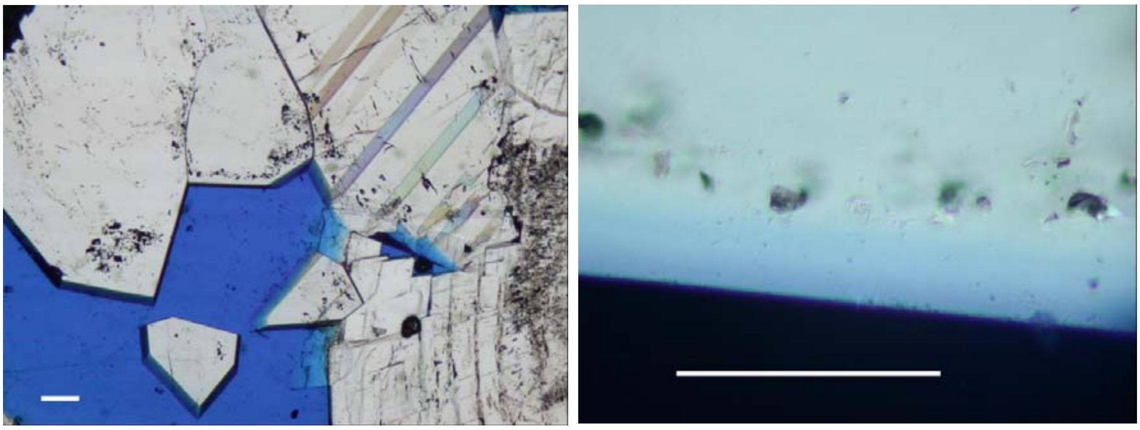

Figure 23. Left: Optical microscopic view of late stage calcite with very late stage growth zones containing supercritical CO_2 and hydrocarbon fluid inclusions. Scale bar is 100 microns. Right: Close up of late stage calcite with very late stage growth zones containing supercritical CO_2 and hydrocarbon fluid inclusions. Scale bar is 100 microns.

Reconstruction of the conditions prevailing during charging of the Montmiral reservoir is very dependent 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 (i.e. obtained at constant volume) data for the inclusion fluids suggests ≈150 °C and 50 MPa. If this is correct 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 overlying limestones 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.

A stable isotope study ($\delta^{13}C$, $\delta^{18}O$ and $^{87}Sr/^{86}Sr$) 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 particular in relation to CO_2 migration events through the cap-rock. Particular emphasis was placed on two distinctive generations of fracture-fill calcite, referred to as early calcite and late calcite. Based on evidence from fluid inclusions, 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 Triassic-Jurassic age, averaging 0 ±1 ‰ PDB for $\delta^{13}C$ and 26 ±2 ‰ Standard Mean Ocean Water (SMOW) for $\delta^{18}O$ (Figure 24). 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-rock 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).

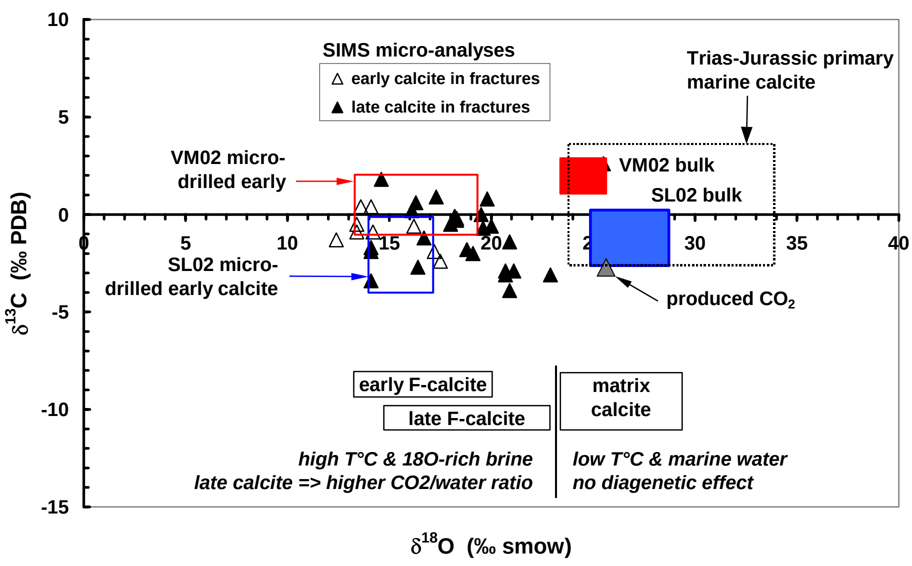

Figure 24. In situ $\delta^{13}C$-$\delta^{18}O$ SIMS micro-analyses of early and late calcite occurring in late fractures (III) in SL02 and VM02 wells, and comparison with $\delta^{13}C$-$\delta^{18}O$ values of bulk fracture (early) calcite (open squares) and bulk-rock calcite (solid squares) in the 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 overlying limestone 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 fractures in the overlying limestones 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 overlying limestones. 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 very little formation of late calcite.

2.3.7 Conclusions

The research on the Montmiral CO_2 field indicates that CO_2 can be successfully trapped for geological timescales and that where leakage has been observed the CO_2 escape has occurred along pre-existing fractures that were re-opened during basin uplift. As CO_2 migrated it entrained hydrocarbons. This is potentially important for man-made CO_2 storage sites as entrainment of oil by migrating CO_2 could lead to the pollution of potable water supplies. It also indicates that the main migration routes for CO_2, as at many of the other studied sites, were through fractures. It is not clear if this migration is ongoing today. The degree of calcite precipitation that could be directly associated with the CO_2 migration along fractures is very small and would probably not lead to fracture sealing. Reaction of CO_2 with porewaters and the sandstone reservoir rocks has caused some increase in porosity, though this has not lead to significant reduction in rock strength or significant mineral trapping.

2.4 A GIANT CO_2 FIELD IN THE PISGAH ANTICLINE, USA

The following description is based almost entirely on the work of Studlick et al. (1990) and Stevens et al.(2004).

Very large quantities of high purity CO_2 occur in underground reservoirs in an area of Central Mississippi, about 100 miles north of New Orleans (Figure 25).

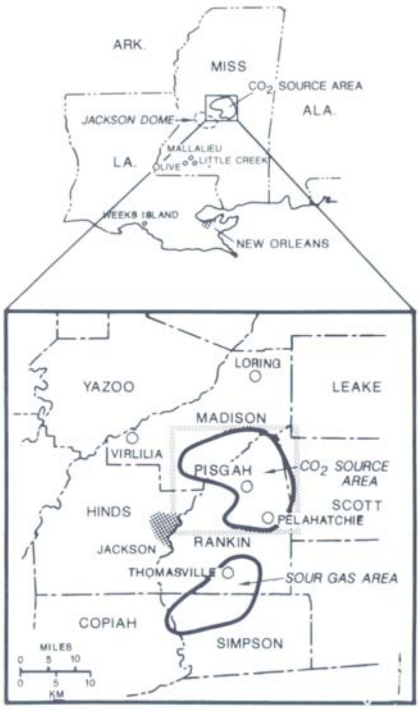

Figure 25. Location of the area of CO_2 fields in Central Mississippi, USA (from Studlick et al. 1990, © Springer). The rectangle with a hatched outline shows the area enlarged in Figure 26.

The CO_2 is found in an area north and east of the Jackson Dome igneous intrusion. It is trapped in the pore spaces of sandstone and dolomite reservoir rocks in a sedimentary basin called the Mississippi Interior Salt Basin. The reservoir rocks have, in places, been folded into anticlines (elongated domes) which form traps for buoyant fluids (Figure 26). The largest of these structures is the Pisgah Anticline. With a crestal area some 29 km (18 miles) long and 8 km (5 miles) wide, it is estimated to contain about 215 Mt of CO_2. This is the same order of magnitude as might be expected in a large man-made CO_2 storage project. The crest of the CO_2 field is at a depth of approximately 4660 m and its base is more than 300 m deeper. In addition to the Pisgah Anticline fields, there are a number of smaller CO_2 accumulations nearby, total CO_2 reserves in the area immediately NE of the Jackson Dome are thought to be in the order of 1.7×10^{11} m^3. The Pisgah (Jackson) Dome produces about 5.5 Mt CO_2 per year (Stevens et al., 2004).

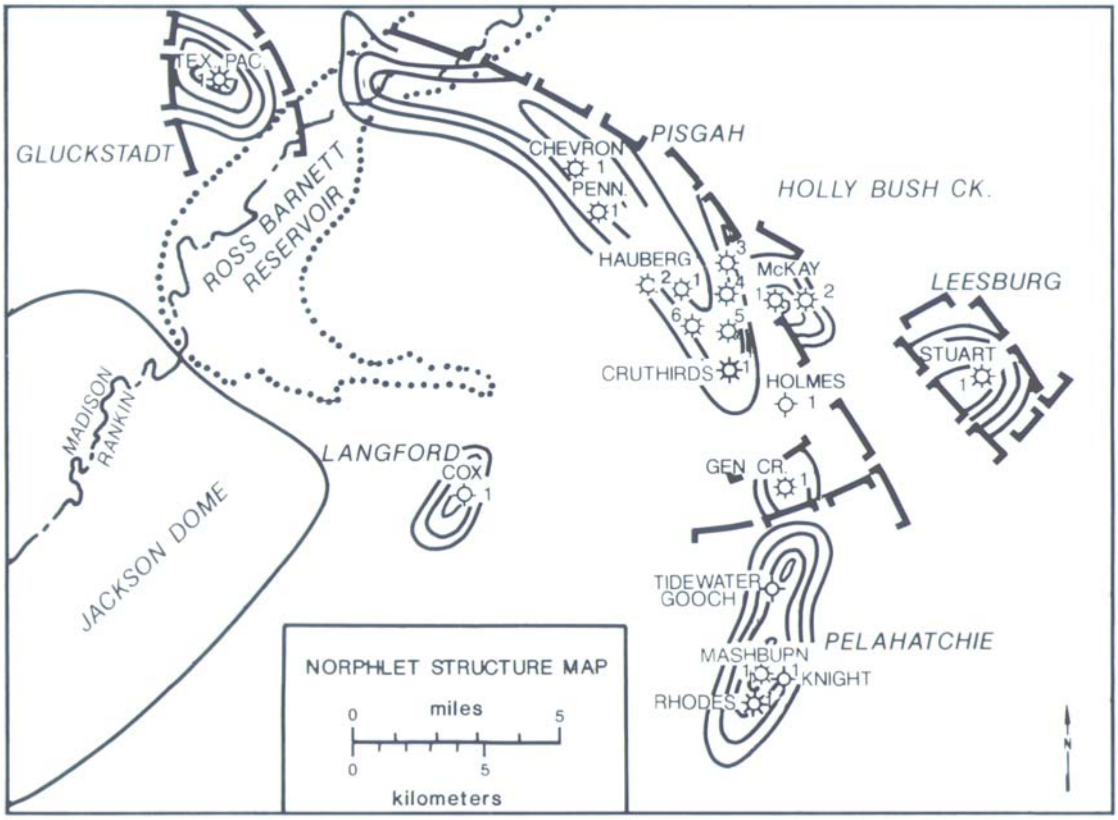

Figure 26. Location of CO_2 fields in the area NE of the Jackson Dome, Central Mississippi. Contours show the area and height of the structures trapping the CO_2 (from Studlick et al., 1990, © Springer).

2.4.1 The reservoir rocks

The CO_2 is found, in ascending order, in the Norphlet, Smackover and Buckner Formations, which are of Jurassic age (Figure 27). The Norphlet Formation consists entirely of sandstone and is 150 – 365 m thick in the Pisgah Anticline. However, its lower part has poor permeability (averaging 1 millidarcy) due to the presence of fibrous illite (a type of clay mineral) in the pore spaces and to patchy cementation by salt. The upper part of the Norphlet, which is 38 – 76 m thick, produces CO_2 and has an average permeability of 10 millidarcies. Porosities range from 8 to 15 %. The Smackover reservoir consists of both sandstone and dolomite and the Buckner reservoir consists of a locally developed sandstone 10 – 30 m thick. Such sandstones are uncommon in the Buckner Formation in Central Mississippi. These reservoirs are separated by a series of low permeability rocks. The Norphlet reservoir is overlain by the dense carbonate rocks of the Lower Smackover. The Smackover reservoir is overlain by anhydrite in the lower part of the Buckner Formation. The highest reservoir, the Buckner sandstone, is overlain and underlain by the low permeability carbonate and evaporite rocks that make up most of the Buckner Formation.

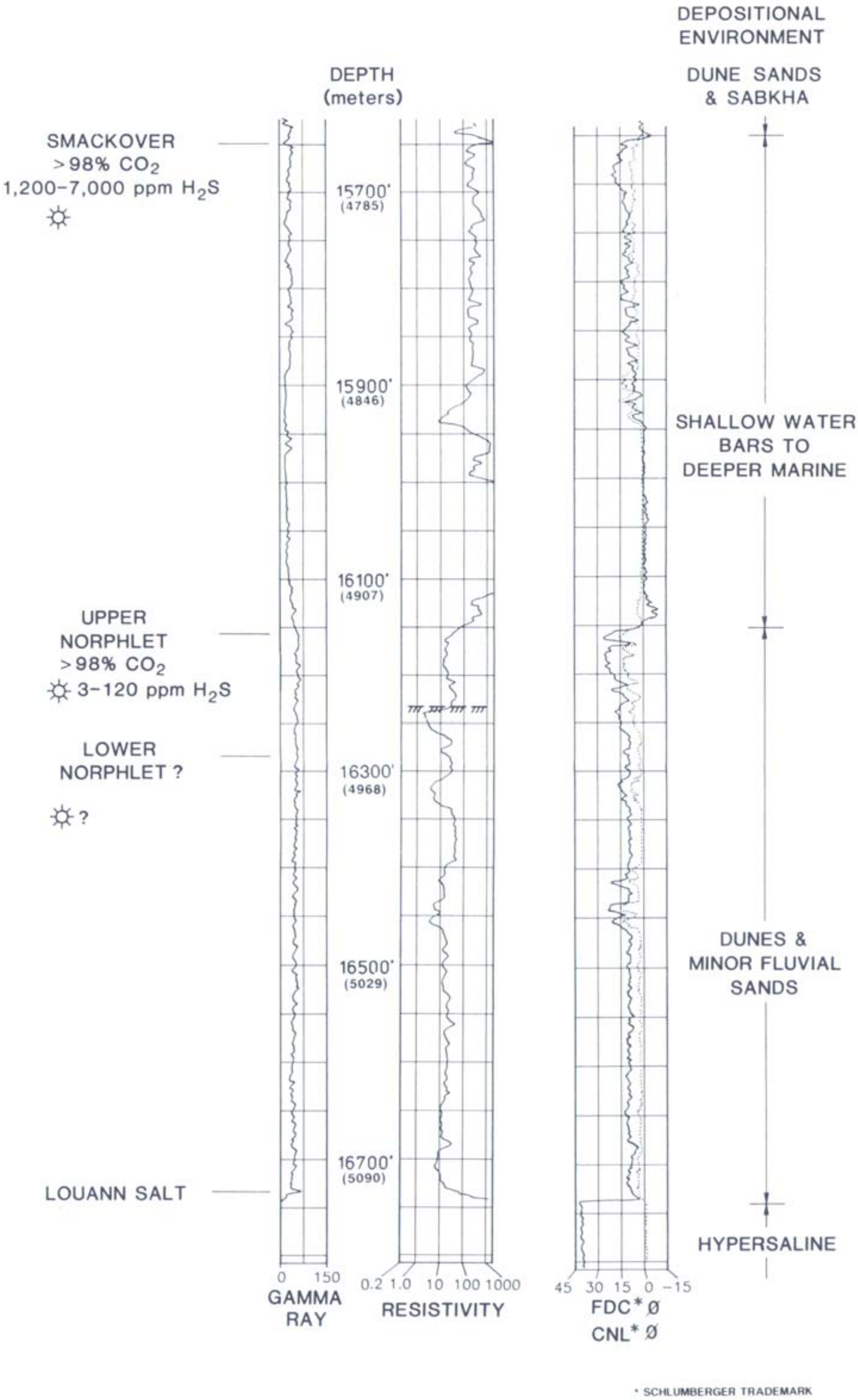

Figure 27. Geophysical logs and associated stratigraphic (Norphlet and Smackover Formations) and facies (depositional environments) subdivisions of a well in the Pisgah Anticline. Gamma ray log reflects clay content, resistivity logs reflect water content and FDC/CNL (neutron logs) represent porosity. From Studlick et al., 1990, © Springer.

2.4.2 Sealing formations that retain the CO_2

Impermeable carbonates and evaporites in the Buckner and Smackover form an effective top seal to the reservoir rocks in much of the region (Shew and Garner, 1990). An additional seal is provided by the Bossier Shale, an impermeable sub-regionally distributed shale more than 30 m thick that overlies the Buckner Formation. At the Pisgah Anticline, the effectiveness of the Buckner carbonate seal is demonstrated by abnormally high pore fluid pressures (known as overpressures or geopressures) in the Norphlet, Smackover and, to a lesser extent, in the Buckner formations. Above the Buckner, the pressure regime reverts to a normal hydrostatic gradient.

2.4.3 Relevance of the Pisgah Anticline and Associated CO_2 Fields to Man-Made CO_2 Capture and Storage Projects

Duration of storage

The main interest of this field from a Carbon Dioxide Capture and Storage perspective is that the high-purity CO_2 in the area originated from direct mantle degassing, probably associated with the Jackson Dome igneous intrusion (Stevens et al., 2004), which allows the age of CO_2 formation to be inferred and hence the storage duration to be estimated.

Geochemical analyses of 10 gases sampled from production wells across the Pisgah field indicate that the CO_2 is most likely derived from primary mantle sources. The $\delta^{13}C_{CO_2}$ values range from –3.55 to -2.57 ‰. The $^3He/^4He$ ratios range from 4.27 to 5.01Ra, and $^4He/^{40}Ar$ ratios range from 1.26 to 2.52, both indicate a mantle origin. Moreover, the ratio of $CO_2/^3He$ to CO_2 concentration (Figure 28) provides a reliable indication of mantle origin, since the $CO_2/^3He$ ratio is relatively fixed in magmatic gases and is not susceptible to subsequent alteration through geochemical processes.

In addition, analyses of ^{20}Ne concentrations provide evidence for strong CO_2 dissolution into groundwaters. ^{20}Ne is derived from groundwaters. In the 10 samples analysed, there is a very strong negative correlation between $CO_2/^3He$ and ^{20}Ne. This suggests that groundwaters control the $CO_2/^3He$ ratio. Since ^3He is conservative, the variation in $CO_2/^3He$ must be derived from variations in CO_2 concentration, caused by dissolution into the water phase. Stevens et al. estimate that about 75% of the original CO_2 is/was dissolved in the water.

It is known that the Jackson Dome igneous intrusion was emplaced in Late Cretaceous times (Saunders and Harrelson, 1991). It would seem likely that this intrusion was the source of the CO_2, though not as a result of thermal decomposition of limestones as previously suggested by Studlick et al. (1990). Therefore CO_2 generation, and migration into the anticlines, would probably have started in Late Cretaceous times, more than 65 million years ago. Thus the proportion of the CO_2 that migrated into the Pisgah anticline and the other smaller CO_2 fields NE of the Jackson Dome has remained trapped underground ever since. If this hypothesis is correct, it demonstrates that, under favourable circumstances, CO_2 can be stored underground for immense periods of time, far greater than the likely duration of any greenhouse crisis initiated by anthropogenic CO_2 emissions.

Note however, that no active monitoring of CO_2 levels above the Pisgah Anticline is taking place, so it is not known whether there are any indications of leakage through the ground. Stevens et al (2004) report that some faults are not sealing as evidenced from unsuccessful exploration wells that found no CO_2 or hydrocarbons, allowing CO_2 to leak; whereas other faults clearly do seal and prevent CO_2 loss. The controls on fault sealing are poorly understood in this area. It is not known how much CO_2 was generated by the intrusion of the Jackson Dome, but Studlick et al. (1990) made the conservative assumption that only a small amount of whatever was generated was captured in traps. It seems intrinsically likely that much of the CO_2 that was generated would have escaped to the atmosphere, as appears to occur in the Paradox basin (see Section 2.2.2). This is to be expected when the CO_2 source is natural and its location may not be within suitable traps.

