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Methane origins and behaviour

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Copyright and disclaimer

Important disclaimer

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Acknowledgments

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Executive summary

This report attempts to provide a background paper on methane in the subsurface in relation to coal seam gas production. The report begins with a brief overview of the chemical and physical properties of methane, its occurrence in the atmosphere, its global warming potential relative to other species and some of the primary uses of methane in industry. Methane can be from biological and geological sources in nature and both can be trapped in the subsurface and exploited commercially as conventional and unconventional gas resources. The report provides an overview of the primary sources of thermogenic gas (from the action of heat and temperature on buried organic matter) and biogenic gas (methane that has been produced by the action of microbes on larger organic molecules). Models for how these gases can be differentiated between are examined and the limitations of some of those interpretive tools are discussed. Of primary importance is the limited amount of data that gas samples provide, with often only the composition and stable carbon and hydrogen isotopes being the main methods for differentiating between the gas sources.

An overview of the differences between conventional and unconventional gas recovery is provided to illustrate the different approaches to recovery methods and more importantly recovery rates.

There has been increasing amounts of research conducted on the potential for methane to become a virtually renewable resource, by way of stimulating coal or other carbonaceous materials, including oil, by the introduction of microbial communities and nutrients to enhance the rate of biogenic methane production. These activities are briefly reviewed, and it is noted that the information in the literature is reasonably limited at this stage.

Monitoring of methane is discussed partly in the light of established monitoring and verification (M&V) methods, activities and regulations that have been developed for carbon capture and storage (CCS) operations around the world. The focus of CCS M&V methods is the monitoring of carbon dioxide, however approaches and methods are similar to that for monitoring other materials such as methane, where concerns about seepage to surface, monitoring any mobilisation of carbon dioxide and substances mobilised by carbon dioxide into aquifer intervals have many parallels. Both activities require monitoring for understanding processes as technology develops and to provide transparency in the activities to communities where these activities are underway. Therefore there are a number of common approaches and common tools that could be deployed to improve monitoring of methane.

To complete the report, a few examples of the main knowledge gaps have been highlighted and potential new activities noted. This is not comprehensive but tends to highlight that there is further research to be conducted in both areas that would have perhaps been regarded as mature areas of research and more green-field research has been noted as well.

1 Introduction

The purpose of this paper is to provide an overview of methane, including its sources and what the environmental impacts may be, and how they can be addressed. In order to do this, we have to visit the following to set the context:

- What is methane (chemical and physical properties)?
- What is methane used for?
- What are the sources of methane, and how is it produced?
- What is its intensity as a greenhouse gas relative to carbon dioxide?

Methane is a natural product often known for its use in power generation and heating. However in the current times, methane is often associated in the public mind with activities in coal seam gas production (CSG). Methane produced from natural gas fields or as gas dissolved in oil fields is regarded in the industry as coming from “conventional” sources or using “conventional” production methods. Coal seam gas, shale gas and tight gas are regarded as “unconventional” sources of methane. They are regarded as unconventional methods as they use newer technologies to recover the gas, not previously used in the oil and gas industry. Much of the new technology development relates to recovering gas from a “tight” interval meaning that the rock formation containing the methane (or other hydrocarbons) has a limited permeability.

Methane is a hydrocarbon (i.e., it contains hydrogen and carbon atoms only) with a composition of one carbon and four hydrogen atoms and is often presented in text as CH_4 (Figure 1). It is the simplest alkane (saturated hydrocarbon). A fuller description of its behaviour is provided in Section 2.1.

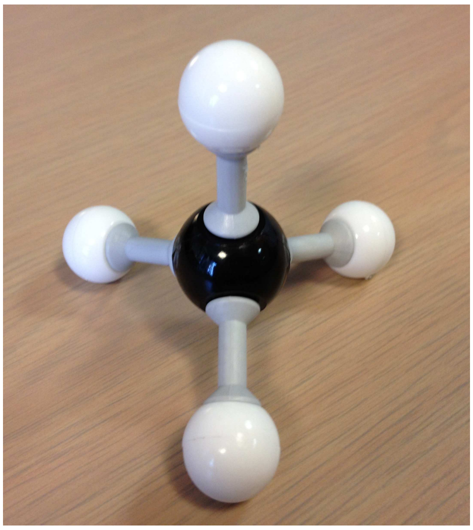


Figure 1 A molecule of methane (CH_4) showing its structure. Hydrogen atoms are represented in white and carbon in black.

Natural gas resources, of which methane tends to be a large constituent, are typically characterised by analysis of the molecular concentration of the gases present (most often presented in a percentage [by mole or by volume] of the total gas). For example, a natural gas may contain large amounts (say 95 %) methane with decreasing amounts of the wetter gases in the following order: ethane, propane, n-butane, iso-butane and pentanes. Wetter gases and liquid hydrocarbons could be dissolved in those gases but often in amounts too low to measure. Non-hydrocarbon gases can be contributors to the overall natural gas and may include carbon dioxide, nitrogen and hydrogen sulphide on occasion.

Characterising the quantities of each of the gases present provides some information on the source of the gas. Further analysis can also be conducted, comparing the stable carbon isotopic composition of the gas. Stable carbon isotopic analysis measures the relative abundance of carbon-12 to carbon-13. The differences in these two are able to be used to track what has happened to the molecules of carbon-rich hydrocarbons and carbon dioxide as they are heated, broken down or altered by microbial consumption. By measuring these ratios in the manner (Equation 1) described in the equation below, it is possible to infer what the source of the methane might be, or what might have happened to the methane over time. These data are used to characterise the source of the natural gas and any secondary processes it may have undergone since its generation. For example, it is possible to say that the methane is from coaly or woody material or from organic matter deposited in an ocean environment.

$$\delta^{13}\mathrm{C}\ \text{‰} = 1000 \times \frac{\left({}^{13}\mathrm{C}/{}^{12}\mathrm{C}_{\ \mathrm{sample}} - {}^{13}\mathrm{C}/{}^{12}\mathrm{C}_{\ \mathrm{reference}}\right)}{{}^{13}\mathrm{C}/{}^{12}\mathrm{C}_{\ \mathrm{reference}}} \qquad \textit{Equation 1}$$

Methods for determining the source of natural gas are discussed in detail in Section 3, but may include the determination of the type of organic matter source that has produced thermogenic gas (gas from deeply buried and heated organic matter trapped in mudstones) to microbial alteration features where naturally generated oil and gas from thermogenic processes is partly consumed by microbes producing biogenic gas.

Methane can be highly abundant in the subsurface, and it is this abundance in reservoirs and coal seams, and an ability to transport it by pipeline easily that makes it an attractive and relatively low cost fuel. As well as occurring in geological formations, where much of the fuel source comes from, methane can be produced by other mechanisms, in particular from biological processes (e.g. microbes) which are why some methane production mechanisms could be regarded in some instances as providing a renewable energy source.

Research, pilot and commercial scale activities to recover methane from biogas facilities occur around the world. These use a variety of organic materials including woody particles, crops, manure/sewage and landfill materials. The organic matter undergoes anaerobic digestion, which involves the introduction of microbes that flourish under an oxygen-free atmosphere, to produce predominantly methane (50-80 %) and some carbon dioxide. This can be harvested and used to supplement or replace fossil fuel methane. For further general information please refer to http://web.archive.org/web/20041124201613/www.eere.energy.gov/consumerinfo/factsheets/ab5.html?print .

Other sources of methane in nature that may be of quantitative significance include livestock such as cows. Estimates have been made that suggest that up to 10% of the total greenhouse gas emissions in Australia are sourced from ruminants (National Greenhouse Gas Inventory, May 2010). Reducing livestock methane emissions is one aspect of CSIRO's research into developing practical solutions to tackle greenhouse gas abatement through better understanding of ruminant microbiology, impact of diet and plant species for the livestock. Natural wetlands and general human activities (waste in particular) contribute to methane emissions overall.