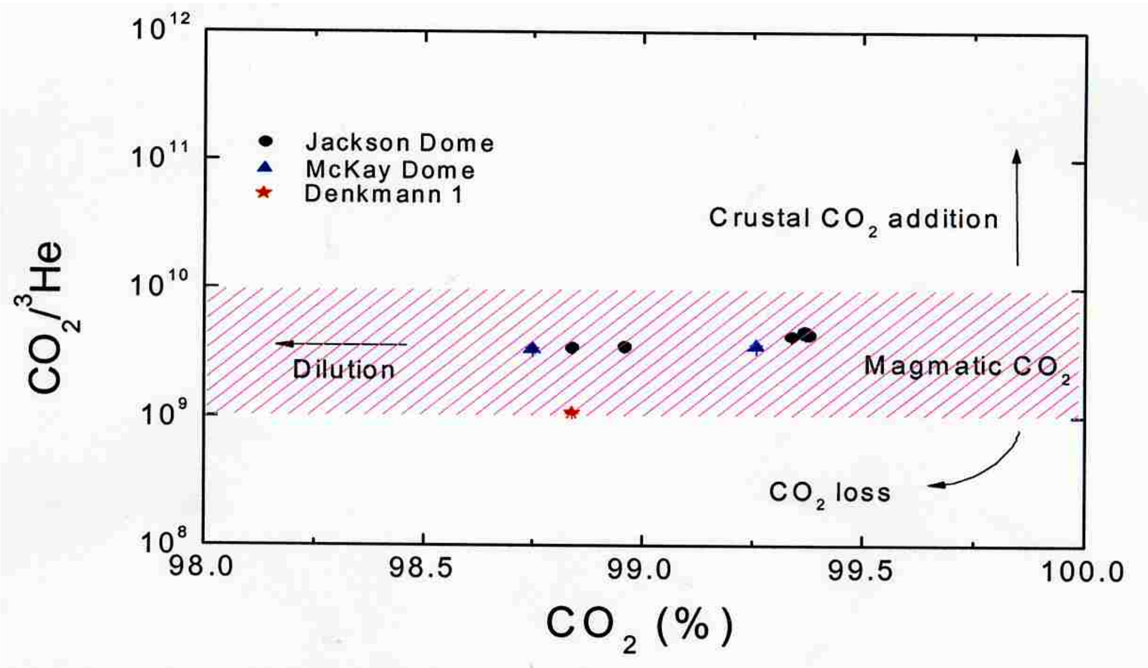

Figure 28. Plot of $CO_2/^3He$ vs. CO_2 concentration at the Pisgah Anticline, indicating the CO_2 is derived from primary mantle degassing. Reproduced by kind permission of ARI Inc.

2.5 NATURAL CO_2 EMISSIONS FROM OFFSHORE AREAS

There are few known natural emissions of CO_2 from the sea bed. However, much is known about the migration and emission of natural gas to the sea bed, which is likely to be analogous in many respects. For example, excellent accounts of natural gas migration and emission mechanisms are given by Schroot & Schuttenhelm (2003a, b), Heggland (1997), Heggland & Nygaard (1998) and Heggland (2005).

One route by which natural gas commonly migrates through lithified strata is via faults and porous and permeable beds. For example, the well known gas seeps above the Tommeliten gas field in the Norwegian sector of the North Sea lie above a salt diapir (Hovland & Summerville 1985). There are deep-seated faults above the diapir that are thought to act as conduits for the gas from depth to the near surface (Hovland 2002), but gas is also widely distributed throughout the upper part of the sediment column; the area of gas-charged sediments above the field is approximately 120,000 m^2. The gas-charged sediments are represented on seismic profiles by a so-called ‘gas chimney' that obscures the imaging of the strata within and beneath it (e.g. Hovland & Summerville, 1985).

Upwards migrating gas may be dispersed to varying degrees in porous and permeable layers along its migration path and form secondary accumulations within them (e.g. Schroot & Schuttenhelm 2003a, b).

In high pressure gas accumulations, gas may seep as a result of hydraulic failure (microfracturing) of the cap rock (e.g. Nordgard Bolas & Hermanrud, 2003) or possibly as a result of transport through the pore system of the cap rock, either in solution in water or as a result of capillary failure (the pressure in the gas column beneath the cap rock may exceed the capillary entry pressure of the cap rock). The cap rock and affected overlying strata thus become partly saturated with gas, which displaces the initially present pore fluid.

Migrating gas may disperse when it reaches the softer sediments that commonly occur close to the sea bed in actively subsiding offshore sedimentary basins. It may migrate along porous sandy or silty horizons and become trapped in normal buoyancy traps beneath less permeable sediments such as clays; or it may disperse through buoyancy in very poorly consolidated sediments. This results in the commonly observed shallow submarine seismic responses known as acoustic blanking, acoustic turbidity and reflector enhancement. When gas (and other fluids) emerges through soft, fine-grained sea bed sediments they commonly produce a pockmark (Hovland and Summerville, 1985; Hovland and Judd, 1988), circular to elliptical depressions on the sea floor, metres to hundreds of metres in diameter. Gas has been imaged emerging from pockmarks (e.g. Hovland & Summerville, 1985). Gas may also emerge through mud volcanoes. These are stratified cones of mud on the sea bed or land surface that originate when overpressured fluids migrate upwards through the less lithified strata in a sedimentary basin by disrupting the overlying strata and rising as a column of fluidised sand, mud, gas, other fluids and blocks of sediment. Major mud volcanoes occur for example around the shores of the Caspian Sea (Huseynev and Guliyev, 2004). At Tommeliten (Hovland & Summerville, 1985), where the sea bed is sandy, the gas emerges in a small part of the area above the gas chimney, covering about 6500 m^2. It emerges at the sea bed as bubbles, through small circular vents c. 10 mm in diameter in the sandy sea floor. The vents commonly have a cone-shaped depression about 20 cm in diameter above them. The gas bubbles have been observed using a remotely operated vehicle and have been imaged on echo-sounder and shallow 3.5 kHz seismic records. Gas may emerge through the sea bed intermittently, in response to changes in hydrostatic pressure or to self-sealing mechanisms (Hovland, 2002).

The best-documented natural CO_2 emission offshore occurs in the Tyrrhenian Sea, offshore from Panarea, one of the Aeolian islands, Greece (Italiano, et al., 2001). Here the emerging fluids generally issue from open fractures in the rocky sea floor as bubbles, although several areas of gas emerging through seafloor sand have also been observed. The fluids emerging from the sea floor have been sampled by scuba divers are dominantly CO_2 with some methane and range from 40 to 95°C. By the time the bubbles reach the sea surface the majority of the CO_2 has dissolved and the bubble gas composition has changed from dominantly CO_2 to dominantly less soluble methane. Bubble sizes decrease from approximately 3-4 cm at emergence to about 0.8 cm over a vertical distance of about 20 m. Thus most of the CO_2 flux is absorbed by the sea water column. A minimum CO_2 output estimated for an area of 15 km^2 of sea bed in the Tyrrhenian Basin is 25,000 tonnes per year, most of which dissolves in the overlying sea water. This clearly has implications for the pH of the sea water, which will likely be lowered by the dissolution of CO_2. The extent to which this affects marine biota will depend on dilution and thus ultimately on the flux through the sea bed.

Speculatively, one difference that might be expected between the Tyrrhenian Sea emissions and CO_2 emissions reaching the sea bed from man-made CO_2 storage sites offshore is that the latter might consist of both gas and water containing dissolved CO_2. This could have important implications for monitoring man-made sites, as detection of bubble trains alone might not be sufficient.

2.6 THE FLORINA NATURAL CO_2 FIELD AND EXPLORATION WELL

The following account of the Florina CO_2 field and exploration well is based entirely on the work of Dr G. Hatzyannis of IGME, for the NASCENT project.

The Florina CO_2 field is located in northern Greece very close to the border with Former Yugoslav Republic of Macedonia (FYROM). Geologically, the Florina CO_2 field lies in the northern part of a NNW-SSE-trending graben, the Florina Basin, which extends to the north as far as the town of Monastiri in FYROM, with a total length of about 150 km. The graben was created during middle Tertiary times and became filled with fluviatile and lacustrine Miocene and younger sediments, which in places exceed 1000 m in thickness. From the geological evidence it is possible that it extends into the FYROM. 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 ground surface (the top of reservoir is at a depth of 300 m), in poorly consolidated sediments and at low pressure with the CO_2 dissolved in the groundwater. This is in contrast to putative storage sites which will be situated at greater depths in consolidated sedimentary rocks. 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 is more than 99.5% pure with traces of methane and other gases. CO_2 occurs in Miocene sands which alternate with silt and clays forming an interbedded reservoir capped by several tens of metres of clay, which form a good but local seal.

In the summer of 1990, the Department of Hydrogeology of IGME (the Greek geological survey) drilled an exploration well for the location of mineral water in the Florina basin, since 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 throughout with a steel tube with an external diameter of 70 mm. Well completion included the installation of a wellhead with a valve (Figure 29). CO_2 occurred along the well from a depth of 97 m to a final depth of 559 m.

Figure 29. Valve-head of well drilled by IGME, 1990 (IGME).

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, 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 by 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 a health cure, by immersion of their feet only in the pool whilst keeping their face about 1.5 m above the water surface. This continued for some years until a fatal accident when a man was asphyxiated when swimming in the pool due to the concentrated CO_2 layer lying just above the water surface. At this point, the local authority prohibited the use of this pool.

In 2000, water and CO_2 were still flowing from the pool, with the flowing water causing a red-brown iron-rich deposit on the banks of small streams created by the flowing water. During field work for the NASCENT project in 2003, the pool and the well were found to be dry. No water or gas was flowing, suggesting that after 12 years of continuous CO_2 flow, the pressure was lowered and/or the borehole collapsed and closed.

From a CO_2 storage perspective, this illustrates that in relatively poorly consolidated successions CO_2 leakage can be induced by drilling wells.

3 CO_2 Emissions from Volcanoes

3.1 INTRODUCTION

CO_2 emissions at volcanoes and associated areas of hydrothermal activity are potentially hazardous to man but they are not close analogues of putative CO_2 emissions from man-made CO_2 storage sites. By their very nature they are areas that are prone to eruptions, ground movements, earth tremors and explosions that can fracture the surrounding rocks. They may also contain magma chambers or other structures capable of storing and suddenly releasing large volumes of CO_2 at high pressure. It is the sudden release of large volumes of pure or nearly pure CO_2 that can flow down slopes and valleys and accumulate in depressions that poses the major threat - that of asphyxiation. In general there are very few large void spaces at depth in sedimentary basins in which CO_2 could accumulate and subsequently be suddenly released. However, where these do occur they should receive special attention in any man-made CO_2 storage monitoring programme and from a health and safety perspective.

Volatiles, such as water and CO_2, are a fundamental part of volcanic activity and play a critical role in determining the behaviour of a volcano. For a given magma composition, higher volatile contents result in increasingly explosive activity (Delemelle and Stix, 1999). Explosive eruptions can emit large amounts of very hot volcanic gases, which may be injected into the stratosphere. In the twentieth century, the most significant eruptions were those of Katmai, Alaska, in 1912, followed by Mt Pinatubo in 1991. The latter, for reference, was 10 times larger than the eruption of Mount St. Helens in 1980.

Explosive eruptions (which include both magmatic and phreatic eruptions, the latter being eruptions driven by superheated water and steam) can be extremely violent , and result in the opening of fissures and craters that can suddenly emit large quantities of concentrated gas, which in many cases comprise almost pure CO_2 (see section 3.4). Fractures may also be opened by less violent events resulting in ground movements. The sudden opening of fractures in this way is considered highly unlikely in tectonically stable sedimentary basins where CO_2 is likely to be stored by man. However, it is recognised that for some countries, risks from tectonic activity will be higher than others and this should be considered during site selection.

Many dormant or quiescent volcanoes contain crater lakes. CO_2 leaking into the bottom of these lakes may dissolve into the lake water. This can result in a gradually thickening layer of denser, CO2-saturated water accumulating on the bottom of the lake and building up towards the lake surface. This results in the density stratification of the lake water. The lower parts of the lake water, as a result of their increased pressure, have increased CO_2 solubility. Disruption of the density stratification resulting in rapid overturn of these lakes can liberate vast quantities of CO_2 in a very short period (see section 3.4.2). This can be highly dangerous and has resulted in at least two natural disasters in the last 20 years. On the other hand, it is highly unlikely to occur in man-made CO_2 storage and, where it is considered a risk, such lakes can be monitored and remediated using a gas lift process, see http://perso.wanadoo.fr/mhalb/nyos/webcam.htm.

CO_2 can also be emitted in a diffuse manner through the soil on the upper flanks of certain volcanoes (see section 3.3.2). Indeed, most of the strata in this position on a volcano are likely to consist of lava flows, volcanic ash and tuffs; the whole being highly porous and permeable - far more so than the sequence of sedimentary rocks overlying a correctly selected man-made CO_2 storage reservoir. Emissions are also associated with faults or other fractures.

Examples are given below of all the types of volcanic CO_2 emissions mentioned above.

3.2 EMISSIONS OF CO_2 DURING EXPLOSIVE VOLCANIC ERUPTIONS – MOUNT PINATUBO AS AN EXAMPLE

Mount Pinatubo (Figure 30), located in the Philippines, [15.13º North, 120.35º East] is one of a chain of composite volcanoes that constitute the Luzon volcanic arc. The arc parallels the west coast of Luzon and results from eastward-dipping subduction along the Manila trench to the west. Mount Pinatubo is among the highest peaks in west-central Luzon. Its former summit, at 1,745 m elevation, may have been the crest of a lava dome that formed about 500 years ago. This was reduced to 1,485 m (the highest point on the caldera rim) during the most recent major eruptive episode (Wolfe and Hoblitt, 1996). The 1991 eruption marked the re-awakening of the volcano after a 500-year period of quiescence. During the climactic eruption a giant ash cloud rose 35 km and injected a minimum of 17 Mt of SO_2 into the stratosphere – the largest stratospheric SO_2 cloud ever detected, and more than an order of magnitude more SO_2 than could have been dissolved in the 5 km^3 of erupted dacite at pre-eruptive conditions. Experimental studies, geobarometer results and the H_2O and CO_2 contents of glass inclusions indicate that the magma was saturated with a water-rich vapour prior to its ascent and eruption, and modelling of the vapour composition suggest that volatile emissions derived from this pre-eruptive vapour phase also included *at least* 42 Mt of CO_2 (Gerlach et al., 1996). In comparison, it can be estimated from fumarolic gas compositions and SO_2 emissions (Casadevall et al., 1983), that CO_2 released during the 18 May 1980 eruption of Mt. St. Helens was between 4.8 and 22 Mt.

The CO_2 from such major eruptions, however, does not pose a danger (independent of that of the explosive eruption itself) to man or the local natural environment. Much of the gas emitted in such eruptions is extremely hot and is carried upwards into the upper parts of the atmosphere where it disperses by mixing with the surrounding air.

Figure 30. The explosive eruption of Mount Pinatubo, 12 June 1991 (USGS photo by D. Harlow).

3.3 DIFFUSE FLANK DEGASSING

Magmatic gases are released rapidly from the central conduit(s) of volcanoes during violent eruptions, as described above. However, it has recently been recognised that non-eruptive diffuse degassing may be the principle mode of gas release from both active and quiescent volcanoes. Gases can percolate to the surface through porous zones on volcano flanks. Gases emitted in this manner are generally non-reactive, and do not contain highly acidic species such as SO_2, HCl, and HF, and also tend to be emitted at low temperatures, often through the soil and through springs. The main gases emitted in this manner are CO_2 and He. Diffuse emissions of CO_2 are known to be large around some volcanoes and hydrothermal areas, although published estimates of these emissions vary dramatically. At present there is no real consensus about the relative importance of this mode of degassing and its full contribution to atmospheric loading (Delemelle and Stix, 1999) and, to date, diffuse emissions of CO_2 have only been studied in any detail on a limited number of volcanoes. Nevertheless, as more studies are made of these emissions, the importance of faults and fractures in degassing has become increasingly apparent, and the presence or absence of faults with surface expression appears to be the principle control on whether a volcano can degas through its flanks, in addition to established summit craters or vents.

Diffuse flank degassing can be significant on active volcanoes. For example diffuse emissions from the upper flanks of Mt. Etna, Sicily (see Section 3.3.2) appear to be of similar magnitude to those emitted from the crater plume, and the isotopic composition ($\delta^{13}C$ and $^{3}He/^{4}He$) of these emissions is consistent with a mantle, i.e. magmatic, origin, (e.g. Allard et al., 1991). An example of diffuse CO_2 emissions is at the quiescent Mammoth Mountain volcano (see Section 1), California, where tree kills were observed as a result of degassing along fault zones on the volcano's flanks (e.g. Farrar et al. (1995) following a period of enhanced seismicity in 1989 interpreted as an episode of dyke intrusion). Diffuse degassing has also been found to take place on other quiescent volcanoes, such as the Somma-Vesuvius volcano, Italy (Aiuppa et al., 2004).

Both hot and cold springs are a common feature in volcanic regions and diffuse degassing may result in significant amounts of gas becoming dissolved in the local groundwaters, from which these springs rise. The gas is predominantly CO_2 with trace amounts of other non-reactive gases (e.g. N_2, CH_4 and noble gases such as He). An example of this was documented at the Albani Hills, Italy, where >0.2 Mt/yr CO_2 rises from the depths and subsequently dissolves into shallow groundwater (Chiodini and Frondini, 2001), which can become oversaturated. The presence of shallow CO_2-oversaturated groundwater can explain several episodes of sudden gas release in the area, which has been documented by historical chronicles since Roman times. Magmatic CO_2 discharge through cold groundwaters is thought represent a significant fraction of the carbon discharge globally from volcanoes.

Whether the released CO_2 is derived directly from degassing due to depressurisation of new magma entering the shallow subsurface, or whether it is the result of the disturbance of a pre-existing reservoir of CO_2 by the seismic activity accompanying the magma injection, is the subject of debate. The presence of gas reservoirs beneath volcanoes has been inferred from the presence of shallow seismic anomalies which have been interpreted as porous, gas-filled rock at Mammoth Mountain (Foulger et al., 2003) and the Yellowstone volcanic field - another example of an area of diffuse degassing during a period of volcanic quiescence (Husen et al., 2004). The presence of large CO_2 reservoirs at shallow depths could also lead to rapid expulsions of CO_2 volumes far exceeding that which could be derived from the magma volumes erupted during volcanic eruptions.

Whilst diffuse flank degassing appears significant on many volcanoes, by no means all volcanoes degas in this way, and those that do may show intermittent periods of flank degassing. The overall control appears to be the structure and stress-field of the region. This is illustrated at the Popocatepetl volcano, Mexico, where the current phase of activity began in December 1994. Whilst the volcano is actively degassing from its summit crater, there is no evidence of an active geothermal system or a diffuse gas component on the volcano's flanks (Varley and Armienta, 2001).

Quantification of diffuse emissions is arguably a major issue when attempting to estimate the global emission rate of CO_2 from subaerial volcanism, and with the present paucity of data, remains extremely difficult. Nevertheless, Morner and Etiope (2002) present a conservative estimate of around 50 Mt/yr (out of a total volcanic emission rate of 300 Mt/yr) for diffuse degassing from emissions from the 500 or so historically active subaerial volcanoes.

Three examples of diffuse CO_2 emissions are described in more detail below:

1. Mammoth Mountain, California, USA

Mammoth Mountain, in central eastern California, USA, is a large volcano with a long history of volcanic activity that began some 200,000 years ago and has produced phreatic eruptions as recently as 700 ±200 years ago, although it currently displays only weak fumarolic activity and no summit activity (Farrar et al., 1995; Sorey et al., 1998). Areas of tree kill (and/or heavier than normal needle drop during the summer months) began to appear around the volcano in 1990, around the same time as a reported incident of near-asphyxia in a confined space; indicative of an increase in diffuse flank emissions of CO_2, such as have also been recorded at Mount Etna and Vulcano (Allard et al., 1991). CO_2 and He with isotopic compositions indicative of a magmatic source ($\delta^{13}C$ = -4.5 to -5‰, $^3He/^4He$ = 4.5 to 6.7 relative to the atmosphere) have been found to be discharging at anomalous rates, both as cold soil gas emissions and from steam vents, and dissolved in groundwaters both prior to and subsequent to the tree kills. Nevertheless, the rate of gas discharge increased significantly in 1989 following a 6-month period of persistent earthquake swarms and associated strain and ground deformation attributed to dyke emplacement beneath the mountain. Additionally, an increase in $^3He/^4He$ in vapour discharged from a fumarole on the north side of the mountain (Sorey et al., 1998; Sorey et al., 1993) reinforced the inferred presence of new magma beneath the area. Tree kills presently affect an area of some 360,000 m^2, which is additionally characterised by diffuse cold soil CO_2 emission. A soil gas survey, begun in 1994, revealed CO_2 concentrations of 30-96% in the area of the tree kills (Farrar et al., 1995). The total area affected by diffuse CO_2 degassing on Mammoth Mountain is about 480,000 m^2 (Gerlach et al., 2001). Both the tree-kill areas and a further notable area of CO_2 discharge above the tree line occur in close proximity to fault zones, which may provide conduits for gas flow from depth. It has been estimated that the total diffuse CO_2 flux from the mountain is approximately 520 tonnes per day, and that a further 30-90 tonnes per day of CO_2 are dissolved in cold groundwater flowing off the flanks of the mountain (Evans et al., 2002; Gerlach et al., 2001).

The compositional (isotopic and chemical) homogeneity of both soil and fumarolic gases suggest a common gas reservoir whose source is probably a combination of magmatic degassing and thermal metamorphism of metasedimentary rocks (Sorey et al., 1998). Whilst the onset of tree kill coincided with the episode of shallow dyke intrusion, the magnitude and duration of the CO_2 flux indicates that a larger, deeper magma source and/or a large pre-existing reservoir of high-pressure gas has been tapped throughout (Farrar et al., 1995). The presence of a gas reservoir is supported by the presence of a seismic (low-V_p/V_s) anomaly extending from the surface to ~1 km below sea level beneath the region (Foulger et al., 2003). Temporal variations in structure showed that significant changes in both V_p and V_s were consistent with the migration of CO_2 into the upper 2 km or so beneath Mammoth Mountain and its depletion in peripheral volumes that correlate with surface venting areas. It would also suggest that should the area be subject to stronger earthquake activity, a more rapid, high volume escape of gas could result. Episodes of increased emission rates have been recorded on a number of occasions; for example, during 1997 at Horseshoe Lake (McGee et al., 2000), at which time direct degassing from a shallow intrusion of new magma is considered implausible since the released gas was cold and barren of other magmatic gases (except He). McGee et al. (op cit) propose that increased compressional strain on the area south of Mammoth Mountain, driven by movement of major fault blocks in the Long Valley caldera, was responsible for triggering the increased degassing from the reservoir to the surface via faults and other structural weaknesses. Nevertheless, recharge of the gas reservoir by CO_2 emanating from the deep intrusions that probably triggered deep long-period earthquakes may also have contributed to the 1997 degassing event.

Although the CO_2 is thought to migrate from a reservoir towards the ground surface via faults and fractures, which are essentially linear features in plan view, the nature of CO_2 discharge at the soil-air interface is more diffuse because it is dispersed within the porous High Sierra soils and by meteorological processes (McGee et al., 2000; Rogie et al., 2001).

3.3.2 Mount Etna, Sicily

Mount Etna, in Sicily [37.734°N , 15.004°E], is Europe's highest volcano, reaching 3350 m above the city of Taormina on its NE flank (Figure 31). From a structural point of view, the volcano lies above the boundary between the Eurasian and African plates in the central Mediterranean. Etna has one of the world's longest documented historical records, dating back to the 2nd millenium BC. Historical lava flows cover much of the surface of this massive, 60 × 40 km wide basaltic stratovolcano, and extend to the sea. Persistent explosive eruptions, sometimes with minor lava emissions, take place from one or more of the three prominent summit craters. Flank vents, typically with higher effusion rates, are less frequently active and originate from fissures that open progressively downward from near the summit (usually accompanied by Strombolian eruptions at the upper end). Cinder cones are commonly constructed over the vents of lower-flank lava flows. Lava flows extend to the foot of the volcano on all sides and have reached the sea over a broad area on the SE flank.

Figure 31. Mount Etna. Photo by Jean-Claude Tanguy, University of Paris.

Etna is also one of the world's most actively degassing volcanoes (Allard et al., 1991; Gerlach, 1991), and large quantities of CO_2, H_2O, SO_2 and other species are released from the summit crater. CO_2 output has been calculated at 13±3 Mt/yr (Brantley and Koepenick, 1995; D'Alessandro et al., 1997). Large amounts of CO_2 have been observed escaping from the volcano's flanks; estimates of the mass of flank emissions vary from 1 to 13 Mt per year (Delemelle and Stix, 1999). Additional CO_2 is dissolved in Etna's aquifers and it has been estimated that approximately 0.25 Mt per year escapes this way (D'Alessandro et al., 1997). Study of the carbon isotope composition ($\delta^{13}C$) of the CO_2 and He isotopic ratios from both the flank and summit emissions on Etna suggest a minor contribution of organic carbon, whilst at the most active sites of gas emission, the isotopic data are consistent with a mantle origin for both gases (De Gregorio et al., 2002). The spatial distribution of soil gas anomalies have also been studied over a wide area (approximately 110 km^2) on the SW flanks of Mt. Etna by De Gregorio et al. (2002), and the highest soil emissions were found to delineate the existence of an active fault system.

3.3.3 Yellowstone volcanic field, Wyoming, USA

The Yellowstone volcanic field [44.43°N, 110.67°W] has developed through three volcanic cycles spanning two million years that included some of the world's largest known eruptions. It is underlain by the Yellowstone hotspot, recent manifestations of which have included volcanism, active crustal deformation, extremely high heat flow (about 30 times the continental average), and intensive earthquake activity (Smith, R. B. and Braile, 1994). Voluminous (1000 km^3) lava flows have been erupted within the Yellowstone caldera over the last 150,000 years. However, no magmatic eruptions have occurred historically, although phreatic eruptions have occurred near Yellowstone Lake and the most recent activity is thought to have occurred around 1050 BC. Yellowstone is presently the site of one of the world's largest hydrothermal systems including Earth's largest concentration of geysers (Figure 32), and active degassing continues.

Figure 32. An eruption of Old Faithful, perhaps the world's best known geyser, rises above Yellowstone's Upper Geyser Basin, which contains more geysers than are known altogether in the rest of the world. The forested ridge in the background is underlain by massive post-caldera rhyolitic lava flows of the Madison Plateau. Photo by Lee Siebert (Smithsonian Institution).

Surface measurements suggest that 16 ±0.6 Mt per year CO_2 are released from Yellowstone due to diffuse degassing, comparable to the CO_2 contribution from other large subduction-related volcanic systems and the combined contribution from the Hawaiian hot spot (Werner and Brantley, 2003). Likewise, the CO_2 flux from Yellowstone (on average 0.0001 Mt CO_2 per km^2 per year) is comparable to other large volcanic and hydrothermal systems worldwide. Analyses of carbon and helium isotopes suggest that around 50% of the CO_2 emitted is derived from sedimentary sources at locations outside the caldera, whereas locations inside the caldera have a lower contribution from sedimentary sources (< 30%). Earthquake tomography suggests a volume of porous, gas-filled rock is located at shallow depths of < 2.0 km in the northwestern part of the Yellowstone volcanic field (Husen et al., 2004). The close spatial correlation of the observed anomalies and the occurrence of the largest earthquake swarm in historic time in Yellowstone (1985) additionally suggest that this gas may have originated as part of magmatic fluids released by crystallization of a body of magma lying beneath the Yellowstone caldera.

3.4 SUDDEN EMISSIONS OF CO_2

Epsiodic releases of CO_2 gas from volcanic centres occur following a build-up of gas. This can occur where the CO_2 concentrates either as a free gas or in a supersaturated state. Rapid release then occurs following a destabilisation of the system. Two examples are described, the Dieng volcanic emissions and the Lake Nyos emissions.

3.4.1 Dieng Volcano, Indonesia

The "Dieng Volcanic Complex" encompasses both the "Dieng" and "Butak Petarangan" volcanoes listed in the Catalogue of Active Volcanoes of the World. The complex (Figure 33) consists of two or more stratovolcanoes and numerous small craters and cones of Pleistocene-to-Holocene age and covers an area of 6 × 14 km on the Dieng plateau in Java. The maximum summit height attained is 2565 m (8,415 feet) at 7.2°S, 109.9°E. Its products range in composition from andesite to rhyodacites (Allard et al., 1989). It forms part of the Suda Volcanic arc of Indonesia which has been active since the mid-to-late Tertiary and is the result of the subduction of the Indian oceanic plate under the continental margin of SE Asia.

Figure 33. The Dieng volcanic complex from the southeast (Photo by Sumarma Hamidi, 1973, Volcanological Survey of Indonesia).

Activity in historical times has been restricted to minor phreatic eruptions, sometimes associated with gas emissions, which have caused fatalities. The area is volcanologically complex, and the relationships between its numerous and closely spaced volcanic features are uncertain. The complex also represents a significant geothermal prospect, and hydrothermal features such as fumaroles, solfataras, mud pools and hot springs are abundant, defining the extensive fissure system and active eruptive centres. A 60 MW geothermal power plant has been built but is currently not operational. Another typical feature of the complex are sites of persistent emission of almost pure CO_2 (moffettes), especially in the western sector where in places emanations frequently destroy vegetation which the local people refer to as "death valleys".

In February 1979, rapid CO_2 emanations leading to 142 deaths were preceded by a phreatic explosion at Sinila (on the SW portion of the Dieng volcanic complex) which resulted in the formation of a new crater and the reactivation of a pre-existing fracture. CO_2 effusion occurred from both the fracture and the crater, and flowed down to the plain below as a dense sheet (Le Guern et al., 1982). Emanation of CO_2 continued over the next few months at a much reduced flow rate (see hazard zonation map, Figure 34).

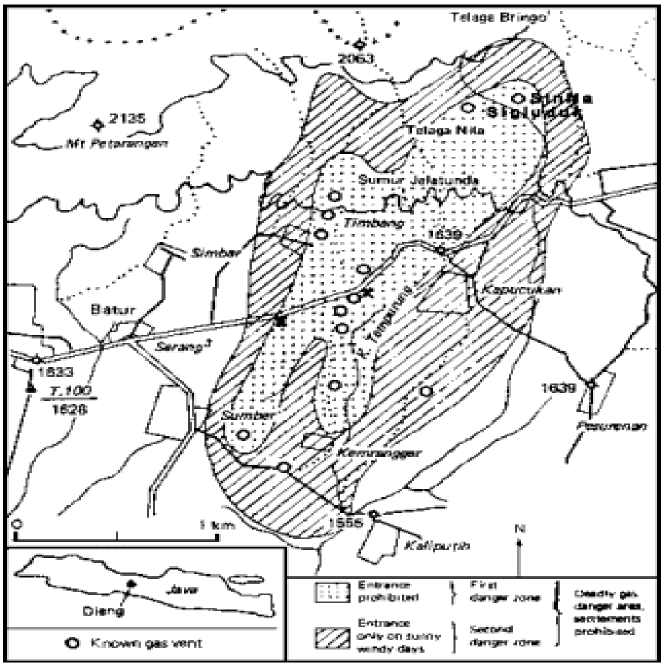

Figure 34. Hazard zonation map showing the SW portion of the Dieng Volcanic Complex. Entry is prohibited to the first danger zone (dotted pattern); entry is permitted to the second danger zone (diagonal lines) only on sunny, windy days. Known gas vents are represented by circles; fatalities are marked by x. Courtesy of Adjat Sudradjat, VSI, (SEAN 1979).

It is estimated that the total CO_2 output associated with this eruption may have approached 0.1 km^3, approximately 0.18 million tonnes at atmospheric pressure and 25°C (Allard et al., 1989). The gas emitted was analysed by Le Guern et al. (1982) and found to be almost pure CO_2 (98-99%) with subordinate amounts of CH_4 and S-compounds. Phreatic eruptions by definition, release steam and superheated water with only subordinate amounts of CO_2. Thus an eruption of this type can only lead to effussion of pure CO_2 if this gas is already emplaced in a shallow local reservoir, probably trapped in fractures, pore spaces or aquifers and probably in the form of a high density fluid. The $\delta^{13}C$ of the CO_2 and the He/CO_2 ratio of the gas was found to be almost identical to the nearby Merapi volcano (Allard et al., 1989), and within the range of mantle derived carbon in MOR magmas (Pineau and Javoy, 1983). A magmatic origin is therefore plausible and it is thought that magmatic CO_2 had accumulated beneath the Dieng volcanic complex, and its effusion was then triggered by pressure release generated by the phreatic eruption. It has also been shown that effusion of concentrated CO_2 occurs frequently within eroded calderas or volcano-tectonic depressions and may account for the major hazard posed by phreatic eruptions within these structures (Allard et al., 1989).

The 1979 event demonstrated that the depressurisation of accumulations of CO_2 at shallow levels beneath volcanoes may represent a major hazard (for local populations) associated with phreatic eruptions, whether it be a trigger or a consequence. The hazard from ongoing CO_2 emanations at Dieng, however persists even between eruptions, as evidenced by the death of four workers at a geothermal well in 1988 ([Sean], 1975-89).

Most recently, on 18 March 1992 a sudden gas emission occurred from a fracture close to the 1979 eruption site, which resulted in one death by asphyxiation. Surface gas measurements the next day indicated high concentrations of CO_2 and O_2 (40 and 15 weight %, respectively), and lesser concentrations of H_2S and HCN; 200 and 197 ppm, respectively (Activity Report, Bulletin of the Global Volcanism Network, 1992).

3.4.2 Emissions of CO_2 from Crater Lakes: Lake Nyos and Lake Monoun, Cameroon

During the 20th century, twelve volcanic disasters each involving over 500 deaths occurred in nine countries worldwide, with a total loss of life of about 78,000. In only one case, at Lake Nyos in Cameroon (see Figure 35), was the main cause of death a gas outburst that asphyxiated people, whereas in the other eleven cases pyroclastic flows or mud flows were the cause of the fatalities.

On the evening of 21^{st} August 1986 a large amount of CO_2 gas erupted from Lake Nyos, a crater lake located in the northwest of Cameroon. The gas subsequently covered the local villages in the downstream area along the valley, resulting in the deaths of 1746 inhabitants and a large number of livestock (Kling *et al.*, 1987). In August 1984, 100 km south of Lake Nyos, a similar but smaller scale gas outburst occurred at Lake Monoun, which is also a crater lake in Cameroon, resulting in the deaths of 37 people (Sigurdsson *et al.*, 1987). These cases were a new and unknown type of unprecedented natural disaster and created much interest in the scientific community and general public. Although the geological setting is different, a high CO_2 lake water content was also reported at Lake Kivu located in the East African Great Rift Valley district (Tietze *et al.*, 1980).

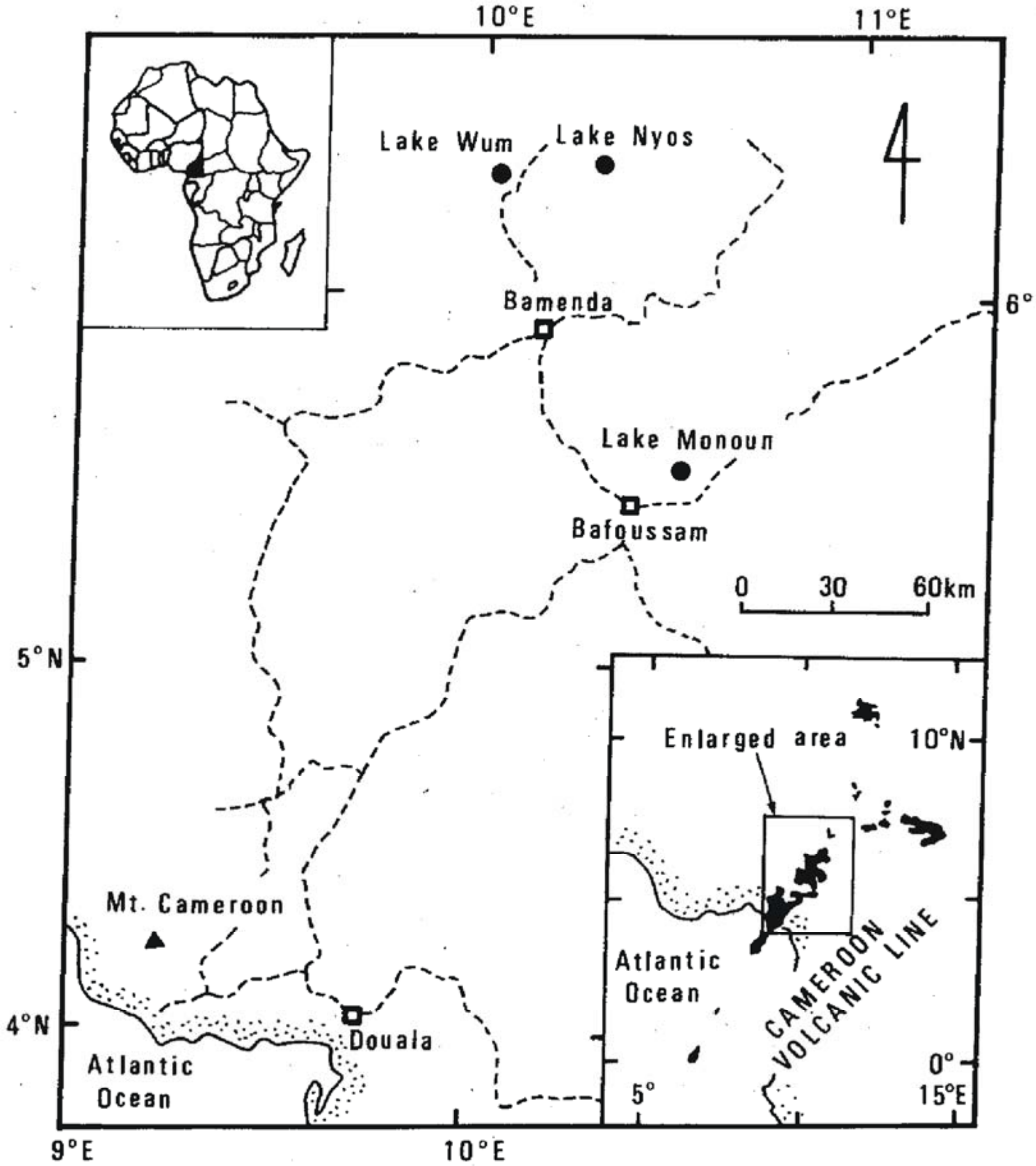

Figure 35. Index map showing localities of Lake Nyos and Lake Monoun in northwestern Caeroon, West Africa. The inset shows the Cameroon volcanic line (Kusakabe et al., 1989).

Disaster relief mission teams from various countries, including US, UK, France, Germany, Japan, Italy and Switzerland, were sent to Lake Nyos. Most teams included volcanologists, specifically volcanic gas experts, because the news reports indicated that a large scale volcanic gas disaster had occurred there. The news coverage probably reflected the initial "phreatic explosion hypothesis" of Dr. Haroun Tazieff, a famous French volcanologist (Tazieff, 1989). A Japanese scientific mission was sent to Cameroon in October 1986 to conduct the lake surveys on Lake Nyos and Lake Monoun. One and a half months after the gas release at Lake Nyos, deep water turbidity was less than at the surface, indicating that the lake sediment had not been agitated recently. There was no indication of the soluble component of volcanic gases in the lake water, such as chloride (Cl^-) or sulphate ions (SO_4^{2-}), and CO_2

contentrations were found to increase with depth and a large amount of CO_2 gas remained in the deep water mass, even at the time of the survey.

Based on this geochemical evidence, Kusakabe *et al.* (1989) concluded that the gas eruption was not caused by the phreatic eruption penetrating the bottom of the Lake, but by a large amount of self-accelerating spontaneous gas exsolution from the lake water. After these scientific surveys on the Lake Nyos case, the self-accelerating spontaneous gas exsolution process was named "limnic eruption". A thermodynamic and fluid dynamic understanding of the process was presented by Zhang (1996), where the dynamics of a CO_2-driven lake water eruption was analyzed by deriving an equation of state for gas-liquid mixtures. Zhang found that under certain conditions these eruptions can be violent: the lake-surface exit velocity of an initially gas-saturated water may reach 89 m/s for Lake Nyos and 51 ms^{-1} for Lake Monoun. Thus, the violent limnic eruption witnessed in both Cameroonian lakes was confirmed by theoretical analyses requiring only a gas exsolution mechanism without a volcanic eruption.

At an international meeting on the Lake Nyos disaster, held in Yaounde, Cameroon in 1987, two hypotheses were proposed to explain the cause of large scale CO_2 gas release from the lakes, the "phreatic eruption" and "limnic eruption". In the former hypothesis, CO_2 was emitted as a "jet" from beneath the lake floor, through the 200 m water column and the lake played only a passive role. The mechanism of the disaster would be similar to the case of the Dieng Plateau, Java, Indonesia, 1979 (Le Guern et al., 1982). On the other hand, in the "limnic eruption" hypothesis, the gas burst was due to rapid exsolution of CO_2 that had been stored in the lake's hypolimnion. If the latter were the case, we would have the chance to forecast and mitigate future disastrous events. The meeting was the start of planning the mitigation strategy. Thereafter, over 15 years regular surveys on Lake Nyos and Lake Monoun were carried out which further supported the "limnic eruption" hypothesis and led to the successful "benign gas release" remediation programme (Halbwachs, 2001).

3.4.2.1 Bathymetry

Lake Nyos is a deep volcanic crater lake with a surface area of 1.8 km^2, a flat bottom, and a maximum water depth of 208 m. The first bathymetric map of Lake Nyos was presented by German limnologist (Hassert, 1912) who plumbed its depth. In 1988, Nojiri *et al.* (1993) carried out 15 lines of profiling of the lake bottom topography using a seismic profiling system and constructed a new bathymetric map. A north-south elongated asymmetric morphology, having a steeper wall in the western part of the lake, was revealed. The compiled bathymetric map is illustrated in Figure 36, showing shallow shelves (0 – 50 m deep) developed in the northern, eastern and southern part of the lake. The depth-area relationship shown in Table 3.1 was calculated from the contour map. A comparison of the calculated total volume by various authors is given in Table 3.2.