These sources of methane can impact on the composition of the atmosphere. Current measurements of methane (Table 1) in the atmosphere are 1.75 ppm (in dry air) as measured at the Cape Grim Baseline Air Pollution Station (CGBAPS) in Tasmania. Note that this is far lower than for carbon dioxide in the atmosphere at the same location.

Table 1 Methane (CH_4) and carbon dioxide (CO_2) measured values from the Cape Grim Baseline Air Pollution Station (CGBAPS). Data from http://www.csiro.au/greenhouse-gases. Data released in June, 2013.

Date	CH_4(ppb)*	Standard Deviation(ppb)	CO_2(ppm)**	SD(ppm)
15/04/2013	1753.83	1.76	391.97	0.07

*ppb = parts per billion

**ppm = parts per million

The primary greenhouse gases include methane, carbon dioxide, nitrous oxide, water vapour and chlorofluorocarbons (CFCs) listed in Table 2. In terms of impact on the atmosphere, these chemicals are compared using a measurement called global warming potential (GWP). GWP is a relative measure of the amount of heat it traps per mass of gas and also includes a time component so that it can be related to the duration of a chemical or compound in the atmosphere. The GWP is expressed relative to carbon dioxide which has a GWP of 1. While the methane concentrations in the atmosphere are far lower than for carbon dioxide (Table 1), methane's GWP is 21 times higher. Methane has a greater efficiency in trapping radiation than carbon dioxide, but remains in the atmosphere for far less time (i.e. about 12 years for methane versus 50-200 years for carbon dioxide). This is why there is much discussion about fugitive emissions calculations for methane in the environment currently. Sources of carbon dioxide include electricity generation, transport, industry, commercial and residential activities. Nitrous oxide emissions come primarily from agriculture and soil management, transportation and industry and also have a high GWP but relatively lower concentrations in the atmosphere.

Table 2 includes the GWP of a few examples of fluorinated gases. CFC gases clearly indicate a far higher GWP than any of the standard gases such as carbon dioxide, methane or nitrous oxide. None of the fluorinated gases are naturally occurring and they tend to have very long atmospheric lifetimes which results in the amplification of their strength as greenhouse gases. These gases have been used in industry, designed to be replacements for ozone-depleting gases, by-products of industrial processes or used in transmission and distribution of electricity (sulphur hexafluoride).

Table 2 Summary of global warming potential (GWP) of primary greenhouse gases, including methane. Data are from a variety of sources, illustrating the calculated ranges available.

Compound	Formula	Lifetime (years)[1]	20Yr[1] GWP	100Yr[1] GWP	500Yr[1] GWP	20Yr[2] GWP	100Yr[2] GWP	500Yr[2] GWP
Carbon Dioxide	CO_2	Variable (50-200)[3]	1	1	1	1	1	1
Methane	CH_4	12	72	25	7.6	56	21	6.5
Nitrous oxide	N_2O	114	289	298	153	280	310	170
CFCs examples (chemistry is quite varied)								
CFC-11	CCl_3F	45	6730	4750	1620			
CFC-12	CCl_2F_2	100	11000	10900	5200			
Sulphur Hexafluoride[4]	SF_6	3200		23900				

[1] http://www.ipcc.ch/publications_and_data/ar4/wg1/en/ch2s2-10-2.html

[2] http://unfccc.int/ghg_data/items/3825.php

[3] http://epa.gov/climatechange/ghgemissions/gases/co2.html

[4] http://epa.gov/climatechange/ghgemissions/gases/fgases.html

Table 3. A comparison of different methane gas sources (conventional and unconventional) and how these reservoir types impact on depth of reservoir, gas composition, recovery methods and resources. Reproduced from NSW Chief Scientist & Engineer (2013) and extensive references made there.

	Coal seam gas	Shale gas	Tight gas	Conventional gas
Source rock (Organic matter origin)	Coal (peat)	Low permeability fine grained sedimentary rocks (silt mudstones & shale mudstones) (Algae, plant and animal derived organic debris deposited as muds in estuaries and in deep basins)	Various source rocks have generated gas that has migrated in to low permeability sandstone and limestone reservoirs	Porous and permeable reservoir rocks, such as sandstones (Algae, plant and animal derived organic debris deposited as muds in estuaries and in deep basins)
Depth	300-1000 m	1000 – 2000+ m	>1000 m	1000-6000 m
Gas occurrence	Adsorbed on coal organic matter including pores of coal	Stored within pores and fractures but may also be adsorbed on organic matter	Within pores and fractures	In geological structures or traps (e.g. anticlines)
Gas composition	Usually > 95% methane. Small amounts of CO_2 and other gases may be present	Mostly methane but may also contain significant higher qualities of higher hydrocarbons (condensate)	Mostly methane	70-90% methane 0-20% ethane, propane, butane Trace pentane 0-8% carbon dioxide 0-5% nitrogen 0-5% hydrogen sulphide
Extraction technology	Vertical or directional wells; hydraulic fracturing is sometimes required	Hydraulic fracturing and horizontal wells are is usually necessary	Large hydraulic fracturing treatments and/or horizontal drilling are required	Vertical wells; natural pressure drives gas to the surface
Water usage	Water must be pumped from seams to reduce reservoir pressure and allow gas to flow. If hydraulic fracturing is necessary, water is required for the fracturing process.	Water is required for hydraulic fracturing	Water is required for hydraulic fracturing	Little or no water produced initially but water production rates increase with time
Extraction challenges	Removal of seam water and its subsequent disposal	Overcoming low permeability Minimising the amount of water required for hydraulic fracturing Reducing infrastructure footprint	Reducing infrastructure footprint	Often located offshore

Previously summarised in NSW Chief Scientist and Engineer Initial Report (2013) and reproduced in Table 3 is an overview of, among other differences between the reservoir types, information on the potential gases that coexist with methane. In the case of coal seam gas production, methane is not the only gas present, but is likely the major hydrocarbon gas present. Higher hydrocarbons such as ethane, propane and butane may also be present to greater or lesser degrees. Other gases are less likely due to the nature of the thermogenic production of methane. However, non-hydrocarbon gases can also be trapped in the same units where methane has been trapped and can include carbon dioxide, nitrogen and hydrogen sulphide. These are often regarded as contaminants and have to be removed from the gas stream for transport (carbon dioxide and hydrogen sulphide [H_2S] being corrosive) and all reducing value of the methane gas stream.

While not obvious, methane can potentially become a renewable resource. Studies on how to convert (reduce) carbon dioxide back to methane using microbes has been undertaken in recent years, for example a Microbially Enhanced Coal Seam Methane program at CSIRO (http://www.csiro.au/Outcomes/Energy/Energy-from-coal/Microbially-enhanced-coal-seam-methane-brochure.aspx). One company, Luca (http://lucatechnologies.com/company.php) based in Colorado, USA, has developed technology where they have used microorganisms and nutrients to conduct bioconversion of coal, oil and oilshales to methane. However in spite of an active test of “methane farming” in the Powder River basin in Wyoming, USA, Luca have subsequently declared bankruptcy in August of this year (http://wyomingpublicmedia.org/post/luca-technologies-files-bankruptcy). This is possibly due to the reduction in the price of gas caused by the increase in supply from the unconventional gas industry in the US making a more novel, and likely higher cost approach to methane generation being impacted.

Other research in a similar vein has looked at harvesting methane from landfill sites and the use of other waste conversion (silage, sewerage etc.,) as a mechanism to capture methane, though these methods are not discussed here. However, by capturing this methane, not only are emissions of this greenhouse gas abated, but it also provides a local source of fuel and energy.

Some of the major issues relating to the commercialisation of unconventional gas, such as coal seam gas, shale gas or tight gas, are the potential impacts on the subsurface or near-surface environment. The production of coal seam gas is often particularly associated with groundwater issues, but there could be other potential impacts such as micro-seismic events or increases in fugitive emissions. Many of these aspects are covered in other reports such as Cook et al, (2013) and not discussed further here.

2 Methane Properties and Sources

2.1 Definition

Methane, or CH_4 is a hydrocarbon (i.e., a compound containing only carbon and hydrogen atoms). Its atomic weight is 16.043 g/mol (in other words with one carbon atom of 12 atomic mass units [amu] and four hydrogen atoms at 1 amu). Other key properties and behaviours are included in Table 4.

Table 4 Selected properties of methane gas. Data from http://encyclopedia.airliquide.com/Encyclopedia.asp?GasID=41 with fuller details in the MSDS shown in Appendix A.

Gas Properties		
Molecular weight	16.043 g/mol	or 16 atomic mass units (amu); one carbon of 12 amu & four hydrogen of 1 amu each
Solid phase	Melting point	-182.5°C
Liquid phase	Liquid density (at 1.013 bar & boiling point)	422.62 kg/m^3
	Boiling point (at 1.013 bar)	-161.6°C
Critical Point	Critical temperature	-82.7°C
	Critical pressure	45.96 bar
Gas phase	Gas density (at 1.013 bar & boiling point)	1.819 kg/m^3
	Gas density (at 1.013 bar & 15°C)	0.68 kg/m^3
	Compressibility factor (at 1.013 bar & 15°C)	0.998
	Specific gravity [air = 1] (at 1.013 bar & 21°C)	0.55
	Specific volume (at 1.013 bar & 21°C)	1.48 m^3/kg
	Heat capacity at constant pressure (1 bar & 25°C)	0.035 kj/(mol.K)
	Heat capacity at constant volume (1 bar & 25°C)	0.027 kj/(mol K)
	Viscosity (at 1.013 bar & 15°C)	0.0001027 Poise
	Thermal conductivity (at 1.013 bar & 0°C)	32.81 mW/(m.K)
	Solubility in water (at 1.013 bar & 2°C)	0.054 vol/vol
	Autoignition temperature	595°C

Methane is the simplest of the alkanes (Figure 1), that is molecules consisting of carbon and hydrogen only, and all having single bonds (also known as saturated hydrocarbons). Methane exists as a gas at standard temperature and pressure (STP = 0°C and 100 kPa or 1 bar). Under these conditions the gas is colourless and odourless. The smell of methane in domestic use is due to the addition of specific chemicals to aid in its identification if leaking (chemicals such as tert-butylthiols or mercaptan). Its distinguishing feature to us is that it burns to provide heat and energy.

Its combustion products are carbon dioxide and water (Equation 2).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \text{Equation 2}$$

2.1.1 COMPOSITION OF METHANE AND OTHER GASES IN THE ATMOSPHERE

The amount of methane is just less than 2 parts per million (ppm) in the atmosphere (Table 5 and Figure 2).

Table 5 Atmospheric concentration of major gases. # gases are of variable concentration. For example, the carbon dioxide concentration of 330 ppm in 1990 versus the reported breach of 400 ppm in recent months but can vary geographically as well. So too for water vapour. Data from Pidwirny, M. (2013).

Components of atmospheric air		Volume %
N_2	Nitrogen	78.08
O_2	Oxygen	20.95
#H_2O	Water vapour	0 to 4
Ar	Argon	0.93
#CO_2	Carbon dioxide	0.036
Ne	Neon	0.0018
He	Helium	0.0005
#CH_4	**Methane**	**0.00017**
H_2	Hydrogen	0.00005
#N_2O	Nitrous oxide	0.00003
#O_3	Ozone	0.000004

2.1.2 INTENSITY AS A GREENHOUSE GAS

Relative to carbon dioxide, methane has a far higher intensity as a greenhouse gas with global warming potential (GWP) of 21 times that of carbon dioxide (Table 6). In terms of emissions however, it is understood that methane is a lower carbon dioxide emitter than if coal were used to generate the equivalent amount of power. Methane concentrations have been shown to be on the increase in the atmosphere as well as carbon dioxide, with data from CSIRO showing rapid increases since the start of the industrial revolution (Figure 2). Prior to that, changes in land use had already begun to impact on concentrations over time.

Relative to other gases, as shown in Table 6, methane has a relatively low GWP, say compared with the worst greenhouse gas, sulphur hexafluoride (>20,000 years), however at about 2ppm, it is orders of magnitude more abundant in the atmosphere than sulphur hexafluoride (predicted to be about 5 ppt (parts per trillion) in 2005; Fraser et al, 2004). While there are increased efforts to find substitutes with lower GWP, not all high value gases have been banned as yet. Sulphur hexafluoride is monitored along with fluorinated gases at Cape Grim Baseline Air Pollution Station (CGBAPS) in Tasmania by CSIRO because of their impact and increase in abundance.

Because of the high abundance of methane relative to carbon dioxide and fluorinated gases, and concerns about ongoing fugitive emissions of methane, there is increased interest in the monitoring of methane in relation to climate change. Methods for this are discussed later (Section 6).

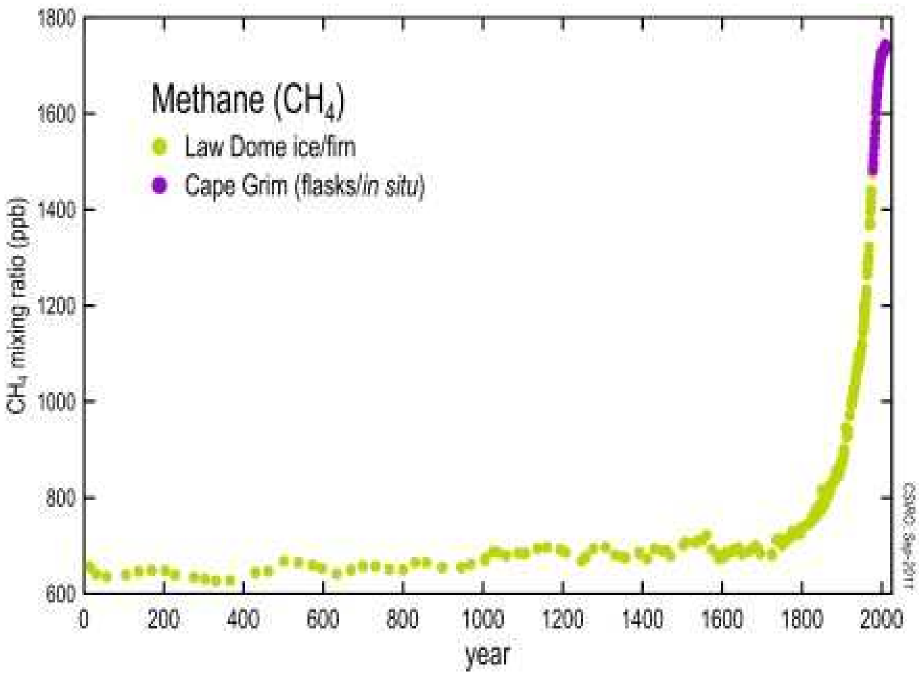


Figure 2 Data from CSIRO showing the atmospheric concentrations of methane as measured at Cape Grim Baseline Air Pollution Station (CGBAPS) in Tasmania and extrapolating this data back in time using ice core data. From http://www.csiro.au/greenhouse-gases/#Methane.