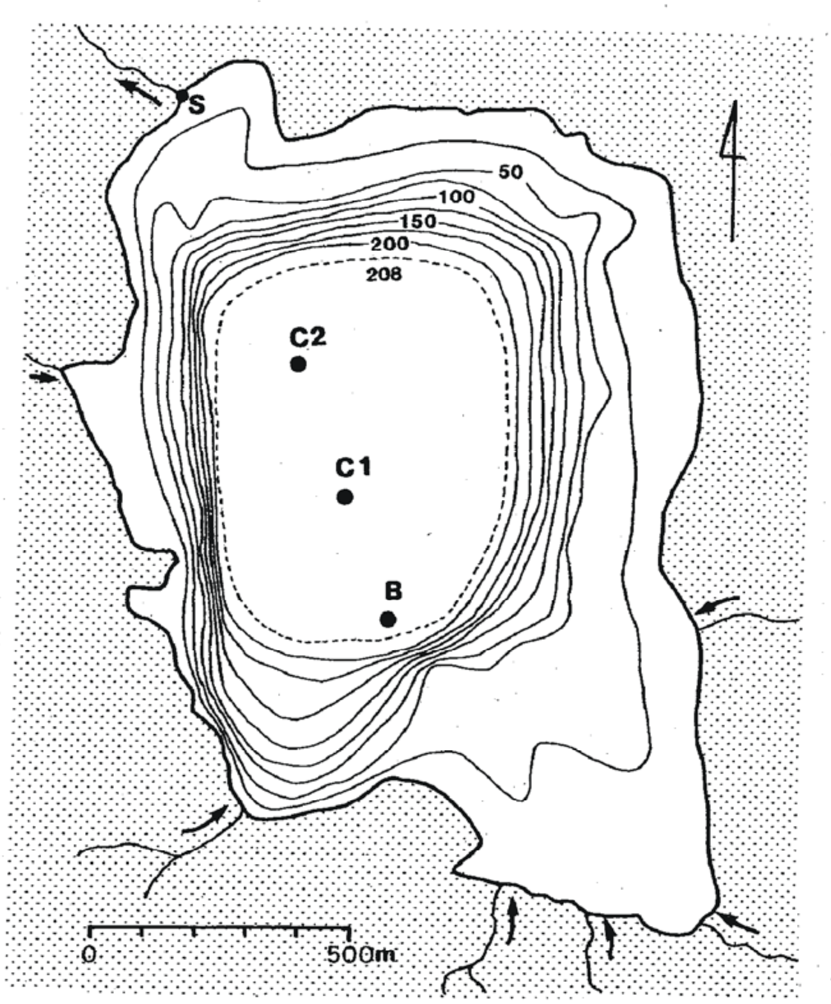

Figure 36. Bathymetric map of lake Nyos (Nojiri et al., 1993).

Table 3.1 Depth-area relationship for Lake Nyos.

Depth (m)	Area (km^2)
0	1.58
25	1.03
50	0.80
75	0.69
100	0.63
125	0.58
150	0.54
175	0.49
200	0.44
208	0.33

Lake Monoun is also a maar type crater lake and both the craters belong to the northeast-southwest trending 1,600 km long Cameroon volcanic line (Fitton, 1983) near the Cameroon-Nigeria border. Lake Monoun, is 1.5 km across east to west and 0.5 km north to south, and is also up to 100 m deep.

These crater lakes were created by the activity of geologically very young monogenetic basaltic volcanoes. Professor Aramaki described the formation of Lake Nyos as follows (Kusakabe *et al*. ,1989):

Lake Nyos appears to have formed by a series of phreatomagmatic eruptions occurring in the southern part of a north south trend of fissure vents. At least two scoria cones were formed in the higher altitude southern region, while in the northern, lower altititude area, a series of hydrovolcanic craters produced a depression which forms the present Lake Nyos. Complex, cross-cutting pyroclastic surge deposits around the lake indicate the presence of multiple vents possibly aligned along the fissure. At Malam Jae's home (which stands 150 m above the southern shore of the lake) conspicuous laminae of surge deposits are exposed, showing the high reach of the surge cloud.

The ejecta from Lake Nyos consists of augite-olivine basalt lapilli and lithic fragments such as granitic rocks and spinel lherzolite. The basalt is very heterogeneous in groundmass texture as well as in the kinds of xenolith and xenocryst.

Table 3.2. Estimate of the lake water volume of Lake Nyos

Volume (km^3)	Reference
0.150	Nojiri *et al.*, 1993
0.159	Hassert, 1912
0.176	Kling *et al.* 1989
0.128	Kanari, 1989
0.153	Freeth 1990
0.162	Tietze 1992

3.4.2.2 Lake water sampling

Collecting deep water samples from these lakes was difficult because the CO_2 content was high enough for free gas to exsolve inside the water sample bottle during the sample collection. This resulted in a loss of part of the sampled gas and/or water as the lid of the sample bottle was forced open due to the internal gas pressure before the bottle reached the lake surface. The first attempt to collect complete samples was made in Lake Nyos by the Japanese scientific mission (Kusakabe *et al.* 1989). They were able to collect the deep waters without losing the exsolved CO_2 by introducing the gases into a plastic bag attached to the Niskin water sampler (Figure 37). A more accurate technique was adopted for total CO_2 analysis in a 1988 survey on Lake Nyos (Kusakabe *et al*. 1990), with which total CO_2 could be fixed in situ into a sodium hydroxide solution that had been placed in the syringe.

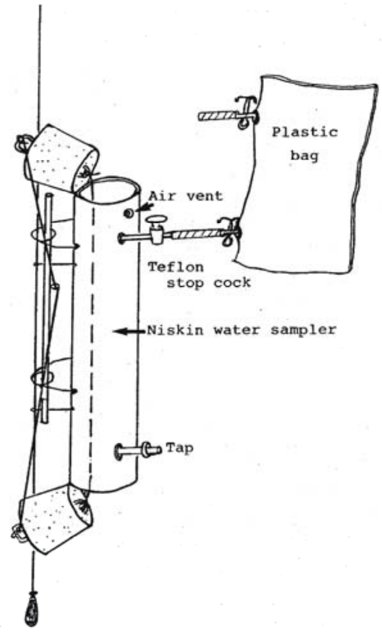

Figure 37. Niskin water sampler with a plastic bag to accommodate the gases exsolved from deep waters. Air in the bag was pumped out as much as possible before sampling.

3.4.2.3 CHEMICAL COMPOSITION

Table 3.3 shows the chemical composition of deep waters of Lake Nyos and Monoun in December 2001 (Kusakabe, 2002). The lake waters are characterized by high concentrations of dissolved species; major cations are Mg^{2+}, Ca^{2+} and Fe^{2+}, and anions are overwhelmingly dominated by the bicarbonate ion (HCO_3^-), though the concentration of total dissolved carbon is much higher than that of HCO_3^-, indicating the presence of H_2CO_3 or CO_2(aq) as additional major chemical species.

Table 3.3 Chemical composition of Lake Nyos and Monoun in December 2001.

Depth m	Temp.	Electric Cond. micros/cm	pH	Na^+ mg/L	K^+ mg/L	NH_4^+ mg/L	Mg^{2+} mg/L	Ca^{2+} mg/L	Fe^{2+} mg/L	Mn^{2+} mg/L	SiO_2 mg/L	Cl^- mg/L	NO_3^- mg/L	SO_4^{2} mg/L$^-$	HCO_3^- mg/L	CO_2(aq) mg/L
Lake Nyos																
165.0	23.604	1008	5.26	18.2	4.1	8.6	64	46	87	1.8	62	0.66	0.44	<0.05	739	5950
170.5	23.680	1025	5.26	17.6	4.2	8.3	65	46	92	1.7	63	0.63	0.11	<0.05	753	6110
175.0	23.765	1043	5.26	17.8	4.5	8.3	68	47	93	1.7	65	0.58	<0.10	<0.05	772	6310
177.5	23.861	1065	5.21	18.4	5.2	8.3	69	47	93	1.7	65	0.62	0.21	<0.05	781	6600
180.0	23.986	1098	5.23	18.5	4.9	8.4	73	49	97	41.8	69	0.63	0.15	<0.05	818	7120
182.5	24.142	1134	5.21	19.2	5.6	8.5	76	50	98	1.8	71	0.63	<0.10	<0.05	836	7780
185.0	24.354	1181	5.18	19.8	5.2	8.9	80	53	104	1.8	72	0.59	0.22	<0.05	886	8840
187.5	24.669	1299	5.11	21.4	6.0	9.5	87	58	116	1.9	75	0.74	0.20	<0.05	969	12350
190.0	25.036	1425	5.04	24.9	7.2	11.3	99	66	140	2.1	83	-	0.33	<0.05	1121	-
195.0	25.178	1444	5.04	24.4	6.4	10.7	100	67	144	2.1	84	0.70	<0.10	<0.05	1134	14980
200.0	25.200	1452	5.04	24.8	6.8	10.9	101	67	146	2.1	83	0.73	0.18	0.06	1148	14920
205.0	25.230	1474	5.04	24.8	6.4	10.5	101	66	148	2.2	82	0.79	<0.10	<0.05	1150	14690
208.0	25.377	1678	5.09	25.4	6.6	11.4	107	68	180	2.4	90	0.71	0.24	<0.05	1257	-
Lake Monoun																
35.0	21.601	1834	6.00	18.6	4.0	17.4	27	33	531	4.1	91	1.55	<0.10	0.19	1517	2340
45.0	22.051	1902	5.93	18.4	3.8	17.2	25	33	523	4.0	89	1.71	<0.10	0.25	1487	2880
55.0	23.100	2273	5.79	23.9	14.9	27.7	32	48	702	4.8	116	2.31	0.20	<0.05	2009	7000
60.0	23.280	2306	5.76	24.1	4.9	27.9	32	48	697	4.8	116	2.42	0.23	<0.05	2003	7240
65.0	23.298	2308	5.61	23.9	4.9	27.8	32	48	695	4.8	114	2.55	<0.10	<0.05	1997	6990
70.0	23.305	2308	5.61	23.9	5.4	28.1	32	48	711	4.9	115	2.33	<0.10	<0.05	2033	6880
85.0	23.309	2309	5.61	24.4	5.8	28.9	32	49	688	4.8	115	2.42	<0.10	<0.05	1991	6860
95.0	23.517	2466	5.60	2.2	5.6	36.2	34	51	867	6.1	125	2.58	<0.10	<0.05	2425	6630

In both lakes, the dissolved carbonate system is controlled mainly by the equilibrium, $H_2CO_3 = H^+ + HCO_3^-$. In addition, since over 99.8% of the total molar equivalent anion concentration is occupied by HCO_3^-, it carries half of the measured electrical conductivity. Hence, the free carbon dioxide content (H_2CO_3) profile can be calculated using the profiles of H^+ (pH measurements) and HCO_3^-, which have a linear relationship with the electric conductivity of the lake waters. Kusakabe *et.al.* (2002) determined the relationship between the measured and calculated H_2CO_3 contents, as shown in Figure 38. Based on this monitoring data, Kusakabe *et.al.* (2002) determined the evolution with time of temperature, electrical conductivity (at 25°C) and CO_2 profiles at Lake Nyos after the 1986 gas disaster (Figure 39).

We can identify the chemoclines at the depths of 50.5 m and 188 m in Lake Nyos at present. The striking feature of the profiles is the evolution with time of temperature, electric conductivity and H_2CO_3 concentration in the bottom water at depths below 180 m, indicating a common source of heat, salinity and CO_2, most probably derived from the CO_2-rich spring with high salinity at the lake bottom. Kusakabe *et al.* (2000) estimated the supply rate of CO_2 at the bottom of Lake Nyos from the time evolution of the CO_2 profiles and concluded that the present rate of CO_2 supply to the lake water is 100 ±50 x10^6 mole/yr (4400 tonnes per year).

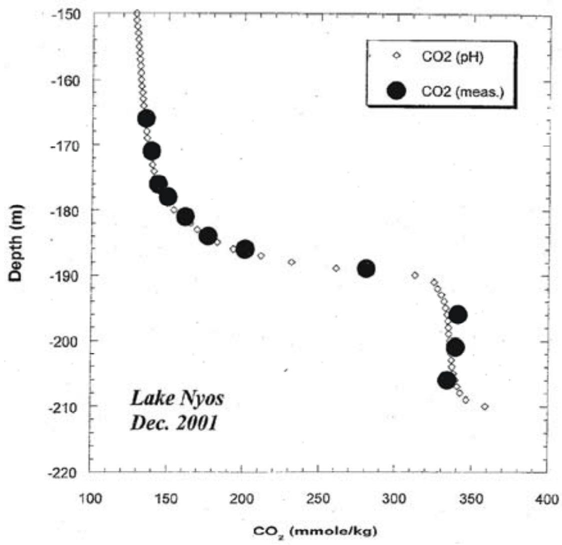

Figure 38. Comparison between the measured and calculated CO_2 concentrations at Lake Nyos in December 2001 (Kusakabe, 2002).

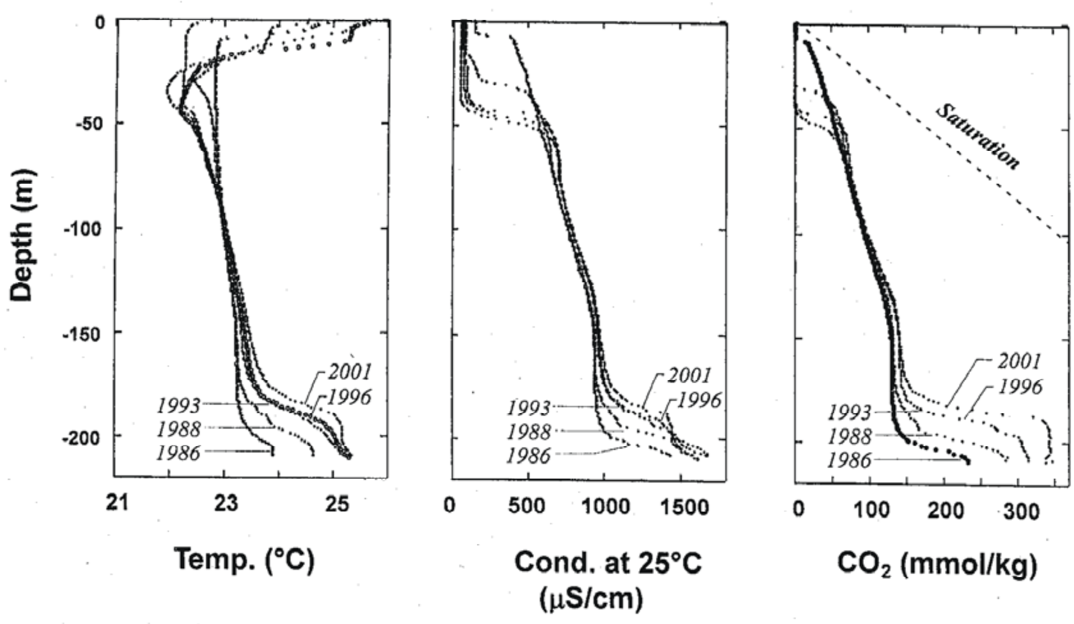

Figure 39. Evolution with time of temperature, electrical conductivity (at 25 °C) and CO_2 profiles at Klake Nyos after the 1986 gas disaster (Kusakabe, 2002).

3.4.2.4 ESTIMATION OF TOTAL GAS VOLUME ERUPTED FROM LAKE NYOS IN AUGUST 1986

Based on the CO_2 content observed in the lake waters of Nyos and Monoun in October 1986, Kusakabe *et al.*(1989) estimated the maximum possible volume of CO_2 erupted during each event. For Lake Nyos, it is estimated that 0.63 km^3 at standard temperature and pressure (STP) or 1.24 Mt of CO_2 were emitted, whereas Lake Monoun could have emitted 0.024 km^3 (STP) or 47,000 t of CO_2. The former value is not inconsistent with the estimated gas volume of 1 km^3 spread over the damaged area, given by French scientific team, on the basis of the three-dimensional distribution of the human fatalities and dead cattle in the area (Tazieff *et al.,* 1986).

3.4.2.5 ORIGIN OF CO_2

A compilation by Kusakabe (2002) of isotopic data of the dissolved gases from Lake Nyos, Lake Monoun, Lake Kivu and others are given in Figure 40, and indicate that these CO_2 gases are mainly derived from the mantle and mixed with a small amount of air and the gas of limestone decomposition. Kusakabe and Sano (1993) discussed the process of CO_2 accumulation in conjunction with basaltic magma properties as follows:

It was proposed by Chivas *et al.* (1987) that expansion of high-density CO_2 fluid at the Earth's surface is responsible for the formation of some maars. Mount Gambier, South Australia is an example of a recent maar volcano which was formed in this way. A similar formation mechanism of the Lake Nyos maar has been suggested by Lockwood and Rubin (1989) who believe that considerable amount of CO_2 from the initial eruption (maar formation) may still be trapped in the highly permeable diatreme deposit beneath Lake Nyos. Accumulation of CO_2 near the Earth's surface results from preferential exsolution of a CO_2-rich fluid from an ascending magma due to low solubility of CO_2 in basaltic melts at low pressures (Sloper and Holloway, 1988). The variation in H/C and S/C ratio of the Kilauean and Icelandic volcanic gases is found to increase generally with time following a path which can be expected when only CO_2 is removed from the original gases (Gerlach, 1983). Such preferential outgassing of CO_2 from a sustained magma at a shallow level has been demonstrated form compositional variation of gases in basaltic magmas of Kilauea (Gerlach and Graeber, 1985).

They claimed that it is probable that magmatic CO_2 and other insoluble gases, originally present in the silicate melt, can accumulate at a shallow depth in the Earth's crust. This process might also be applicable to the Okinawa-trough, where CO_2-rich fluid forms a clathrate-hydrate following in situ reaction with seawater (Sakai *et. al.* 1990). Based on the low temperature phase relations for the CO_2-H_2O system (Takenouchi and Kennedy, 1965) shown in Figure 41, Kusakabe and Sano (1993) suggested that liquid CO_2 (the 1°C per 100 m geotherm) or supercritical CO_2 (the 5°C per 100 m geotherm) will migrate upward due its buoyancy to reach the bottom of Lake Nyos. Here it leaked into the bottom of the lake at a slow rate, allowing it to dissolve and increase concentration in the bottom waters.

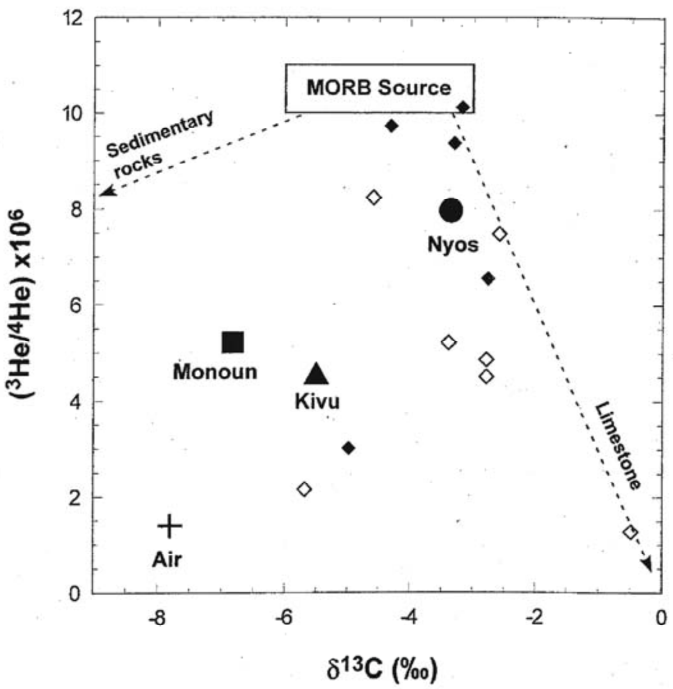

Figure 40. A plot showing $^3He/^4He$ ratio and $\delta^{13}C$ values of dissolved gases in the lakes Nyos, Monoun and Kivu and soda springs from the Cameroon Volcanic Line

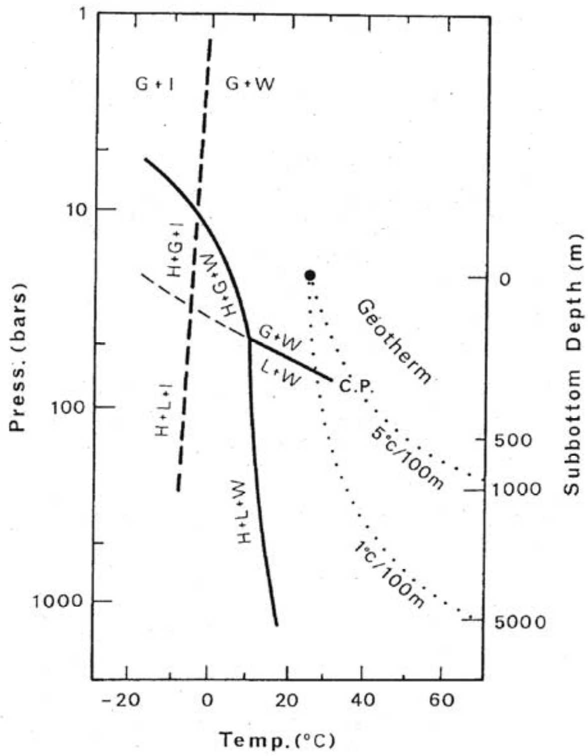

Figure 41. Phase relations in the CO_2-H_2O system. H=CO_2 hydrate, L=liquid CO_2, G= gaseous CO_2, W=liquid water and I=ice. C.P. indicates the critical point of CO_2 (31.1°C and 73.4 bar). Geotherms with different thermal gradients, starting from the lake bottom P/T conditions, are shown by dotted curves.