Table 6 Global warming potential (GWP) of selected gases used industrially. Table reproduced from Stalker et al., (2009a). Note that (a) the data are averaged in some cases and (b) the data are modelled from the Bern Carbon Cycle model. Therefore different organisations may calculate these values differently via models and numbers are not always consistent (e.g. compare with Table 2).**

Chemical	Atmospheric Lifetime (Years)	GWP
CO_2*	Variable	1
CH_4*	12 ± 3	21**
Sulphur hexafluoride (SF_6)	3200	22,850**
Chlorofluorocarbons		
CFC-11 (CCl_3F)	45	4000[#]
CFC-12 (CCl_2F_2)	100	8500[#]
CFC-113 (CCl_2FCClF_2)	85	5000[#]
Perfluorocarbons		
PFM (CF_4)	Up to 50,000	6500[##]
PFE (C_2F_6)		9200[##]
PFM (CF_4)	50,000	6000[#]
PFE (C_2F_6)	10,000	11,000[#]
PFCB (c-C_4F_8)	3200	9600[#]
PFB (C_4F_8)	2600	8100[#]
Hydrofluorocarbons		
HFC-23 (CHF_3)	265	12,000[#]
HFC-134a (CH_2FCF_3)	14.1	1300[#]
HFC-152a ($C_2H_4F_2$)	1.4	130[#]
Hydrochlorofluorocarbons		
HCFC-21 ($CHFCl_2$)	1.7	180[#]
HCFC-22 (CHF_2Cl)	12	1700[#]
HCFC-123 (C_2HFCl_2)	1.3	95[#]

* http://unfccc.int/ghg_data/items/3825.php

**based on an average of three values from the EPA Website from 20, 100 and 500 year life cycles.

[#] based on GWP4 (40 CFR) presented by the U.S. EPA (U.S. EPA Class I Ozone-Depleting Substances Website: http://www.epa.gov/Ozone/ods.html or http://www.epa.gov/Ozone /ods2.html

[##] http://www.eia.doe.gov/oiaf/1605/ggrpt/gwp_gases/html or http://glossary.eea.e.int/EEAGlossary/C/carbon_dioxide_equivalent

2.1.3 COEXISTENCE OF METHANE WITH OTHER GASES IN RESERVOIRS

Frequently other gases and hydrocarbons are found with methane in various types of reservoirs, such as in coal seams, shale or tight gas units or in conventional hydrocarbon reservoirs (Table 3). Often the majority of the coexisting compounds are heavier n-alkanes (straight chain compounds containing carbon and hydrogen atoms with single bonds also known as saturated hydrocarbons) such as ethane, propane, n-butane, etc., with formula C_nH_{2n+2} where "n" is the number of carbon atoms. However there can be heavier n-alkanes present but do not exist in the gaseous phase and other hydrocarbons with different structures that are co-generated during the thermal alteration or maturation of organic matter.

Often methane coexists with carbon dioxide in reservoirs, produced naturally along with water, as a part of the natural heating and burial of organic matter trapped in sediments. The amount of carbon dioxide varies depending on the input organic matter type. Terrestrial, woody or coaly organic matter tends to have relatively more oxygen present, so can contribute higher amounts of carbon dioxide than that of organic matter from marine or lacustrine sourced organic matter. However the total generation potential of carbon dioxide from organic matter under catagenesis (i.e., on reaching temperatures likely to cause oil and gas generation) is limited by the relatively higher thermal stability of the oxygen-rich molecules that are less prone to break down to carbon dioxide so the overall contribution from the organic matter is not great (Stalker, 1994).

Rather, higher concentrations of non-hydrocarbon gases, including carbon dioxide tend to come from sources other than the organic matter (Stalker, 1994). In the case of carbon dioxide, relatively high (8-16%) concentrations can be seen around Gorgon-Io-Janz fields and the Rankin Trend of the off shore North West Shelf area of Australia (Boreham et al, 2001). The source of carbon dioxide is from far deeper hotter zones which might have undergone thermal decomposition of carbonates where faulting has acted as conduits to transport some of the carbon dioxide to shallower intervals where the gas has been trapped. This is seen in other cases around the world such as at the Sleipner Field, Norwegian North Sea (James, 1990). Carbon dioxide may be derived from volcanic or magmatic origins (as is the case for the southern Sydney Basin; Faiz et al, 2003). Analysis of helium isotopes (found in trace amounts in reservoired gases) can provide some information about the source of the carbon dioxide (or in some instances deep methane).

Other gases that may "contaminate" the hydrocarbons in coal seams or other reservoir intervals may include hydrogen sulphide. While some contribution may come from the organic matter generating the methane and other hydrocarbons, hydrogen sulphide can often occur due to the addition of other gas sources that are not related to the maturation of organic matter. If a source rock has undergone some washing from saline waters (ingress from the ocean) higher amounts of sulphur can become incorporated. But again typically high volumes of hydrogen sulphide (and carbon dioxide) may have been generated from thermochemical sulphate reduction (Reaction 1: Stalker, 1994 and references therein) as is seen in areas with high amounts of evaporates (rocks deposited via evaporation leaving rocks rich in salts such as halite (NaCl), gypsum [$CaSO_4.2H_2O$] or anhydrite ($CaSO_4$) in areas in Alberta, Canada (Krouse et al, 1988).

$$4CH_2O + SO_4^{2-} \rightleftharpoons 4CO_2 + H_2S + 6H^+ \qquad \text{Reaction 1}$$

However, while rare, hydrogen sulphide has been observed in coals from NE Asia, France, USA and Australia (Gillies et al, 2000). Significant occurrences have been found in mines in Queensland (Bowen Basin). Sulphate addition from seawater that is not removed by pyrite formation, due to lack of iron, is a likely process that leaves free sulphate to be reduced by bacteria. Stable sulphur isotopic data can show the pathway resulting in the trapping of hydrogen sulphide in coals (Gillies et al., 2000 and references therein). Interest in understanding and anticipating the presence of hydrogen sulphide is due to the threshold limits for hydrogen sulphide being 10ppm for an 8 hour exposure, or 15 ppm for a 15 minute exposure, and where 500ppm will induce death.

In the case of conventional oil and gas reservoirs, there can be a sliding scale of the amount of higher hydrocarbons dissolved in gas versus gas dissolved in oil (condensates). In some cases the gases may contain abundant aromatics or waxes, for example some of the cases in the Otway basin (Boreham et al, 2008). Gases from terrestrially derived organic matter (i.e., woody or coaly material) can also have notable amounts of nitrogen and examples of high nitrogen gases include those in Germany from Carboniferous Coals (Krooss et al, 1995) in the Rotliegend and Buntsandstein reservoirs, but are also observed in wells in Otway, for example (Katnook-1 has 78% nitrogen (Boreham et al, 2001). Nitrogen is also found in some parts of the Adavale, Bonaparte, Cooper/Eromanga, Gippsland and Perth Basins in the range 20-50%, and > 50% in parts of the Cooper Basin (Boreham et al, 2001 and references therein). The source of the often abundant nitrogen could be from primordial, volcanic, magmatic, radiogenic, atmospheric, organic or inorganic origin (Krooss et al, 1995). High temperatures in the interval where the organic matter resides was believed to be a major component of the presence of high levels of nitrogen. However, so far, it has been difficult to attribute source of nitrogen using stable nitrogen isotopic data to date. In the case of NSW, the predominant secondary gas in coal seams in the area is carbon dioxide (Faiz et al, 2003 and references therein).

2.1.4 GAS COMPOSITION IN NSW

There is some open file information on the gas composition of coal seam gases in NSW (Faiz, 1993; Pallasser and Stalker, 2001; Faiz et al., 2003; Pinetown et al, 2008; Pinetown et al, 2009; Saghafi and Pinetown, 2011; Pinetown, 2013) as well as data lodged at Geoscience Australia. Some examples of the data from the Southern Sydney Basin are used to illustrate identification of source and alteration of gases in Section 3.4.

2.1.5 MATERIALS SAFETY DATA SHEET (MSDS) INFORMATION

MSDS, or materials safety data sheets, are useful tools to identify potential hazards or handling issues with chemical compounds. There are a number of companies who have these MSDS sheets on their websites. Laboratories will have these printed out and available for all chemicals they use, including gases. Appendix A contains a copy of the scientific MSDS for methane to show the sort of information available. This information has been used in part to populate Table 4.

2.1.6 HAZARDS

Simply put, methane, as with most gases, can be an asphixiant; in other words when it leaks it displaces air (containing oxygen) to such an extent that the oxygen contents of the air in the immediate area is reduced from its normal levels to a level unable to sustain life. It is an asphixiant rather than a toxic substance to animal life and can induce death in plants also to displacement of oxygen in the root zones. The other major hazard is that of its flammability. It does require an amount of oxygen present and an ignition source to provide a flame. As with most gases, the other major hazards are related to the pressure the gas may be stored under. If the vessel is over pressurised, it could be prone to failure, resulting in a rupture of the vessel and projectiles being propelled, or for a stream of high pressure gas to hit an individual. Sudden pressure drops can cause freezing around pipes and cause significant freeze burns.

The flammable range for methane, i.e., the concentration of a gas or vapour that will burn or explode if an ignition source is introduced (conditions of 20°C and atmospheric pressure) range from 5-15% (Table 7).

Table 7 Lower and upper flammable limits for methane and other well known organic materials.

Compound	Lower explosive or flammable limit (LEL/LFL) %	Upper explosive or flammable limit (UEL/UFL) %
Methane	5	15
Ethane	3	12.4
Gasoline	1.4	7.6
Methyl alcohol, methanol	6.7	36
Turpentine	0.8	
Diesel fuel	0.6	7.5
Acetic acid	19.9	

From http://www.engineeringtoolbox.com/explosive-concentration-limits-d_423.html

2.2 Uses of Methane

2.2.1 INDUSTRIAL

The primary use of methane is as a fuel source. This may be in the form of natural gas which is often used for energy generation at power plants. Alternatively the methane gas can be converted to liquefied natural gas (LNG) which can then be used in vehicles with suitable tanks. The LNG process is mainly to facilitate transport of large volumes of natural gas to market more efficiently through conversion to a denser liquid. Methane (and other hydrocarbons) is also able to be processed to join the smaller molecules into longer chain higher value products such as gasoline or diesel fuel by Gas-to-Liquid (GTL) processing. The conversion process (Figure 3) is still a subject of major research and of interest in locations where there may be an absence of liquid hydrocarbons stocks, such as here in Australia.

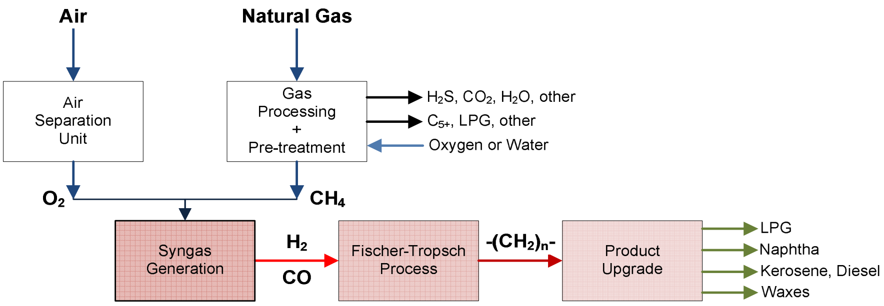


Figure 3 Methane used in the process to convert gas-to-liquids (GTL) as a means of generating hydrocarbons of larger molecular weight (V. Sage Pers. Comm).

Methane is also used as the feedstock for the generation of methanol and other organic solvents and hydrogen.

2.2.2 LABORATORY AND ANALYSIS

Methane in a mixture with argon is used in analytical tools such as Geiger counters. It is also used in x-ray fluorescence (XRF) as a quenching gas during analysis. It is also used as a calibrant in gas mixtures to measure an array of other organic compounds in the petrochemical industry, in equipment for conducting oil and gas surveys and for measurement of trace impurities.

3 Geological Sources of Methane

3.1 How to Assign the Source of Methane and Other Hydrocarbons

There is often a degree of difficulty in assigning the source, maturity and impact of secondary alteration to a body of natural gas. This is because there are far fewer compounds present in a gas field to analyse and assess than for an oil sample because of their smaller carbon number and limited configuration of these small molecules into different chemical species. But, assuming that a given gas sample contains C_1 (i.e., methane) to C_5 (pentanes) and carbon dioxide there are a number of analyses and interpretation tools that can be used, with caution, to ascribe some geological information about the source of gas sample.

3.1.1 COMPOSITIONAL ANALYSIS

Gas compositional analysis is usually conducted by gas chromatography (GC) using a variety of detector types. It is assumed suitable calibrations are conducted on the instrumentation and the results are usually expressed in normalised percent values either by mole or by volume. The results are often used to generate ratios such as;

- Dryness, expressed as $C_1/(C_1 + C_2 +\ldots+ C_n)$, or alternatively,

- Wetness, expressed as $((C_2 + C_3 + iC_4 + nC_4 + iC_5 + nC_5)/(C_1 + C_2 + C_3 + iC_4 + nC_4 + iC_5 + nC_5))$ X 100

Where “C” is a carbon atom (i.e., C_1 = methane), “i” is the iso-alkane (i.e., iC_4 is iso-pentane) and “n” is the number of carbon atoms.

These ratios give geologists and geochemists information on the amount of methane relative to the heavier or wetter hydrocarbon gases in a sample. “Dry” samples have a lot of methane and little else. A dry sample may be interpreted as being from a very mature (heated to a greater degree, see Table 8) or be dry because most of the wet components have been consumed by bacteria leaving only methane behind.

One example of using gas dryness is presented (

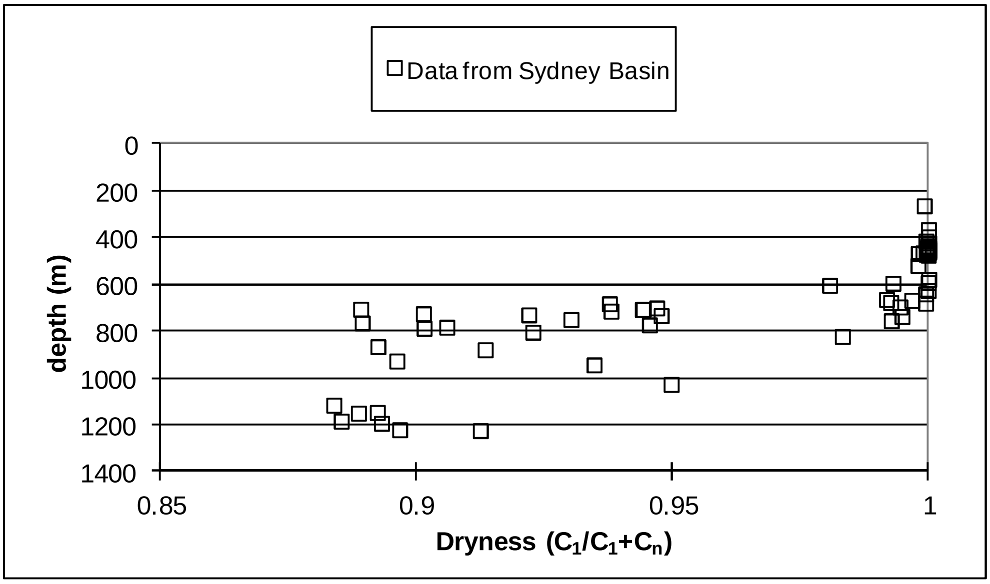
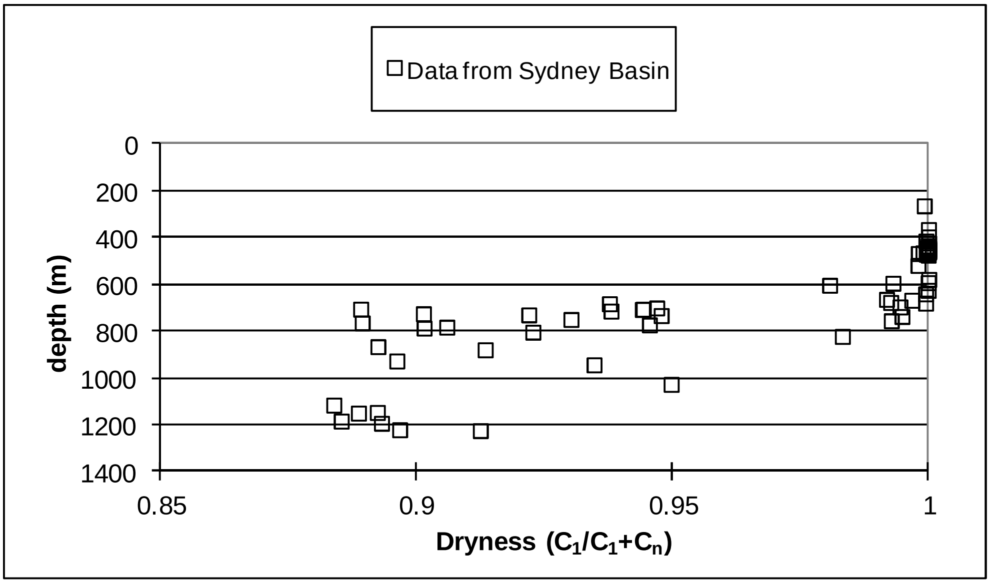


Figure 4) which shows that there can be strong relationships between the depth and amount of methane to wet hydrocarbons in gas samples. In the case of the southern Sydney Basin example (Figure 4) there is a clear change from very dry gas at depths of 200 to 600m (biogenic) and a rapid transition to wetter gases below that depth that relates to the increased contribution from deeper thermogenic sources of methane.