3.4.2.6 Density profiles in the lakes

The density effect of solutes in water can be explained in terms of the partial molar volume of solute components, *i.e.* cations, anions and neutral species such as free CO_2 (Kusakabe *et al*., 1989). Cations and anions are in approximate equilibrium in both Nyos and Monoun lakes and the water density stratification depicted in Figure 42 is due to the residual effect of free CO_2. The free CO_2 density effect was large enough to override the thermal expansion effect.

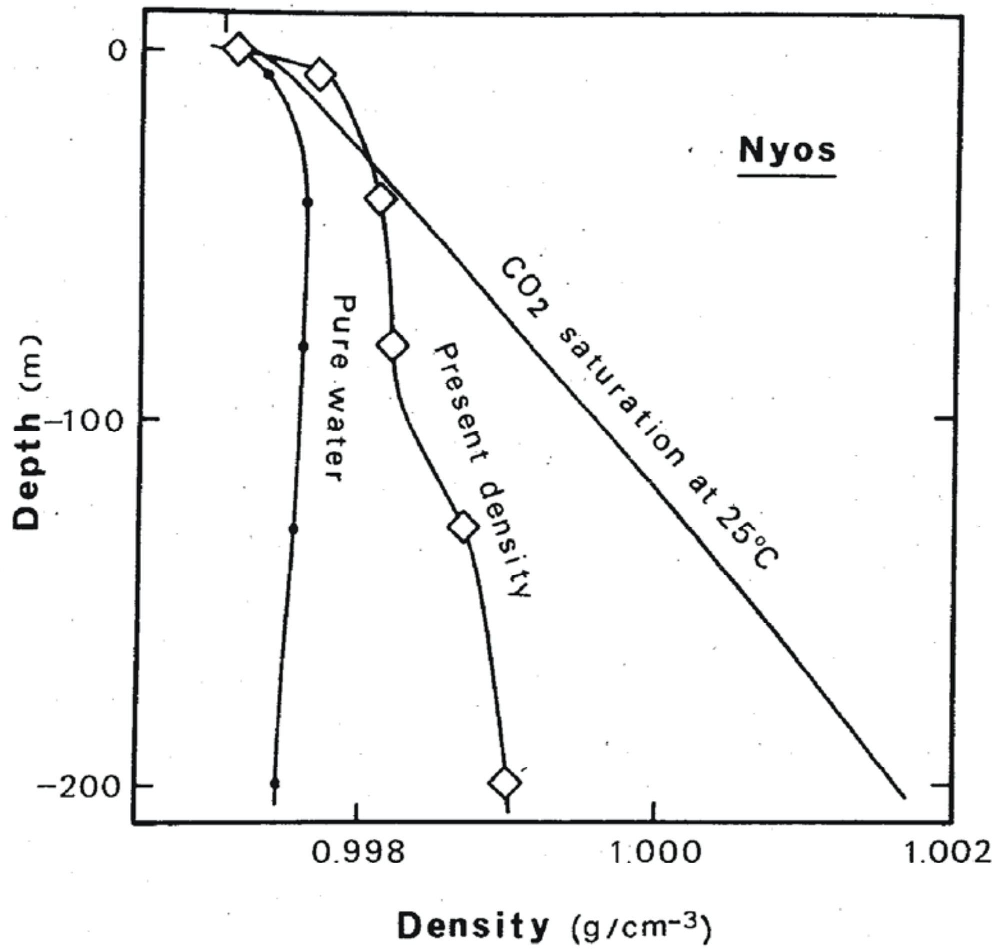

Figure 42. Density profile of October 1986 at Lake Nyos calculated from temperature distribution, chemical composition and partial molal volume of the dissolved species (Kusakabe et al., 1989).

Comparisons between the solute gas pressure and the hydrostatic pressure (Table 3.1) shows that the deepest water of Lake Nyos contains 340mM of free CO_2, which could be interpreted as a CO_2 fugacity (f_{CO2}) of 10.71 bar using the modified Henry's law (Weiss, 1974);

$$[CO_2] = K_0 \ f_{CO2} \ exp \ [\ (1\text{-}P) \ v'_{CO2} / \ \mathrm{RT} \ ]$$

where $[CO_2]$ is the molar concentration of dissolved CO_2 in the deepest lake water, K_0 is the modified Henry's law constant of CO_2, P is the total pressure and v'_{CO2} is the partial molar volume of CO_2 (= 31.0 cm^3/mole, Ohsumi *et al.,* 1992). Evans *et al.* (1993) used a pressure probe (a gas permeable silicone tube connected via steel tubing to a pressure transducer) for dissolved gas partial pressure measurements. With this technique, recent measurements at 198 m depth at Lake Nyos shows a CO_2 partial pressure of about 13 bar, which is over 60% of the bottom hydrostatic pressure (21 bar). The difference between observed gas partial pressure (13 bar) and calculated CO_2 partial pressure is attributed to the methane content, which has a lower solubility than CO_2. Kusakabe (2002) presented CO_2 profiles at Lakes Monoun, Nyos, and Kivu (Figure 43). The common feature among these three cases is that water is well mixed below the chemocline (a shoulder of the CO_2 content profile). At Lake Monoun the shoulder almost reaches the CO_2 saturation curve, which means that small external turbulences could make the stratification unstable.

Figure 43 shows that the bottom layer in Lake Nyos is similar to those in Lakes Monoun and Kivu. To predict gas outbursts in these lakes therefore requires an understanding of the development of the density structure.

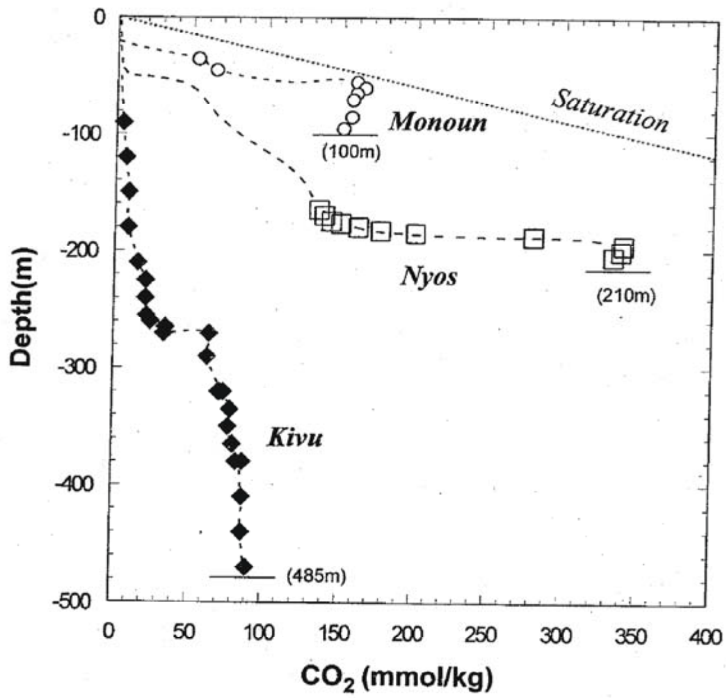

Figure 43. CO_2 profiles at Lakes Monoun, Nyos, and Kivu. The data for Lakes Monoun and Nyos represent those in December 2001. The data for Lake Kivu were taken from Tietze et al. (1980).

3.4.2.7 Trigger for the gas outburst

Reliable witnesses suggest that the gas outburst at Lake Nyos probably lasted a few hours. Damage to vegetation on the lake shore was caused by large waves resulting from the outburst. This may have been exacerbated by the seiche phenomenon - the resonant oscillation of the water within the lake. No earthquakes were observed associated with the gas outbursts at either Lake Nyos or Lake Monoun. The most persuasive explanation of the trigger for the gas outburst in the Lake Nyos case is that the long period of cloudy days before the event resulted in the formation of a significant mass of cold water which then sank and disturbed the stratification of the lake.

3.4.2.8 Conclusions

A massive release of cold CO_2 over several hours, with a typical scale of several tens of thousand tonnes of gas, occurring in a populated area, could result in a disaster such as the Cameroonian cases. This requires a trap and accumulation mechanism, combined with sudden explosive release to the surface free water body. However, tropical lakes without a seasonal overturn provide the only documented cases. In higher latitudes, seasonal lake overturns (where the water body is mixed as surface waters heat up during the summer and cool down during the winter) may prevent the build-up of CO_2-saturated bottom waters. Direct release of pure CO_2 into the deep part of the water body, driven by its buoyancy, might result in some dissolution of CO_2. In the crater lake cases in Cameroon, a conduit, (diatreme) associated with the volcanism, provided a permeable path for CO_2 into the lake water.

4 Some Current Underground CO_2 Storage Sites

4.1 INTRODUCTION

This chapter very briefly describes some current man-made CO_2 storage operations. It is intended to give a flavour of the sort of projects that are likely to develop in the next few years.

From a potential leakage perspective, these operations have a number of features in common:

- They are all in sedimentary basins, large stable areas where reservoir rocks are commonly found, interbedded with low permeability fine-grained rocks that form seals. Oil and natural gas fields are found in many sedimentary basins, proving the reservoir rocks can retain fluids for very long periods of time (thousands to millions of years).
- They all involve storing CO_2 in the pore spaces between the grains of porous and permeable sedimentary rocks.
- They are all at depths of over 800 metres. At about this depth reservoir temperatures are typically such that the CO_2 will be held in the reservoir in the supercritical phase. Supercritical fluids have gas-like properties but liquid-like densities, which means they will occupy less space in the subsurface.

Three of the four operations described below already are, or will be, associated with major research projects. These projects all have approximately the same objectives. In essence, they aim to characterise the site and surrounding area, create geological and numerical models of the site, simulate the injection of CO_2 at the site, simulate the migration of CO_2 during and after the injection period, monitor the distribution of CO_2 during the injection process and use the results of the monitoring and other data acquisition opportunities to iteratively improve the models. Additional activities such as risk assessment may also be undertaken.

Three of the four projects described below are in oil or gas fields, where fluids have remained trapped probably for millions of years prior to the start of CO_2 injection. The fourth is in a saline water-bearing reservoir rock that did not previously contain gas. Possible leakage from the reservoir has been detected at only one site - Rangely. The estimated mass and nature of the leakage is described below. The oldest site is Rangely, where CO_2 injection started in 1986. The Sleipner project has been injecting CO_2 since 1996, the Weyburn operation started injecting in 2000 and at In Salah, injection started in 2005.

In addition to those described, up to commercial 48 acid gas (H_2S and CO_2) injection projects have been undertaken in the Alberta Basin of Western Canada, of which 41 are still active (Bachu and Haug, 2005). From 1989 to 2003, approximately 2.5 Mt of CO_2 and 2 Mt of H_2S have been injected into deep saline formations (26 sites) and depleted hydrocarbon reservoirs (18 sites) in western Canada. Reservoir depths, which are both carbonate and siliciclastic, vary between 1100 and 2300 m.

4.2 THE SLEIPNER PROJECT, NORTH SEA, OFFSHORE NORWAY

4.2.1 Project description

The Sleipner gas field complex is situated in the centre of the North Sea, in the Norwegian sector, close to the UK/Norway median line (Figure 44) and approximately 200 km from land. The main fields in the complex are Sleipner Vest (West) and Sleipner Ost (East). Both are gas fields.

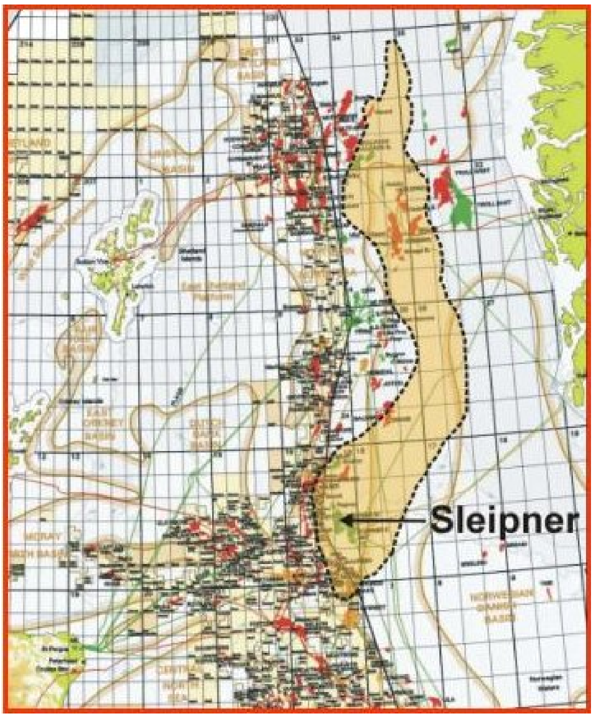

Figure 44. Map showing the location of the Sleipner West gas field, North Sea and the distribution of the Utsira Sand reservoir into which the carbon dioxide is injected.

The Sleipner West field lies closest to the centre of this part of the North Sea basin. Its reservoir is in the Hugin Formation and is of Middle Jurassic age. The Sleipner West natural gas reservoir is faulted, with different pressure regimes and different fluid properties in the various fault blocks. The natural gas in the reservoir includes between 4% and 9.5% CO_2 (Korbul & Kaddour, 1995; Baklid, Korbul & Owren, 1996).

The Sleipner East field lies further towards the eastern basin margin and the main reservoir is the Palaeocene Heimdal Formation. This reservoir contains around 0.3% CO_2 (James, 1990).

To get the natural gas to saleable quality, the amount of CO_2 has to be reduced to 2.5% or less. In order that the gas can be exported through the Zeepipe export pipeline to Zeebrugge, which passes through Sleipner, this operation is carried out offshore. The gas from Sleipner West is produced via 18 production wells drilled from a wellhead platform (Sleipner B) and transported to a process and treatment platform (Sleipner T) connected to the main Sleipner A platform (Figure 45).

Figure 45. The Sleipner Platforms. The platform on the left is the Sleipner T gas-processing platform, where the CO_2 from the Sleipner west field is separated from the methane. The concrete-legged platform on the right is the main Sleipner A production platform from which the CO_2 is injected underground via a 3 km long deviated well, see Figure 46. (Photo Statoil).

Around 1 million tonnes of CO_2 is separated from the natural gas annually. This amounts to some 3% of total Norwegian CO_2 emissions. CO_2 injection started in August 1996 and will continue for the life of the field. Rather than vent this CO_2 to the atmosphere, the operators of the field, Statoil, and partners took the decision to store it underground in the Utsira Sand. This is a sandstone reservoir approximately 150 – 200 m thick, at a depth of between 800 and 1000 m (Figure 46).

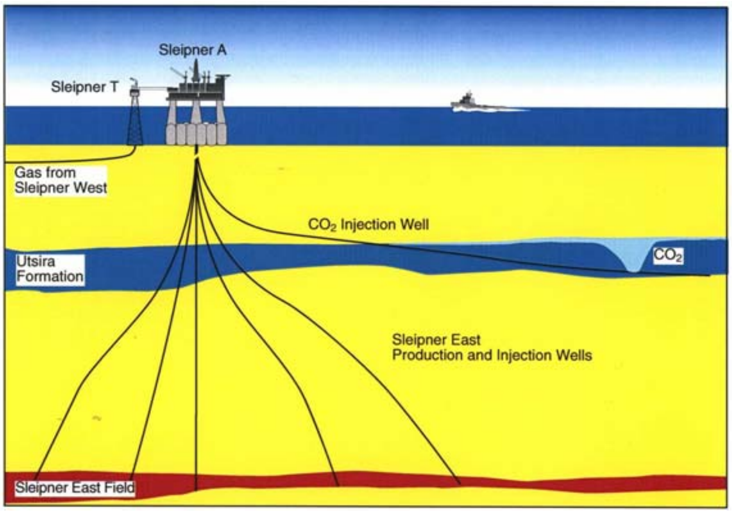

Figure 46. Diagrammatic cross-section through the Sleipner CO_2-injection project (courtesy of Statoil). Gas is brought in to the Sleipner T platform from the Sleipner West gas field and the CO_2 is removed by an amine stripping process. It is then sent to the Sleipner A platform where it is compressed and injected into the Utsira Sand via a 3 km-long deviated well.

A series of demonstration projects (the former SACS and SACS2 projects and the current CO2STORE project), jointly funded by successive EU Framework Programmes, industry and national governments, was initiated shortly after injection started and have been monitoring and evaluating the geological aspects of the subsurface storage operation ever since. These projects have characterized the site and surrounding area (Chadwick et al., 2004; Zweigel et al., 2005), built geological, geochemical and numerical reservoir models to simulate CO_2 migration within the reservoir and predicted the future performance of the site. They are also monitoring the subsurface dispersal of the CO_2 within the reservoir using time-lapse seismic techniques (Arts et al., 2001, Pearce et al., 2001; Lindeberg et al., 2001 and Chadwick et al., 2004a, 2004b, 2005). The monitoring results are "history matched" to the predictive models, to improve performance prediction and identify what further geological data is needed to help improve and verify the models. Seismic and reservoir modelling is currently being used to more accurately verify independently the mass of CO_2 in the reservoir and predict its future behaviour.

4.2.2 Caprock

At the injection site, the caprock consists of two parts; firstly a lower unit consisting of more than 100 m of shales, the "Lower Seal" that immediately overlies the reservoir, and secondly the remainder of the strata above the Lower Seal (the Middle and Upper Seal) which also appear to consist dominantly of mudstones or silty mudstones (Figure 47). These strata effectively prevent the CO_2 from leaking back to the seabed and thus to the atmosphere.

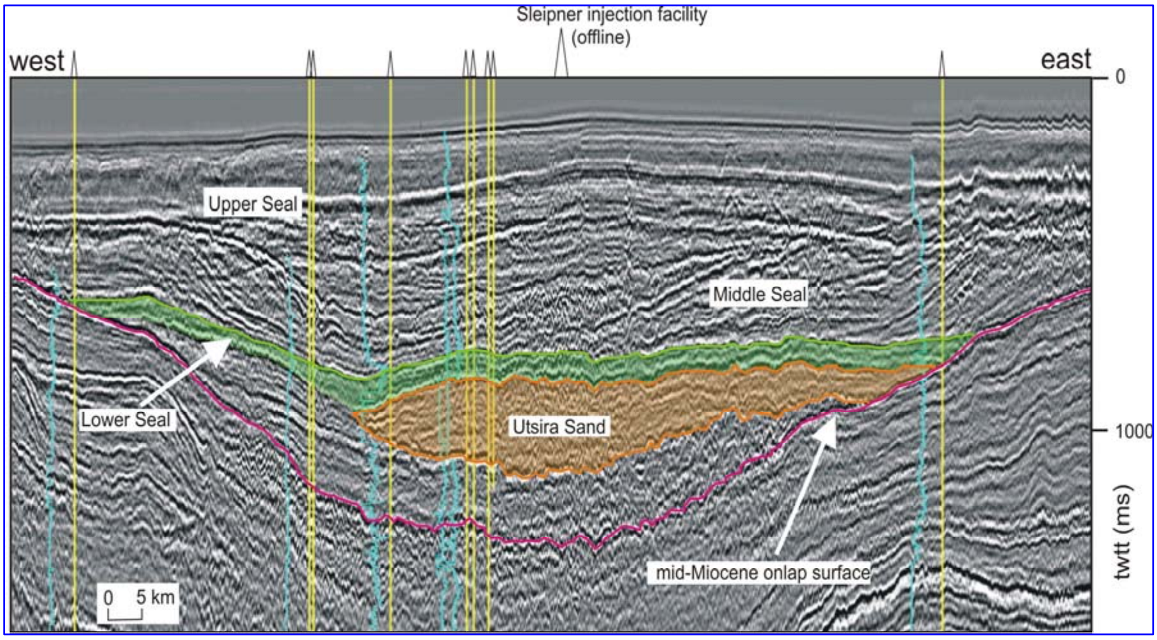

Figure 47. E-W Seismic profile in the centre of the North Sea showing the Utsira Sand and its overlying cap rocks. Vertical exaggeration approximately x 55. Seismic data courtesy of WesternGeco.

A core has been taken from the lower Seal in a nearby well. This has a permeability of less than 0.001 millidarcies, which means it is an effective cap rock, provided there are no through-going fractures. There is no evidence of faults or fractures in the cap rock above the injection site on seismic surveys and no evidence that CO_2 is leaking from the storage reservoir on any of the seismic surveys, the latest of which was acquired in 2002, some six years after injection started (Arts et al., 2004).

4.2.3 Reservoir

The reservoir rock itself is approximately 200 m thick around the injection point. A core taken in a nearby well consists predominantly of poorly cemented loose sand, which contains a few shell fragments (Figure 48).