However, the compositional data provides only limited data. It can be complemented by the measurement of the stable isotopes of the gases, that is carbon ($\delta^{13}C$) and hydrogen (δD), discussed in the next section.

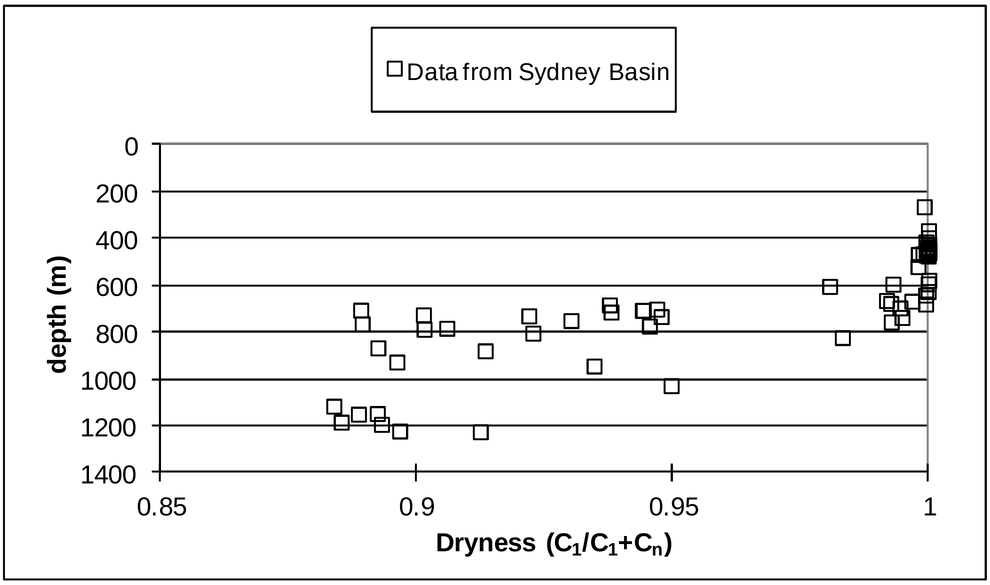


Figure 4 Example of coal seam gas dryness for samples versus depth from wells in the southern Sydney Basin. Data from Faiz (1993), Faiz et al, (2003) and Stalker unpublished results.

3.1.2 STABLE ISOTOPES

“Isotopes may be defined as atoms whose nuclei contain the same number of protons but a different number of neutrons” Hoefs, 1973. While many people are aware of unstable or radioactive isotopes, there are also a group known as stable isotopes that do not generate radiation.

STABLE ISOTOPES OF HYDROGEN

Hydrogen has two stable isotopes: ^{1}H (hydrogen) which makes up 99.9844% of all hydrogen and ^{2}H (also known as ^{2}D or deuterium) which makes up 0.0156% of all hydrogen (Hoefs, 1973). Hydrogen contains one proton versus deuterium containing one proton and one neutron. This large difference in mass results in large isotope effects. For example the density and other physical properties of these molecules have a large impact. In the case of comparing H_2O with D_2O (water and heavy water) the density of H_2O is 0.9982 g cm^{-3} versus that of D_2O at 1.1050 g cm^{-3} (Hoefs, 1973). Other properties change resulting in what is known as “isotope effects”. It is these effects that allow scientists to compare the hydrogen (and indeed carbon) isotopes of compounds to work out source and alteration effects undergone by mapping the ratios of “heavy to light” isotopes.

STABLE ISOTOPES OF CARBON

Carbon has two stable isotopes: ^{12}C (carbon-12) which makes up about 98.89% of all carbon and ^{13}C (carbon-13) which makes up 1.11% of carbon (Hoefs, 1973 and references therein). While ^{12}C has six protons and six neutrons, ^{13}C has an extra neutron. Again depending on the distribution of the different types of carbon (i.e., ^{12}C to ^{13}C), molecules can undergo isotopic effects. One of the best known is the fractionations caused by different plant type metabolic processes (i.e. how the plant types fix carbon during photosynthesis). Because these pathways (one known as the C3 pathway and the other is known as the C4 pathway) are quite different, the isotopic effects are different and the different plant types end up having very different ratios of ^{12}C to ^{13}C. C4 plants include maize, sugar cane and other angiosperms. C3 plants include rice, barley and olive trees as examples.

MEASURING STABLE ISOTOPE RATIOS

Stable carbon and hydrogen isotopes in gases and oils are often measured today using a gas chromatograph-isotope ratio-mass spectrometer (GC-IR-MS) with a combustion furnace to convert the materials to hydrogen for δD data and carbon dioxide for $\delta^{13}C$ data. A gas or liquid is introduced into the gas chromatograph to separate out individual compounds, and in the case of measuring carbon, the compounds are passed through a high temperature furnace to be fully converted from the hydrocarbon compound into carbon dioxide. This carbon dioxide is introduced to the isotope ratio mass spectrometer where the different isotopes are measured and corrected for. The delta or δ-values are compared with international standards as follows:

$$\delta \ in \ ‰ = \frac{R(sample) - R(standard)}{R(standard)} \times 1000$$

Where the isotope ratio measurement is the delta value (δ) given in per mil (‰) i.e. parts per thousand and R represents the isotope ratio. The delta-values are reported relative to international standards. Currently, carbon isotopes are reported relative to Vienna Pee Dee Belemnite (VPDB), a mixture that is distributed to laboratories with a known value. Hydrogen isotopes are reported relative to Vienna Standard Mean Ocean Water (VSMOW).

The isotopic measurements on their own or in conjunction with the chemical composition of gases are used to characterise their source and maturity in geochemical studies of oil and gas. In one example, the carbon isotopic composition (in VPDB) is plotted against sample depth for coal seam gases in the Southern Sydney Basin (Figure 5). In this case, at shallow levels, there is a broad range of stable carbon isotopic compositions from isotopically "light" or depleted in ^{13}C up to δ^{13}C –80‰ (biogenic) to as low as the "heavy" or enriched in δ^{13}C values of -23‰ (thermogenic). Below about 600m, the samples all tend to hover around δ^{13}C -45- to -50‰ indicating that the gases are of a thermogenic origin, that is, generated from the action of deep burial to heat and alter the original organic matter. This observation has been seen in many hydrocarbon bearing basins around the world and this empirical approach generally works well.

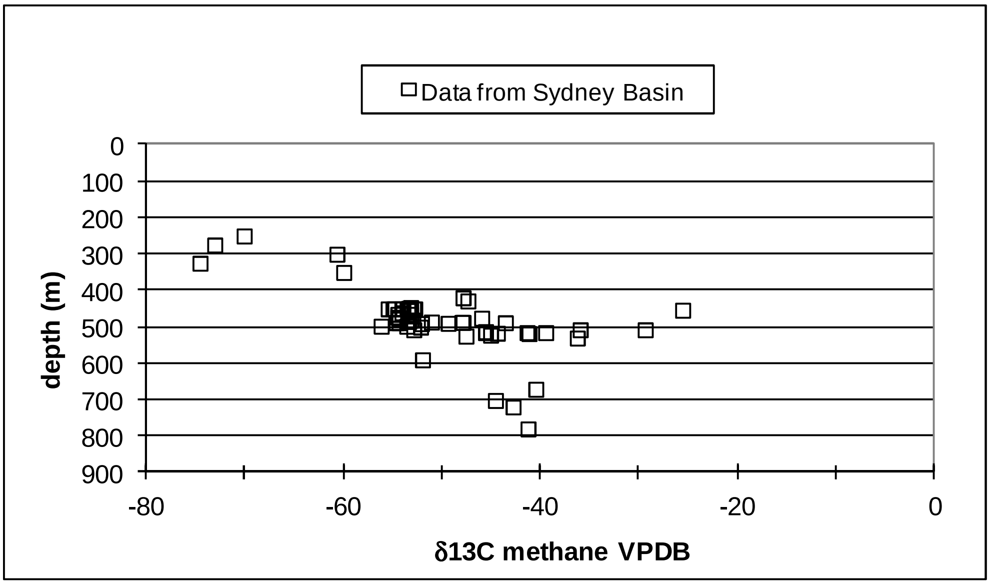


Figure 5 Example of coal seam gas stable isotopic carbon distribution of gases for samples versus depth from wells in the Southern Sydney Basin. Data from Faiz (1993), Faiz et al, (2003) and Stalker unpublished results.