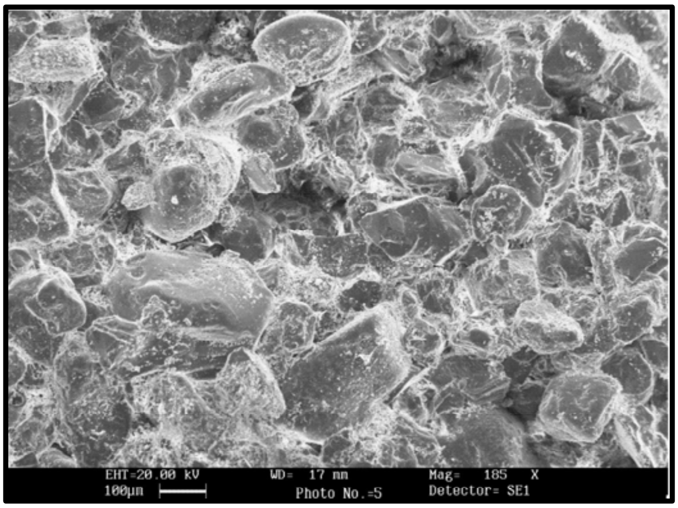

Figure 48. SEM image of the Utsira Sand

The Utsira Sand has a permeability of about 1-3 Darcies and an estimated porosity of 35-40%. Interbedded with the sand are a number of relatively thin mudstone horizons typically around a metre but up to 5 metres thick. None of these are present in the core but they are clearly identified on well logs in nearby wells (Figure 49).

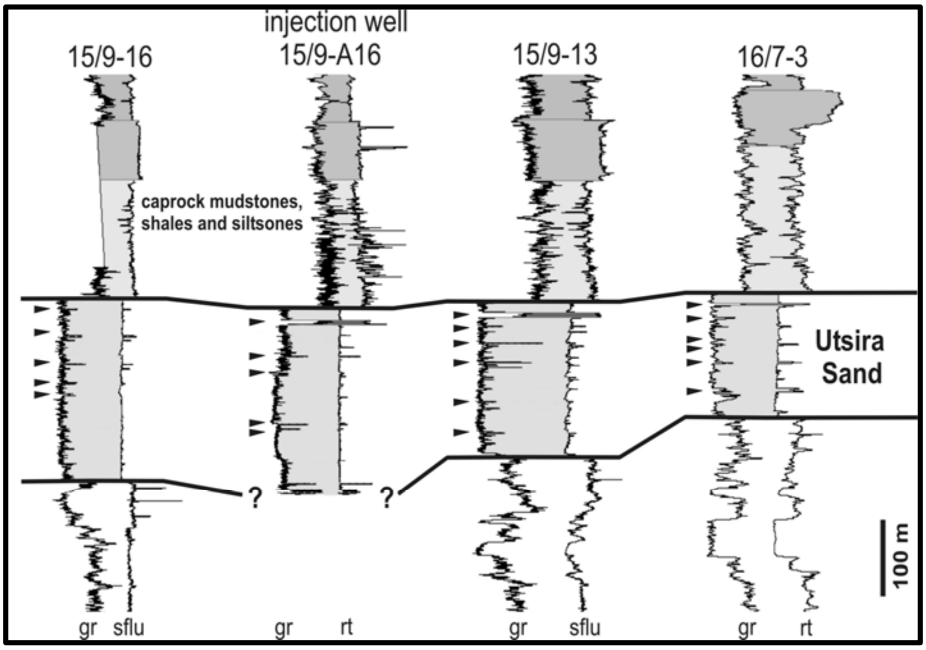

Figure 49. Well logs through the Utsira Sand and overlying strata near the injection point. Note the thin shale beds (arrowed) including the thicker, more continuous shale bed near the top of the reservoir sand.

The lateral continuity of the thinner shale beds is probably low, because they do not obviously correlate between adjacent wells, However, one near the top of the reservoir appears to be continuous across the injection site and the immediately surrounding area.

The injection point is close to the base of the Utsira sand, which behaves as an infinite aquifer; fluid is being displaced from the pore spaces above the injection point without a significant pressure increase measurable at the wellhead.

The pressure and temperature at the top of the reservoir are estimated to be 8.6 MPa and 29°C respectively, suggesting that the CO_2 is in supercritical phase and has a density of about 744 kg/m^3 at the top of the reservoir. There is significant uncertainty in the temperature (and hence density) estimates however.

4.2.4 Monitoring programme

A series of 3D seismic surveys have been acquired over the injection and storage area (Figure 50). The first of these was acquired in 1994, prior to any CO_2 injection. The subsequent surveys were acquired as injection progressed between 1999 and 2002. The clear difference in reflectivity between the baseline survey acquired in 1994 and the later surveys is due to the presence of CO_2 in the pore spaces of the reservoir rock.

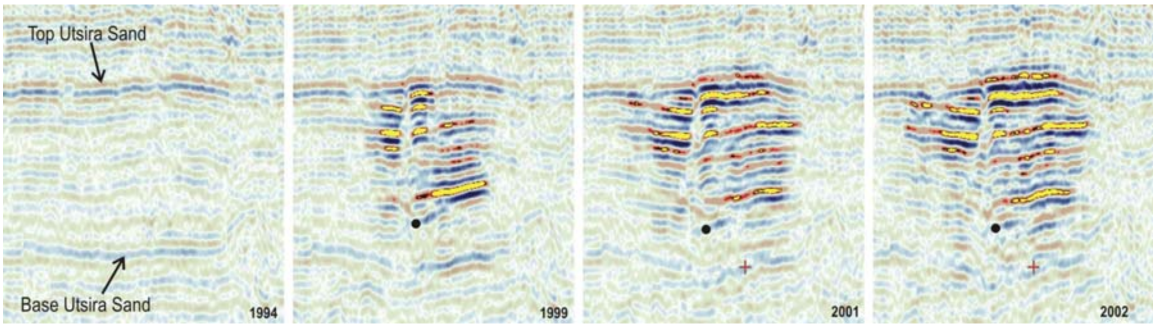

Figure 50. Time-lapse seismic profiles through the Utsira Sand and CO_2 plume at the Sleipner CO_2 injection site. The black dot marks the location of the injection point. Seismic data shown courtesy of SACS and CO2Store.

Many further details can be seen within the plume of CO_2, e.g.:

- The CO_2 has spread out laterally from the injection point in a series of discrete layers. It is thought that these layers are trapped beneath the thin shale beds within the reservoir.
- There is a central chimney of CO_2 rising through the middle of the plume to the base of the cap rock. This is thought to contain relatively high CO_2 saturations and act as a conduit by which CO_2 reaches the top of the reservoir. It appears to pass through the thin shales within the reservoir.
- The CO_2 has penetrated through the ~5m thick shale layer near the top of the reservoir.

Modelling of the plume indicates that the average permeability of the thin shales found within the reservoir is many times greater than the measured permeability of the cap rock core. A possible inference from this is that the thin shale beds within the reservoir are discontinuous or heterogeneous on a very local scale or contain fractures that dramatically increase effective permeability.

The 2002 seismic survey indicates that the CO_2 is migrating northwards from the injection point, as predicted by seismic mapping of the upper surface of the reservoir.

Long term simulations of the injection site suggest that the CO_2 plume will gradually (over hundreds of years) dissolve into the native pore fluid (a brine with approximately the same salinity as sea water). The resulting CO_2-saturated brine is approximately 1% denser than the native pore fluid, so simulations predict that it will slowly sink through the reservoir and accumulate at its base. Once this has happened there will be little if any chance of CO_2 leakage back to the atmosphere.

4.3 THE IN SALAH PROJECT, ALGERIA

4.3.1 Project description

The In Salah gas project is a joint venture between BP, Sonatrach and Statoil. It is a multi-field natural gas development sited in the central Sahara Desert in southern Algeria that will produce about 9 billion cubic metres of gas per year (Riddiford et al., 2003).

The project consists of 8 separate gas fields. Their production will be phased, with the initial production being from the three northern fields; Krechba, Teguentor and Reg. These fields will have a plateau production period of about 10 years, after which the southern fields will be brought on stream to maintain the plateau production from the project as a whole.

The natural gas in the In Salah fields contains between 1 and 9% CO_2. The sales specification for the gas is that it should contain less than 0.3% CO_2, so it has to be removed. This results in the production of a stream of high purity CO_2 which is stored underground rather than being vented to the atmosphere. Up to 1.2 million tonnes of CO_2 a year will be stored in this way to mitigate the greenhouse gas emissions from the project (Riddiford et al., 2004). The project is expected to last about 25-30 years.

A central CO_2-stripping facility has been installed at the Krechba field. Gas from the Teguentor and Reg fields is taken there by pipeline and the CO_2 is removed prior to export. The CO_2 is injected into the same reservoir rock that hosts the natural gas field but beyond the field limits (Figure 51). Reservoir simulation predicts that the CO_2 will not move up into the natural gas reservoir until after it is fully depleted and has been abandoned.

The reservoir rock at Krechba is thin (approximately 20 m thick) and has relatively low permeability. Consequently the gas is produced from wells that penetrate the reservoir horizontally. Similarly, three wells, each with more than 1000 m of horizontal section in the reservoir, have been drilled for the CO_2 injection. Two wells are being used to inject the CO_2 and the third provides some spare capacity if needed. The gas/water contact at the base of the field is at about 1840 m below ground level and the seal is provided by approximately 950 m of Carboniferous mudstone. The Carboniferous mudstones are overlain by a further 890 m of Cretaceous sandstones and mudstones which form a regional aquifer.

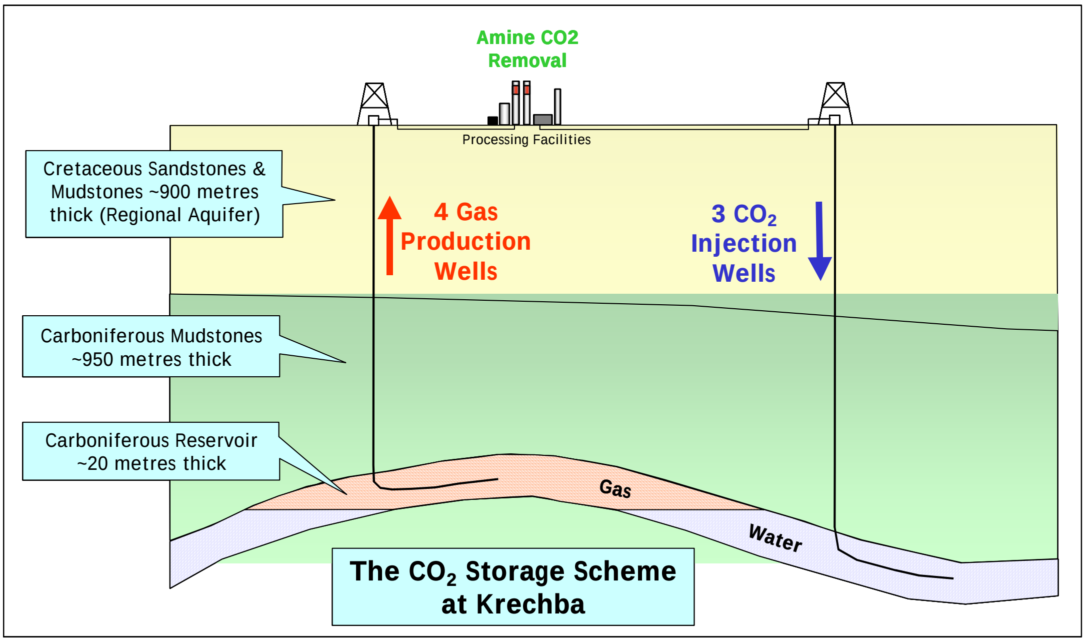

Figure 51. Schematic of the In Salah gas production and CO_2 storage project, Algeria. *Courtesy of BP.*

4.3.2 Monitoring Programme

CO_2 injection at the In Salah gas field will be closely monitored. A 5-6 year $30 million 'In Salah Gas CO_2 Storage Assurance Joint Industry Project' has been proposed (Riddiford et al., 2004). This will be a public demonstration of CO_2 storage assurance and will address the key issues of understanding the long term storage performance and, in particular, the duration of storage. Baseline data acquisition for this project started in 2004.

The monitoring programme will be designed to monitor the distribution of CO_2 in the deep subsurface both at and around the injection site, and CO_2 levels in the soil, at the ground surface and in the atmosphere just above the ground surface at the site. Initially it will determine background fluxes of CO_2 at the site and subsequently will monitor for the presence of any leakage of CO_2 from underground.

4.3.3 Most likely leakage pathways

CO_2 leakage from underground is considered extremely unlikely. There is no reason to believe that there has been any natural gas leakage from the undisturbed geology as, prior to discovery, the reservoir rock retained the natural gas in the Krechba field for millions of years. The CO_2 is being injected into the same reservoir rock that successfully contained the natural gas. The wells will be drilled, completed and abandoned in accordance with appropriate best practice. Nonetheless, a risk assessment will be undertaken to determine any possible leakage pathways for the injected CO_2, and the monitoring programme will be designed to take this into account.

Similar risk assessments performed for other sites have indicated it is possible, although unlikely, that the disturbance of the natural geology in any field by man could result in the development of leakage pathways. This could occur either as a result of the injection of CO_2 that, in the presence of water, has the potential to react with certain rocks, or as a result of changes in pressure in the reservoir rock associated with CO_2 injection or natural gas production that might induce faulting or re-open cracks in the overlying strata. There might also be leakage associated with the wells. Potentially a well could provide a man-made pathway all the way from the reservoir rock to the ground surface. Therefore, although the risk assessment process has yet to be completed for In Salah, the production and injection wells seem intuitively the most likely sources of any leakage. These will be closely monitored.

4.4 THE WEYBURN CO_2-ENHANCED OIL RECOVERY PROJECT

4.4.1 Project description

The Weyburn oil field was discovered in 1954 in Saskatchewan, Canada, it covers an area of 180 km^2 (70 square miles), and lies at a depth of approximately 1450 m. Approximately 1.4 billion barrels (221 million m^3) of sour 25-34 °API oil were estimated to have been initially in place within the field.

The Weyburn field is currently undergoing CO_2 injection to enhance oil recovery. It is the subject of an intensive programme to research and monitor the CO_2 injection from a CO_2 storage perspective (Wilson & Monea, 2004). The research programme consists of 4 themes:

- Geological characterisation.
- Prediction, monitoring and verification of CO_2 movements.
- CO_2 storage capacity and distributions, and the application of economic limits.
- Long-term risk assessment of the storage site.

The overview given below is abstracted from the much more detailed and comprehensive account presented by Wilson & Monea (2004).

4.4.2 Production history

The Weyburn field has undergone three phases of production, each characterised by a different production method. It underwent primary production (i.e. the fluids in the reservoir were produced naturally to begin with and then later probably by pumping the oil out of the reservoir) until 1964. It was placed on secondary production by water flood, water being injected into the reservoir to help keep up the pore fluid pressure and drive fluids (oil and water) towards the production wells. In 2000, the field was placed on tertiary production, whereby a WAG (water alternating with gas) process was initiated, in which water and CO_2 are injected alternately into the reservoir. The CO_2 mixes with the oil, lowering its viscosity and increasing its volume and enabling it to move more easily. Water is then injected to help push the CO_2/oil mixture towards the production wells. Some of the CO_2 is recovered from the production wells with the oil and is separated and re-injected into the reservoir, but some remains trapped underground. The CO_2-flood was targeted specifically at the Marly zone of the reservoir. Over the lifetime of the field it is estimated that some 18-20 million tonnes of CO_2 will be stored in the field. The CO_2 used for the CO_2-flood is anthropogenic, coming from the Dakota Gasification plant near Beulah, North Dakota, USA and is transported to Weyburn by a specially-built 320 km pipeline.

The oil reservoir at Weyburn is the Midale Beds, which are of Carboniferous age. It has a maximum thickness of 30 m in the Weyburn field. It consists of fractured carbonate rocks which can be divided into two units, the Vuggy zone (0-20 m thick), which consists primarily of highly fractured and permeable limestone, and the overlying Marly zone, a low permeability marly dolomite. Fractures are present throughout the Midale reservoir, but they are more common in the Vuggy than the Marly.

In the area currently under CO_2-flood, the Marly is 3-10 m thick and the Vuggy is 8-22 m thick. The marly has porosity of 16-38% and permeability of 1->50 millidarcies, whereas the Vuggy has 8-20% porosity and 10->300 millidarcies permeability.

4.4.3 Field structure

The field is primarily a structural/stratigraphic trap comprising a dipping reservoir truncated by an unconformity.

4.4.4 Cap rocks

The field is sealed by evaporites that stratigraphically underlie and overlie the Midale reservoir (the Frobisher evaporite and Midale evaporite respectively) and by an altered zone at the subcrop of the Midale Beds beneath the unconformity, and then by the Triassic Lower Watrous Formation that lies above the unconformity surface.

The Frobisher evaporite has a nodular texture and is generally not fractured. Oil staining is present in some studied samples so it may be potentially susceptible to fluid migration. However its sealing properties are shown *de facto* by its role as a seal in the Weyburn field.

The Midale evaporite is a dense anhydrite formation 2-11 m thick. It has clearly been a very effective seal to hydrocarbon migration for the last 50 million years. No fractures in the Midale evaporite have been observed that show any evidence, such as oil staining or mineral precipitation, that they have conducted fluids.

The diagenetically altered zone of the Midale Beds reservoir that lies immediately beneath the unconformity varies between 2 and 10 m thick. There is almost total porosity reduction in this zone, which has developed through a complex diagenetic process.

The Lower Watrous Member is an important sealing horizon to many oil fields in southeast Saskatchewan. In general it has a mixed lithological character, being composed of sandstones, siltstones and mudstones. It contains secondary dolomitic and anhydrite cements and is an effective aquitard, although restricted fluid movement has been observed into this unit elsewhere in basin. No significant fractures have been observed in the Lower Watrous at Weyburn.

4.4.5 Prediction, monitoring and verification of CO_2 distribution

Prediction, monitoring and verification of CO_2 movement was achieved through a comprehensive programme of modelling and monitoring the injection of CO_2, and monitoring for surface emissions of CO_2 at the ground surface. This was followed by matching the observed monitoring results to the predictions from the models. Feedback was then used to improve the models and highlight data gaps needed to better characterise the field.

4.4.5.1 Monitoring for leakage at the ground surface

Soil gas studies were undertaken to measure the natural background concentration of CO_2 and other gases, and to ascertain whether there is any leakage of CO_2 resulting from the CO_2 injection. Three periods of sampling over a 360 point grid took place between July 2001 and October 2003. CO_2, O_2 and CO_2 flux values were measured and the results showed these to be within the normal range of natural soil values. The results can therefore be explained by the normal metabolic processes taking place in soils. Although there is marked seasonal variation in these gases, the statistical distribution of radon and thoron at the grid nodes is very similar from season to season. This provides further support for the hypothesis that CO_2 is not leaking from a deep source as it would be expected that there would be a correspondence of high radon values and high CO_2 values if CO_2 were acting as a carrier for radon and both were being transported together from depth.

A comparison of the results from the Weyburn soil sampling grid with a control site 10 km to the NW showed generally similar background results for all monitored parameters, adding further support to the hypothesis that CO_2 is not leaking from a deep source.

Work was also undertaken on a number of sites that were thought potentially to represent preferential vertical migration pathways from the reservoir to the ground surface. These included two decommissioned wells (one of which was completely abandoned and the other of which was temporarily suspended from production), a river lineament, and a salt collapse structure with associated faulting. Soil gas concentrations for the two wells were well within the range of data from the main soil gas grid, but the suspended well had, on average, somewhat higher CO_2 values than the grid. Although leakage cannot be entirely ruled out, there is no strong evidence for it. The river lineament shows some weak CO_2 anomalies but their positions and the general lack of accompanying higher levels of other gases, support a biogenic origin. There are some helium anomalies on one profile across the lineament that could merit follow-up studies. The salt collapse structure has generally low concentrations of soil gases and no significant levels apart from some anomalous helium results on one profile, that warrant further investigation.

Overall, there is no evidence for escape of injected CO_2 from depth. Further monitoring of soil gases is necessary to verify that this remains the case in the future and more detailed work is required to better understand the causes of variation in soil gas contents, and to investigate further the possible conduits for gas escape.

4.4.5.2 Monitoring for leakage from the reservoir

A seismic monitoring programme was undertaken, primarily to image and quantify the distribution of CO_2 within the reservoir over time. This included time-lapse surface 3D 3-component seismic surveys over the whole CO_2-flood area. This successfully imaged the CO_2 around the horizontal injection wells, the anomalies due to CO_2 injection being particularly clearly seen on amplitude difference maps of the Marly zone. No leakage from the reservoir was detected.

Conventional production data such as injected volumes of gas, oil and water and reservoir pressure were also monitored, and a programme of geochemical sampling of reservoir fluids was undertaken. The primary purpose of these surveys was to determine and quantify the distribution of CO_2 within the reservoir and the chemical processes taking place in the reservoir.

4.4.6 Risk assessment

An important element of the Weyburn project is the long-term risk assessment of the storage site. The site and surrounding area was considered as a complex natural and engineered system comprising the geology of the site and surrounding area, the wells, the characteristics of the fluids within the system boundary and their evolving flow regimes and other factors. This allowed a rigorous and formal systems analysis approach to be adopted. A list of all the features, events and processes that could be relevant to the evolution of the Weyburn system was developed and reservoir simulations were conducted to predict the behaviour of the system 5000 years from the end of CO_2 injection.

The initial results of the simulations of the natural system (i.e. excluding the wells) suggest that 26.8% of the estimated CO_2 in place at the end of EOR (~21 million tonnes) will migrate out of the EOR area. 18.2% is predicted to move downwards to below the reservoir, 8.6% is predicted to migrate laterally in the Midale reservoir and 0.02% is predicted to diffuse into the overlying cap rock. No CO_2 enters the potable aquifers in the region during the 5000 year modelled period.

The estimated maximum cumulative leakage from the estimated 1,000 wells over the 5000 year period was 0.03 million tonnes of CO_2, or 0.14% of the total CO_2 in place at the end of EOR. Significant uncertainty is attached to this estimate however.

4.4.7 Conclusions from the Weyburn Monitoring Project

The monitoring programme demonstrates that there has been no leakage from the reservoir to date. The risk assessment suggests that there will be no leakage of CO_2 from the natural system. However, it predicts that there may be minor leakage from the estimated 1000 abandoned wells over a 5000 year period from the end of EOR operations.

4.5 THE RANGELY CO_2-ENHANCED OIL RECOVERY PROJECT

4.5.1 Project description

The Rangely oil field, Colorado, USA, (Figure 52) was discovered in 1933, underwent primary production up to the 1950s, was converted to water flood in 1958 and then CO_2 flood in 1986 (Bowker & Jackson, 1989). It covers an area of approximately 78 km^2. Since 1986, in excess of 23 Mt of CO_2 has been serendipitously stored in the field, as a result of enhanced oil recovery. Stevens et al. (2000) estimated that ultimately approximately 0.03 Gt of CO_2 would be stored in the reservoir. It may be representative of typical large scale EOR projects that will store CO_2 in the future. The CO_2 is supplied from the LaBarge natural gas field in Wyoming where the CO_2 is removed during natural gas production, enabling the latter to meet pipeline corrosion specifications (Stevens et al., 2000). Rangely contains over 500 injection and production wells plus an unknown number of plugged and abandoned wells (Klusman, 2003a). The reservoir is the Weber Sand Unit at a depth of 1980 m with cumulative production of 850 × 10^6 barrels of oil. The injected CO_2 will be supercritical at this depth.

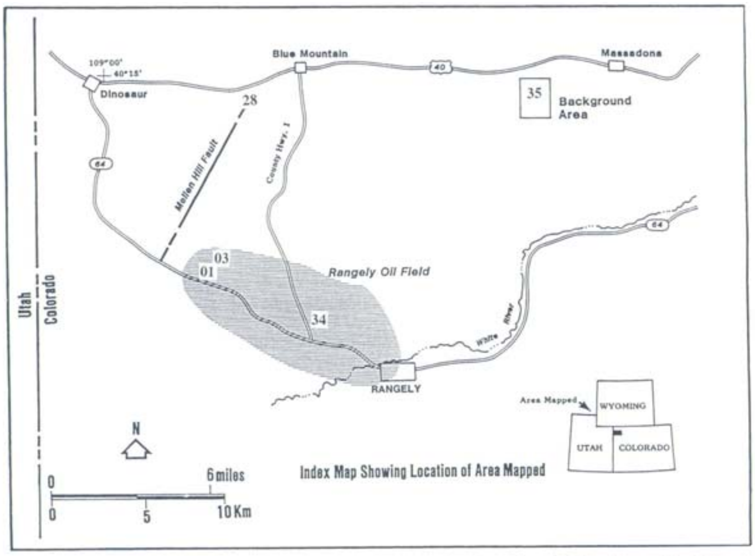

Figure 52. Location of the Rangely Oil Field, background (control) area and Mellen Hill Fault. Numbered locations are "deep" holes drilled for soil gas sampling at a range of depths. Reprinted from Klusman, (2003), courtesy of Elsevier.

4.5.2 Soil gas and soil-atmosphere flux measurements at the Rangely field

Between 2000 and 2002, a survey of the field and adjacent areas was conducted to determine whether any CO_2 was leaking from the field and, if so, quantify the leakage (Klusman, 2003a, b, c, d). CO_2 flux from the soil to the atmosphere is a surface process and, in the absence of a deep source of CO_2, is largely the result of biological processes such as root respiration and microbial oxidation of soil organic matter. Consequently, in the Colorado climate it is subject to large seasonal variations and, in summer, diurnal variations. Also, in the desert environment that prevails at Rangely, CO_2 flux is strongly affected by the amount of moisture in the soil - a burst of activity was detected after rainfall for example. In winter, when the soil temperature is low, more subtle mechanisms such as changes in barometric pressure may be responsible for drawing CO_2 out of the soil into the atmosphere. The lower biological flux in winter makes it easier to detect geological processes.

Preliminary measurements for the purposes of method development and equipment testing were made in the winter of 2000/2001. The main survey took place in summer 2001 and winter 2001/2002. 41 measurement locations on the Rangely field, 16 on a control area with similar vegetation and ground conditions and 2 at the ends of a nearby fault - the Mellen Hill Fault - were studied.

The soil to atmosphere fluxes of CO_2 and CH_4 were measured, and both shallow and deep soil gases were sampled and analysed. CO_2 and CH_4 concentrations were measured, and the proportions of stable carbon isotopes ($\delta^{12}C$ and $\delta^{13}C$), and also the less stable isotope $\delta^{14}C$, were determined.

The results for CH_4 and CO_2 measurements in air above the field suggest the possibility of minor methane leakage from field infrastructure.

The results from deep soil gas sampling in boreholes suggest a deep source of methane and light alkanes in the vicinity of two of the sampling points in the western part of the field, and $\delta^{13}C$ isotopic measurements support a deep thermogenic source for this CH_4. At one of these two sampling points there was a slight shift to heavier carbon isotopes in CO_2, possibly, but not convincingly, indicative of a deep source. However, $\delta^{14}C$ values from the CO_2 at the bottom of this hole indicate a radiocarbon age of 25,000 years, supportive of an ancient, isotopically dead, source for the carbon. Thus there is some evidence of seepage of methane and/or carbon dioxide from the western part of the field.

4.5.3 Estimating the quantity and distribution of seepage of CO_2 and CH_4 from deep sources at Rangely

The mean winter CO_2 flux from the soil to the atmosphere can be taken to be the maximum potential leakage (Klusman, 2003a). The mean figure derived from the sample points was 0.302 g CO_2 m^{-2} day^{-1}. Scaling up to the entire field results in a figure of 8600 tonnes per year for the entire field. However, $\delta^{14}C$ measurements indicate that even in winter more than half of the CO_2 was derived from biological activity, and thus that <3800 tonnes of isotopically dead CO_2 was likely to be leaking from the field. Preliminary analysis of the $\delta^{14}C$ measurements from the deep soil gas samples suggests that the flux of isotopically dead CO_2 could be as low as 170 tonnes per year. Moreover it is likely that a significant proportion, if not all, of the isotopically dead CO_2 is derived from methanotrophic oxidation of deep-sourced methane (Klusman 2003d). Thus the 170 tonnes/yr lower limit for direct leakage of CO_2 from the reservoir may well be too high - indeed it is possible that no CO_2 is leaking from the reservoir.

It is important to note that scaling up the results from the 41 sampling points to the entire 78 km^2 site means that there is the possibility of significant inaccuracy in the 'whole field' flux estimates as there is no means of telling how representative the sample points are. The $\delta^{14}C$ results indicate that the seepage is patchy and that it might take the form of plumes, currently of unknown dimensions.

4.5.4 Airborne survey of the Rangely field

As well as the detailed geochemical sampling of the field described by Klusman (2003a-d), an airborne hyperspectral survey was flown over the field to see if the effects of any local elevated CO_2 concentrations on the roots of plants could be detected (Pickles & Cover, 2004). Such elevated CO_2 concentrations affect the health of the plant because its roots become deprived of oxygen. Its poor health can be detected on images in parts of the visible and infra-red spectra (Figure 53). The technique has been used successfully to detect areas of high soil CO_2 concentrations at Mammoth Mountain, California (Pickles & Cover, 2004). The survey at the Rangely field did not detect any anomalous areas of poor plant health.

Hyperspectral remote sensing identified several ecological habitats at Rangely which were subsequently verified by field observations. Due to the sparse nature and species of the vegetational cover in this area, the vegetation index can identify the location of each plant within the region, though in more densely covered regions this may not be possible. The vegetation index map (Figure 53) provides a baseline of geobotanical conditions that can be compared with future acquisitions to assess possible changes in plant-life that may indicate CO_2 leakage. The semi-arid climate at

Rangely results in plant species that externally appear as dry twigs during much of their life. Ground-truthing therefore becomes necessary, since many areas that could have been interpreted as having less healthy vegetation were in fact very healthy just dormant. This highlights the need for detailed baseline surveys that establish natural variations in plant growth on several timescales associated with seasonal and meteorological, and even diurnal, changes.

58 categories of plant habitat, soil type and mineralisation were discriminated. Subsequent field-validation by walking around the perimeter of these habitats with a DGPS indicated mapping accuracy to 1 or 2 pixels (equivalent to 3-6 metres).

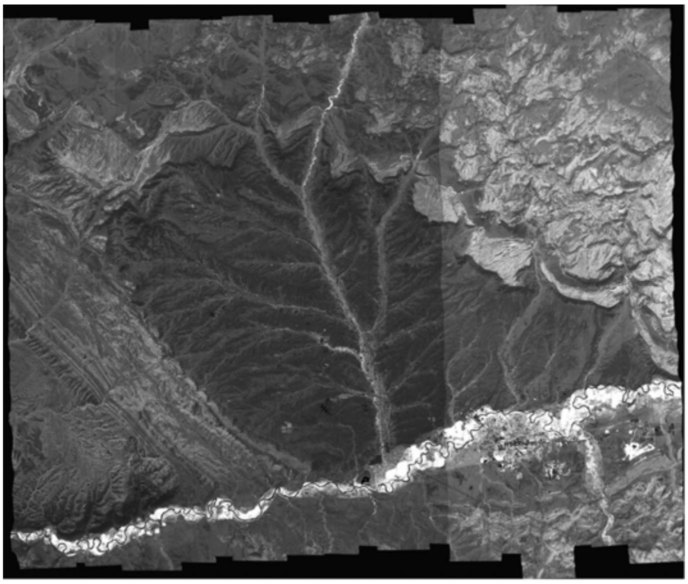

Figure 53. A vegetation index grey scale image map of the Rangely field. The whiteness or brightness of each image pixel means both that there is a higher percentage of plant coverage in the pixel area and/or that the plants are exposing more chlorophyll in their leaves and stems. The right third of the image is brighter because these lines were acquired following a significant rain event, which 'greened' the plants. (Courtesy of Pickles and Cover, 2004, CCP).

5 Comparison of Natural CO_2 Emissions with Putative Emissions from Man-Made Storage Sites.

5.1 DISTINCTION BETWEEN CO_2 EMISSIONS IN SEDIMENTARY BASINS AND THOSE IN VOLCANIC OR HYDROTHERMAL REGIONS

A major distinction can be drawn between the CO_2 emissions that are known to occur in volcanic regions and associated hydrothermal areas and the emissions that may occur in sedimentary basins selected for CO_2 storage.

Volcanic regions are characterised by the presence of magma at variable depth and both volcanic and hydrothermal areas are characterised by the presence in the shallow subsurface of heat and steam, which can lead to very high fluid pressures and explosive activity. They are also tectonically active and subject to ground heave and the development of cracks and fissures in the ground. Natural voids, caused, for example, by the withdrawal of magma, may exist in these areas and can allow the build-up and sudden emission of gases. Moreover, because the topography of recently active volcanic regions is at least partially created by the deposition of airborne particles (ash and larger volcanic fragments) and lava flows, they may have topography that includes more natural hollows and depressions than are likely to be found in sedimentary basins. Also, the tectonic activity in volcanic regions can lead to rapid changes in fluid flow in the subsurface, which can lead to the establishment of new vents or the re-opening of old ones. These factors favour both the sudden, or relatively rapid, episodic emission of gases and the build-up of CO_2 near the ground surface.

Volcanic regions may also contain crater lakes, which represent by far the greatest potential natural CO_2 hazard. As described above (Section 3.4) the very special set of circumstances that is required for these lakes to pose a CO_2 hazard is extremely unlikely to be found in sedimentary basins. Even if comparable circumstances did occur, any lakes above or near a man-made CO_2 storage site could be monitored for CO_2 content and remediated - as is currently happening at Lake Nyos. The amounts of CO_2 emitted from the events at lakes Nyos and Monoun have been estimated to be as high as 0.63 km^3 (STP) or 1.24 Mt of CO_2, and 0.024 km^3 (STP) or 47,000 t of CO_2 respectively.

By contrast, the sedimentary basins that will be targeted for CO_2 storage will lie in stable geological environments, not subject to major tectonic activity, and commonly containing natural fields of gas and oil, which prove their ability to retain buoyant fluids, frequently for millions of years.

5.2 FLUX RATES OF NATURAL CO_2 EMISSIONS IN VOLCANIC AND HYDROTHERMAL AREAS COMPARED WITH THOSE FROM SEDIMENTARY BASINS AND ENGINEERED CO_2 STORAGE SITES

Fluxes from both natural and engineered sites may be of interest from a local health, safety and environment perspective and fluxes from engineered sites are also of interest from a climate change perspective. If leaks from engineered sites become too large then they could potentially become significant contributors to atmospheric CO_2 emissions in their own right. Fluxes from volcanic emissions, some moffettes and leaks in sedimentary basins and the estimated leakage rate at Rangely are compared with anthropogenic emissions in Figure 54. Flux data should be interpreted with caution because they may be averaged over potentially arbitrary areas and/or time periods that may conceal the true nature of the emission. Ultimately it is the concentration (and the duration of any raised levels) of CO_2 in the near surface and the atmosphere or oceans rather than the flux that is most important in terms of biological impacts. Either high or low fluxes could result in build-ups of concentrated CO_2, depending on the environmental setting, e.g. built up areas or confined topographic areas versus windswept open countryside. Even relatively low fluxes have the potential to damage vegetation because they are commonly associated with high levels of CO_2 in soil gas.

In terms of leakage from engineered sites, it is the total mass per unit time rather than the mass per unit area per unit time that is important in terms of emissions performance. A high flux expressed, for example, in tonnes per m^2 per year, may not be significant in terms of overall leakage if it is an average from a very small area, whereas it might be highly significant if it is an average from a very large area.

Local flux rates in volcanic and hydrothermal areas can be extremely high during sudden, episodic events. At Lake Nyos, the flux of CO_2 from the volcano into the lake waters has been estimated at approximately 4,400 tonnes per year. The flux out of the lake waters into the atmosphere during the devastating 1986 event is calculated to have been approximately 1.24 million tonnes from an area of 1.8 km^2 in just a few hours. During the Lake Monoun event in 1984, the flux out of the lake waters into the atmosphere is calculated to have been approximately 47,000 tonnes in just a few hours.

The volume emitted at the 1992 Dieng volcanic event, which resulted in the deaths of 142 people, may have been approximately 0.1 km^3 (equivalent to approximately 180,000 tonnes at STP). Again, this was largely emitted very suddenly but continued for the next few months at a much reduced rate. This flux emerged following a phreatic eruption from two relatively small areas; a crater and a fissure.

Sudden events may also occur in hydrothermal regions associated with quiescent volcanoes, for example at the Alban Hills Quaternary volcanic complex, which extends over an area of about 1500 km^2 to the south-east of Rome and includes the Ciampino area. The Alban Hills volcano is considered quiescent based on the lack of eruptive activity over the last 0.02 Ma, although the occurrence of seismic swarms, gas vents and thermal waters may indicate ongoing unrest. The release of a large volume of CO_2 during a seismic swarm resulted in the death of 30 cows in 1999 in the town of Cava dei Selci. The mass of CO_2 emitted during this event is not known. Subsequently gas flux measurements have been undertaken in the Ciampino area but these are at a preliminary stage and only a few measurements have been conducted. These measurements yielded a point CO_2 flux value of around 2.57 $kg/m^2/day$ in the area near where the 30 cows died in 1999 (Annunziatellis et al. 2003), which indicates the periodic nature of the gas release and close link between it and local seismicity.

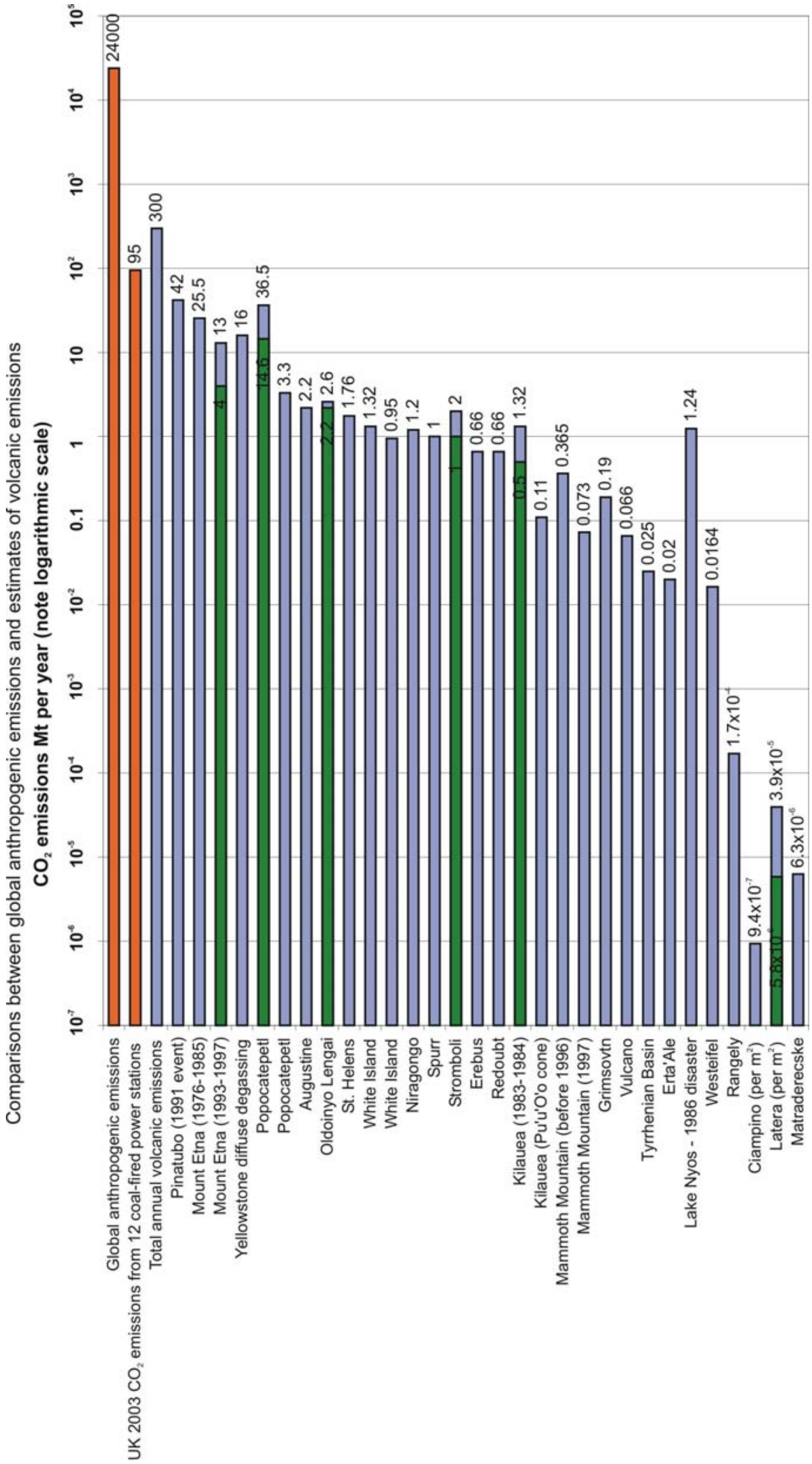

Figure 54. Comparison of CO_2 emissions from volcanoes, moffettes and other natural sources compared with anthropogenic emissions.

In areas of diffuse degassing, daily flux rates from volcanic and hydrothermal areas can be significantly lower. The total CO_2 flux from the Yellowstone hydrothermal area is approximately 45000 ± 1640 tonnes per day (16 ± 0.6 million tonnes per year) or about 10 tonnes of CO_2 per km^2 per day on average.

The total CO_2 flux from the Mammoth Mountain area has been estimated at approximately 520 tonnes per day through the ground, with an additional 30-90 tonnes per day from groundwater flowing off the mountain (Gerlach et al. 2001).