3.2 Sources of Methane

There are a number of sources of methane in the environment, particularly the subsurface, that can be classified as geological and biological sources (Figure 6). The stable carbon isotopic signature of methane is one of the main diagnostic methods used to give some provenance information on the source of the natural gas and is used to good effect for methane and carbon dioxide (Figure 7). Organic matter from marine sediments may be in the range δ^{13}C -40 to – 55‰ while terrestrial organic matter is relatively more enriched in ^{13}C with values of δ^{13}C -25 to -40‰. Permian coals of eastern Australia have been reported to have values that are fairly enriched in ^{13}C as well. However, the carbon isotopes can be impacted by secondary processes such as microbial alteration (Schoell, 1980; Whiticar, 1999). The view has long been held that microbial alteration results in methane that is isotopically depleted in ^{13}C such that any methane with a δ^{13}C value of less than -60‰ is regarded as being of a microbial origin (Figure 6).

The evolution of organic matter from initial deposition, subsequent burial and thermal alteration is well understood and summarised in texts such as Tissot and Welte (1984) or Hunt (1996) and is discussed further in Section 3.2.1.

Other geological sources may be regarded as abiogenic (i.e., non-biological), coming from the degassing of hot magmatic rocks, or emitted with hot geothermal liquids but these may not be quantitatively significant with respect to economic methane accumulations (summarised in Schoell, 1988).

Subsurface biological sources include fermentation and decomposition mechanisms facilitated by microbial organisms in the main. A good general overview of the mechanisms is well presented in a paper by Schoell (1988) and subsequent works discussed in Section 3.2.2.

3.2.1 GEOLOGICAL AND THERMOGENIC METHANE

Mantle degassing from great depth and abiogenic gas generation can produce methane or other hydrocarbons as is reported in the literature (Schoell, 1988). Some methane gas data reported from New Zealand, by way of example, may be in the range of $\delta^{13}C$ -26 to – 30‰ (Lyon and Hulston, 1983). The values indicate the potential for either shallow or deep crustal carbon from inorganic or organic sources. The mode of generation can be at very high temperatures and pressures. In the case of the New Zealand gases, they were believed to be formed at temperatures of 300 to 450°C. In a laboratory simulations, observations of the mechanism of methane generation in the Earth's mantle showing carbonate breakdown (that is the heating of minerals such as calcium carbonate or calcite to the extent that it degrades to a gas) at 5 to 11 GPa (72,5189 – 1,595,415 psi) and temperatures of 500 to 1500°C have been made (Scott et al, 2004). While abiogenic hydrocarbons do persist, they are deeply buried and seldom found in significant quantities and are therefore unlikely to be the source of commercial deposits of hydrocarbons. Abiogenic gas was first postulated in the 1950s by Thomas Gold (Gold, 1992).

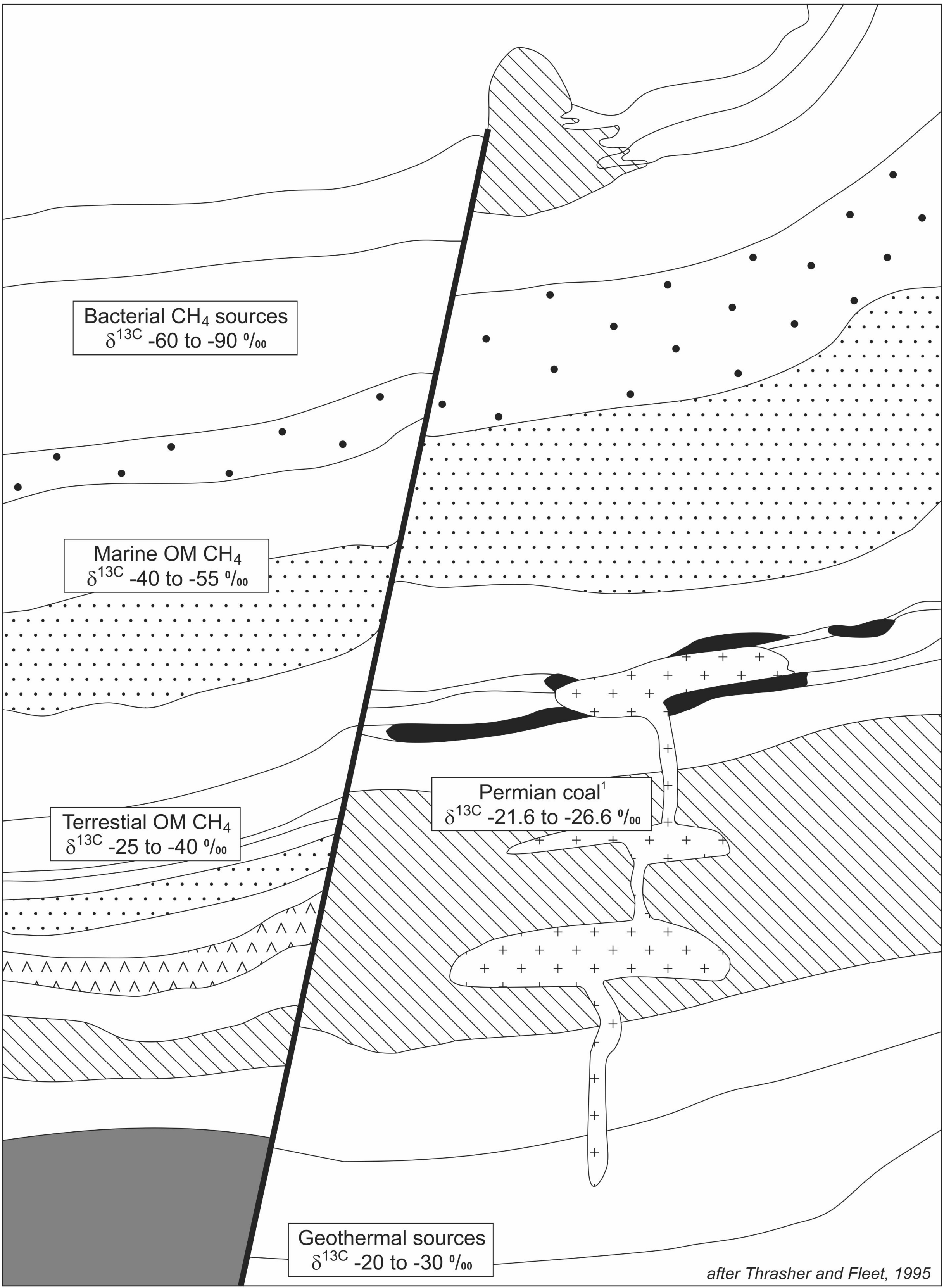


Figure 6 Different sources of methane generation in the subsurface, modified from a figure on carbon dioxide origins by Thrasher and Fleet, 1995. The figure presents ranges of stable carbon isotopes of methane pertinent to differentiating different sources. [1]Data from Smith et al (1982) for Permian coals.