The total flux from a 15 km^2 area of the Tyrrhenian Basin hydrothermal area, offshore Italy has been estimated as at least 68 tonnes per day (25,000 tonnes per year).

There are very few measured CO_2 flux rates in sedimentary basins. However, the average flux of the gas seepage in the area around the village of Mátraderecske in NE Hungary is about 5-10 $l/hour/m^2$, (0.0002-0.0004 $tonnes/day/m^2$) but along faults it can be as much as 400 l/hour (0.017 tonnes per day at STP). These rates are as high as those at Cava dei Selci and Mammoth Mountain. The gas seepage on the surface can be observed as bubbling in wells and in the Almáskút stream, flowing through the village, as well as in the form of strongly carbonated springs.

The fluxes observed to date from man-made CO_2 storage sites are either zero or very low. No flux has been observed from the Sleipner, In Salah (though injection has only just started here) and Weyburn sites. An unevenly distributed but small flux of up to, but possibly much less than, 10.4 tonnes per day is estimated for the Rangely site, which covers 78 km^2. However, it is not know whether this is leaking from the oil reservoir; at least part of it may be due to the oxidation of deep-sourced methane originating from the oil reservoir or overlying strata.

Although CO_2 flux rates in sedimentary basins can, in rare instances, reach levels comparable to those in volcanic terrains, it is the concentration of CO_2 in specific locations around an emission site, rather than the flux, that is important in defining its impact. Moreover, sudden events in which large masses of CO_2 are emitted are the most dangerous to man and animal life, and known examples have occurred only in volcanic areas. A diffuse emission in open countryside of the size calculated at Rangely is unlikely to pose a hazard, whereas a concentrated emission of this size could be dangerous if it was in a confined area such as a hollow in the ground or beneath a building. It should be noted therefore that special attention should be paid to areas in which CO_2 might build up in any monitoring programme established at an engineered CO_2 storage site.

5.3 LESSONS LEARNED FROM THE EXAMPLES

The examples of natural and engineered CO_2 emissions and storage sites were all selected because they illustrate particular aspects of the accumulation, transport or emission of CO_2 in the geosphere. Some of the most important points are:

- The Pisgah Anticline natural CO_2 field demonstrates that large masses of CO_2, in this case over 200 million tonnes, can be trapped underground for tens of millions of years.
- The French carbogaseous area and the Paradox Basin on the Colorado Plateau are examples of sedimentary basins in which natural CO_2 emissions present, at most, only very local hazards to man or the natural environment.
- There is no evidence of leakage from the engineered CO_2 storage sites at Sleipner and In Salah, though injection has only just started in the latter. The Sleipner project has been injecting CO_2 for nearly eight years.

- There is no evidence of leakage at the Weyburn enhanced oil recovery project, which has injected up to 5000 tonnes CO_2 per day since 2000.
- There is a deep-sourced flux of 170-3800 tonnes/yr CO_2 from the Rangely oil field where an enhanced oil recovery project is in progress. It is likely that at least part, if not all, of this flux is due to the oxidation of deep-sourced methane from the oil reservoir, but part of it could be due to the migration of injected CO_2 from the oil reservoir. Approximately 23 million tonnes CO_2 have been injected into the field since 1986.
- Modelling of the fate of CO_2 at the Sleipner injection site suggests that in the long term much of the CO_2 may dissolve in the native pore fluid. As it does so, it will increase the density of the CO_2-saturated pore fluid, which will therefore migrate downwards through the pore system in the reservoir rock and accumulate at the base of the formation.
- Both the previous point and the fact that reservoir pressure is likely to be highest during the injection phase of engineered storage site development, suggest that many CO_2 storage sites will become more, rather than less, stable through time.
- The Colorado plateau and the Florina well case studies indicate that wells may provide leakage pathways to the ground surface from natural CO_2 fields or engineered CO_2 storage sites.
- Natural CO_2 emissions in an area of 15 km^2 in the offshore Tyrrhenian Basin have a minimum flux of 25,000 tonnes per year, most of which dissolves into the sea water.
- The incident involving asphyxiation by CO_2 at the Dieng volcano in Indonesia in 1979 provides an example of the danger presented by sudden CO_2 emissions from volcanoes following an underground build-up of gas. This incident was associated with a phreatic (superheated water and steam) explosion that resulted in the formation of a new crater and the reactivation of a pre-existing fracture. This could not occur in a sedimentary basin because the necessary heat is not present at shallow depths. Moreover, there are commonly few large void spaces in the subsurface in sedimentary basins in which gas could build up.
- The sudden, large emissions of CO_2 from the crater lakes Monoun and Nyos in Cameroon, in 1984 and 1986 respectively, are also examples of the danger presented by sudden CO_2 emissions from volcanoes, in this case following a build-up of CO_2 within crater lakes. They were the result of exceptional circumstances very unlikely to be found at or near engineered CO_2 storage sites, viz: the presence of stratified lakes at considerable elevation compared to much of the surrounding local topography, the presence of a CO_2 leak into the bottom of the stratified lakes, the unobserved CO_2 saturation of the lower layer of the lake waters. Any such combination of features and processes in the vicinity of an engineered CO_2 storage site could be easily monitored to prevent such incidents.
- Current activities at Lake Nyos demonstrate that levels of dissolved CO_2 in stratified lakes into which CO_2 is leaking can be successfully monitored and remediated by a simple gas-lift process so that they do not present a hazard.

- Diffuse degassing through the soil on the flanks of volcanoes such as Mount Etna and Mammoth Mountain does not appear to present a hazard to man unless the mixing of the CO_2 with the ambient air is restricted, for example in buildings or hollows in the ground, or very close to the ground surface.
- In hydrothermal areas diffuse degassing of CO_2 is commonplace. There can be significant variations in emissions from vents in such areas at different times. For example, a sudden emission of an (inferred large) mass of CO_2 associated with seismicity recorded in the Cava dei Sielci area of the Alban Hills in Italy resulted in the deaths of more than 30 animals.
- There is only very sparse CO_2 flux data recorded from sedimentary basins. No records of sudden large emissions of CO_2 from sedimentary basins were found during this study.
- CO_2 found in sedimentary basins can be derived from magma degassing, thermal metamorphism of carbonate rocks and possibly geochemical interactions.

5.4 TYPES OF EMISSIONS FOUND IN SEDIMENTARY BASINS

The commonest natural CO_2 emissions in sedimentary basins are carbonated springs and moffettes. Emissions via faults or other fractures in the bedrock are also recorded but sudden large increases in emission rates are not.

5.4.1 CO_2 emissions along faults and other fractures

The clearest recurring theme from all the examples reviewed in this report is the association between natural CO_2 emissions and faults or other fractures in the bedrock. It should be emphasised that many faults and fractures in sedimentary basins are sealing and do not permit rapid fluid migration either along or through them. This is demonstrated by the many oil and gas fields in which the hydrocarbons are retained by faults. However, it is equally clear that many faults and other fractures are permeable.

In the subsurface, CO_2 will be transported via any porous and permeable pathways that it can enter along its migration path. In sedimentary basins, these are likely to include both porous and permeable rock formations and permeable faults or other fractures. However, permeable faults and other fractures are fast transport pathways that cut across the bedding in a sedimentary basin and can cut through both low permeability caprocks and aquifers or reservoir rocks. Thus they tend to 'short-circuit' the migration of CO_2 along horizontal or sub-beds of porous and permeable reservoir rock. Moreover faults and fractures have a greater tendency to be permeable very near to the ground surface, where the pressure of surrounding and overlying strata is less than at depth. These factors probably account for the observed correlation between natural CO_2 emissions and faults or other fractures in the bedrock. An implication is that CO_2 emissions from bedrock are concentrated rather than diffuse, making them easier to detect and quantify. Whilst none of the examples cited in this report appear to indicate the transport of CO_2 all the way to the ground surface along permeable strata, this should not be neglected as a potential transport route from man-made CO_2 storage sites. There are many examples of natural oil and gas seeps that come all the way to the surface via this route, (e.g. Watson et al., 2000) and long distance lateral transport along permeable beds has to be invoked to account for the distribution of oil and gas in many sedimentary basins.

Once CO_2 has emerged through such a pathway onshore, it tends to be dispersed to varying degrees in the overlying soil and by groundwater processes before emerging through the ground (Oldenburg & Unger, 2003, 2004; Oldenburg et al., 2003). There are several processes that may lead to the attenuation of CO_2 in the vadose zone. These processes include CO_2 solution into porewaters, biogeochemical reactions with microbes and plants and physical trapping on top of the water/soil air boundary. Offshore it is likely to accumulate in the shallow sea bed and, with increasing water depth, the CO_2 is more likely to dissolve.

Surface manifestations of natural CO_2 emissions in sedimentary basins can include travertine deposits (carbonate precipitates created as CO_2-charged springs degas), carbonated springs, dry gas 'moffettes' and areas of stressed or dead vegetation. Offshore gas seeps can produce pockmarks and mud volcanoes.

5.4.2 Carbonated springs

The most common manifestations of CO_2 seeps at the ground surface are carbonated springs, in many cases used as mineral water. CO_2 migrating through the subsurface may saturate groundwater circulating at depth. Because the pressure is lower when the water emerges at the ground surface some of the dissolved gas comes out of solution. In general, there appears to be little danger from such carbonated springs. However, CO_2 leakage into lakes could be dangerous (regardless of whether they are stratified) because CO_2 can build-up above the water, presenting a risk of asphyxiation, in particular to swimmers.

5.4.3 Moffettes

Another typical surface manifestation of CO_2 emissions is a moffette - a site of dry or periodically dry CO_2 emissions. If such sites occur where there are depressions in the ground, such as steep sided valleys, excavations or other confined topographic lows the CO_2 can accumulate and the risk of asphyxiation will increase. Depressions are especially common at CO_2 emission sites where the bedrock is limestone, dolomite or another readily soluble rock type. The acidic groundwater tends to dissolve carbonate rocks and create sinkholes or other depressions around the emissions site. Many emissions sites are barren of vegetation, presumably because it has been killed off by high CO_2 levels in the soil gas.

5.4.4 Borehole sites

Surface CO_2 seeps have been observed at and near borehole sites. This is well documented in the Paradox Basin and also at Florina in Greece. At Florina the initial CO_2 seep was located ~100 m from the wellhead and then gradually migrated towards the well head over a number of weeks. Although favourable water and rock chemistries combined with high CO_2 concentrations can lead to calcite precipitation in fractures offering the potential for 'self-sealing', this effect will be limited because of slow kinetics and the leaking CO_2 may simply be diverted to another point.

Well blowouts, in which fluids emerge either through a borehole or the immediately surrounding strata in an uncontrolled manner, usually during drilling but sometimes as the result of a casing failure, are a well known, if uncommon, phenomenon in the oil and gas production industry. An extreme example of such a well failure occurred at the Yaggy underground natural gas storage site in Kansas. In 2001, 143 Mcf (thousand cubic feet) of natural gas leaked from a failed well casing in the Yaggy underground gas storage facility which was excavated by solution mining in thick salt deposits. The gas migrated up to 9 miles in the subsurface to the town of Hutchinson, Kansas. It travelled this distance in approximately 3 days. The gas formed geysers and resulted in explosions, reaching the surface via abandoned brine wells which were used in the original salt mining. The gas migrated along a narrow (20-30 ft thick) dolostone layer which was heavily fractured due to geological dissolution of the underlying salt which was used for the gas storage at Yaggy. Fracturing is inferred since the dolostones, interbedded with gypsum and thin mudstones, have low matrix porosity. The high pressure of the gas escape at 600 psi, was greater than the fracture entry pressures allowing the gas to open the fractures and migrate the long distance. 57 vent wells and five observation wells were drilled to extract the escaped gas over the region. As the gas was vented, pressures decreased and previously open fractures lost connectivity as apertures were reduced and closed (Watney et al., 2003).

Experience in CO_2 production operations from the USA indicates that CO_2 well blowouts are a rare occurrence. However, at least one has occurred, and was successfully remediated (Lynch et al. 1985). CO_2 blowouts are likely to be less serious and more easily controlled than oil or natural gas blowouts because CO_2 cannot catch fire.

5.4.5 Manifestations of CO_2 leakage to the sea bed

Offshore it is likely that prolonged CO_2 seeps with high flux rates would create pock-marks in fine grained sediments at the sea bed and might create mud mounds or mud volcanoes if they emerged along with muddy fluids. They would also likely be expressed as trains or plumes of bubbles in the sea water column. However these bubbles might dissolve before reaching the surface if the flux was low and the water depth exceeded about 50 m.

5.4.6 Conclusions about the types of emissions that might be expected from CO_2 storage sites

Any of the types of emissions described in Section 5.4 above might be expected at or around leaking CO_2 storage sites, although the probability of an emission is very low. Although it is possible to predict the likely types of emissions that might occur at man-made CO_2 storage sites with some confidence, it is not so easy to predict their likely fluxes. One difficulty in drawing analogies between flux rates from natural CO_2 emissions from sedimentary basins and putative man-made CO_2 storage sites is the fact that there are differences as well as similarities between man-made CO_2 storage sites and natural CO_2 fields. It is possible that because the structures in which natural CO_2 fields are found were probably filled very slowly, CO_2 built up in them to some threshold pressure or fill level and then began to leak at relatively slow rates, maintaining a more or less steady state between accumulation and leakage. Because man-made CO_2 storage sites will be filled at much faster rates it is possible that leaks could be of a different character. For example, leaks from man-made CO_2 fields could be initiated when reservoir pressure was high and forced the opening of a pre-existing fracture or fault. Intuitively it might be expected that such a leak might start as a relatively large flux. However, it would likely lead to a (progressive) decline in pressure in the field and therefore the greatest flux of CO_2 from the seep might be close to the time when it first developed. Examples of the declining height of a geyser at a former borehole site cited in section 2.2.4 suggest that this natural decay or decline in fluxes towards a steady state may occur after a new leakage pathway is initiated. This is an area where further research and modelling is needed. Predictions of this kind can be made using reservoir modelling techniques and analogies can be drawn from man-made leaking natural gas storage sites and well blowouts.

If persistent dangerous or damaging leaks from a man-made CO_2 storage site did occur, as a last resort it might be possible to reduce the emissions to the ground surface by opening the injection wells and lowering the pore fluid pressure in the storage reservoir.

Induced seismicity, where CO_2 injection induces small-scale local seismic activity could be caused by creation of new fractures or reactivation of existing faults or fractures in a caprock. This occurs when the injection pressure exceeds the threshold for fault reactivation (or fracture opening) which depends on the *in situ* stress field. At a CO_2 storage site, the *in situ* stress would be determined as part of normal site characterisation and injection pressures would be capped below this threshold. For example, in gas (methane) storage projects fracture pressures are routinely determined (Perry, 2005) in acid-gas injection projects in Alberta it is a regulatory requirement that injection pressures must be below 90% of the rock-fracturing threshold (Bachu and Haug, 2005).

5.5 IMPACTS OF NATURAL CO_2 EMISSIONS IN SEDIMENTARY BASINS

It should be noted that most of the examples of natural emissions from sedimentary basins pose little danger to man, except in very localised depressions around the emissions site or in buildings. This is because they generally have relatively low fluxes and most of the time they are dispersed by the wind.

Undoubtedly the most dangerous CO_2 emissions are those where large quantities of CO_2 have been emitted from a concentrated source and have not been dispersed by the wind. There are conditions where dispersion of even a small emission would be very slow, for example where the emission point occurs beneath a house or other building. There are examples where CO_2 fluxes are known in urban areas and whilst measures may be taken to mitigate the effects of such emissions, they clearly pose a danger and are undesirable (e.g. Lombardi et al., 2004; Pearce, 2003).

In general, most observed seeps of CO_2 through the ground surface have an impact on vegetation, killing it off where the flux is sufficiently high and damaging it where the flux is lower (Pickles and Cover, 2004, Rogie et al., 2001). In many cases it appears that seeps are actually discovered because of the anomalously dead vegetation. The reader is also referred to Raschi et al. (1997), which provides a detailed and comprehensive review of research carried out at natural CO_2 springs and other sites on plant responses to elevated CO_2, especially elevated atmospheric levels.

The impacts of CO_2 emissions to the sea floor are not well known. However they would lower the pH of sea water at least locally and it is generally considered that this would have a negative impact on marine life (Turley et al., 2004). The Tyrrhenian basin offers an opportunity to assess the impacts of CO_2 emissions from the sea floor on the marine environment.

Changes in barometric pressure can affect the rate of emission from the ground, low pressure resulting in increased emissions (Klusman, 2003a). The main danger appears to be when there is little wind to disperse the emission and it hugs the ground.

5.6 NATURAL ACCUMULATIONS OF CO_2 IN SEDIMENTARY BASINS

The Paradox Basin provides a good example of the geological conditions needed for long-term storage. The caprocks at both McElmo Dome and St Johns field comprise thick evaporite sequences. At McElmo Dome, a 400 m thick evaporite is overlain by a further 300 m of low permeability shales. At St Johns, the 250 to 1000 m sequence of evaporites provides a high quality seal. These thick, low permeability sequences have allowed CO_2, as well as oil and gas, to be trapped for tens of millions of years, despite subsequent rapid (in geological terms) uplift and unloading. The ductile nature of evaporites appears to provide an additional benefit at McElmo Dome, preventing fractures present below the salt from propagating through to the surface.

Clearly, the presence of such thick seal sequences with underlying high quality reservoir rocks would provide ideal potential sites for engineered CO_2 storage. Other geological settings that do not contain thick evaporite sequences above the reservoir are also capable of retaining CO_2, oil and gas for geological timescales, e.g. the Pisgah Anticline natural CO_2 field.

Evidence for leakage at St Johns has been attributed to an overfilling, beyond the closure spillpoint. This can be readily avoided in engineered storage sites.

In contrast to the natural accumulations where no leaks have been observed, the CO_2-rich springs of the northern Paradox Basin suggest that particular attention must be paid to faults that may connect reservoirs to the surface and the relative transmissivities of surrounding damage zones. The CO_2 is thought to occur at shallower depths in this region (above the thick evaporite sequences), in formations that are breached by faults. Although the fault planes themselves are apparently sealed, CO_2 is able to migrate through their surrounding damage zones.

5.7 RECOMMENDATIONS

In order to prevent leaks it is recommended that all engineered CO_2 storage sites should undergo a process of:

1. Geological characterisation of the site and surrounding area.
2. Production of geological and numerical models of the site and surrounding area.
3. Simulation of CO_2 injection into the proposed storage reservoir to model the short term and long term distribution of CO_2 in the subsurface, changes in the physical and chemical state of the reservoir rock and surrounding strata and identify potential migration paths and thus leak points for the injected CO_2.
4. Risk assessment to identify features, events and processes that might lead to the migration of CO_2 out of the intended storage reservoir and/or to the ground surface or sea bed. Iteration between steps 3 and 4 would most likely be required.

5. Establishment of a monitoring plan based on steps 3 and 4 and acquisition of baseline monitoring surveys prior to injection. Monitoring of both the surface and subsurface of the site and surrounding area during injection of CO_2.
6. History matching of the observed results from the monitoring with the models. Acquisition of further data may be required if there are discrepancies between the observed and modelled results.

Every effort should be made to locate and monitor all boreholes in or near a CO_2 storage site, and to plug and abandon new boreholes in a way that will prevent CO_2 emissions for the required storage period of probably thousands of years.

The potential impacts of CO_2 leaks on local ecosystems, at a variety of likely scales, should be assessed. This should include both offshore and onshore ecosystems. Natural emissions sites should form a key part of this assessment.

Carefully selected natural CO_2 emissions sites could be used to validate and build confidence in models used to predict key processes in the long-term behaviour of a storage site.

The potential to test risk assessment methodologies by using analogues as long-term test cases should be investigated. Man-made storage sites are currently performing satisfactorily and so far do not appear to leak. It is therefore difficult to use these sites to verify risk assessment methodologies that might need to predict the consequences of a future escape from a reservoir. Though clearly a site that presents a large risk of leakage is unlikely to be selected for storage, it may still be useful to simulate the likely nature and consequences of leakage at such sites. Careful comparisons with appropriate natural analogues could contribute to this understanding.

Analogues can provide powerful examples to non-specialists of how CO_2 storage might behave and the hazards that a site failure might present. However, these analogues can be abused. They should therefore be used with due care not to overstate or understate their relevance to CO_2 storage processes.

Analogues can be used as testing grounds for the development of monitoring techniques for CO_2 storage sites and their application in this area has not been fully exploited to date.

The two most likely routes for CO_2 migration out of the reservoir are via wells or faults and fractures. The processes that lead to this leakage may be more fully understood by examination of analogue situations. For example, we are aware of research currently underway to understand well cement casing performance over decades or 100 year timescales through studying wells in both oil and CO_2 fields in the US. Other analogues, for example, ancient cements around CO_2 springs, could contribute to this research.

Analogues may also contribute to a more detailed understanding of the migration of CO_2 along fractures through the overburden above a storage reservoir.

Near surface process that may lead to the attenuation or dispersal of CO_2 in the shallow environment require further study. Analogue studies and experimental releases of CO_2 could provide much useful information about these processes.

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