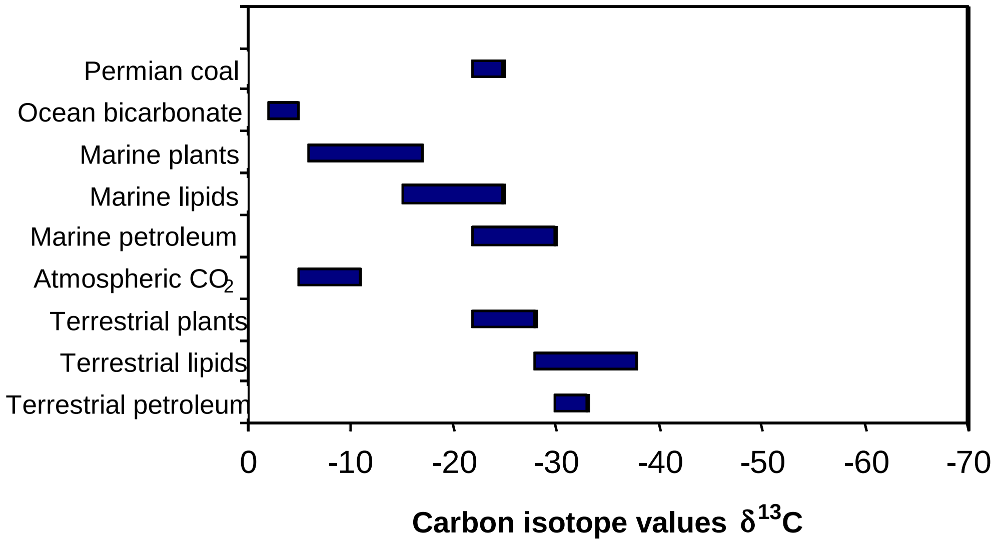


Figure 7 Overview of carbon isotopes of organic matter that can contribute to the formation of methane. For example, the carbon isotopic composition of Permian age coals (derived from land plants at that time) range from δ^{13}C -20 to -30‰. Modern terrestrial plants are similar in range but marine plants are more enriched in ^{13}C. Modified from Stalker et al., (2013) and references therein.

But the most quantitatively significant source of methane that can be harnessed by humans currently is from the drilling of deep structures in the subsurface that have trapped hydrocarbons sourced by the thermal alteration of organic matter or thermogenic methane. The organic matter is typically the matter trapped during the burial of muddy materials associated with marine, lake or peaty deposits, depending on the depositional environment locally. The organic matter is preserved in oxygen-poor or anoxic environments so that the carbon is not directly converted by microbes or decay mechanisms to carbon dioxide.

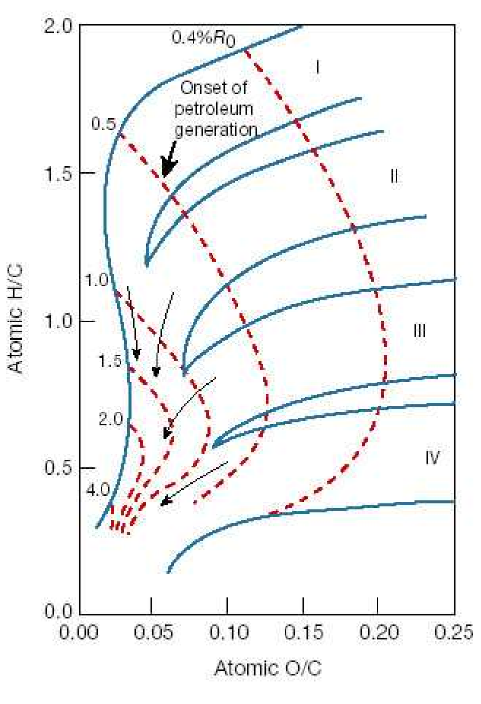
Methane can be the primary component of the hydrocarbons that are matured or expelled from the buried mudstones or shales. Hydrocarbons can have a range of chemical compositions from long chain waxy molecules, aromatic rings or lighter molecular weight gases dissolved in these larger molecules in solution at depths as “oil-associated gas”. Further heating and cracking of the hydrocarbons can cause the reduction in chain length of the molecules ultimately producing methane. Understanding the source of methane in the subsurface is an important factor in anticipating the discovery and definition of a new oil or gas field or whether a coal seam has reached sufficient maturity to produce and absorb methane. This involves understanding the original organic matter type and how much that organic matter has been heated and pressurised to a given level of maturation. Type I/II organic matter that comes from a lake (lacustrine) or marine setting, tends to produce more of the longer chain or “wetter” hydrocarbon components relative to Type III coaly (terrestrial land plant) organic matter (Table 8). Type III organic matter tends to produce both larger quantities of carbon dioxide and drier gas with mainly methane. Peak methane generation from Type III kerogen occurs at deeper/hotter temperatures than Type I/II organic matter. The low temperature methane curve shown in Table 8 relates to shallow biogenic methane generation that occurs at the onset of burial.

While the source of the organic matter has an impact on the chemistry of the gas generated, the maturity (temperature history) of the source rock also influences the composition of the gas. Table 8 shows the types of information used to understand the level of maturity of a source rock as it is buried in terms of temperature (which can be inferred from the geothermal gradient) and how it impacts on the maturity or rank of coal.

Burial depth in kilometres is shown along side the temperature expected for a region where there are no hot spots in the subsurface, for comparison in Table 8. These physical measurements are compared with the vitrinite reflectance values for rocks buried at these sorts of depths and temperatures. Vitrinite reflectance is a measurement of the amount of light a piece of vitrinite coal reflects back under a microscope (Table 8). It provides the maximum heating that the rock received during burial. This information gives geologists information on how mature the organic matter in a sample is and it can be applied to any type of organic matter. Coals are also characterised by “rank” which is a series of parameters that characterises the metamorphosis of the organic matter from peat and lignite (which may only have a low carbon content) all the way through to anthracite which may contain more than 85% carbon. In addition to these methods of characterising organic matter in the subsurface, the elemental composition (from which we can define organic matter into the Type I, Type II and Type III as described in the previous paragraph) also impacts on the metamorphosis of the coal and organic matter as it is buried. This has been documented in the van Krevelen diagram (Table 8) which shows the evolution of the different kerogen types as they are increasingly matured. The hydrogen to carbon ratio shown on the y-axis of the figure in Table 8 is used to estimate the chemistry of the hydrocarbons generated. If there is more hydrogen, there is more likelihood of liquid hydrocarbons generated from Type I and II kerogen, whereas Type III and IV are hydrogen poor, and may generate increasingly drier gases.

All of the information described above and the geological context are all taken into consideration to define the source and maturity of the organic matter source material and the resultant hydrocarbon liquids and gases.

Table 8 Maturation parameters showing the evolution of coaly material as it is altered by the action of heat and temperature during burial. Tabulated data from Hunt (1996). Figure Seewald, 2003.

Depth km	Temperature °C	Vitrinite Reflectance %	Coal Rank	Van Krevelen Diagram showing evolution of kerogen types as maturation increases
0	20	0.3	Lignite	
1	47	0.4		
2	75	0.6	Subbituminous	
3	102	1.0	High volatile bituminous	
4	129	1.35	Medium volatile bituminous	
5	157	2	Low volatile bituminous	
6	184		Semianthracite	
7	211	4	Anthracite	
8	238		Meta-anthracite	
9	266			

3.2.2 BIOLOGICAL OR BIOGENIC METHANE

During shallow burial, methane can be produced in some abundance. However it may be further metabolised and lost if there are microbes and oxygen available to oxidise the methane to carbon dioxide, thus taking most of the carbon into its lowest energy state. If there is an absence of oxygen, this methane can be buried deeply and may be later discovered as a source of biogenic gas. Alternatively, the organic matter is preserved more completely and taken to deeper depths to be affected by thermal maturation.

There is a pattern of microbial action that occurs during the progressive burial of sediments that is particular to the burial conditions (i.e., presence of nutrients and oxygen in particular; Whiticar, 1999). An illustration of the mechanisms of microbial alteration of organic matter in near surface environments is presented in Figure 8. There are differences in the microbial pathways depending on the location of the organic matter. In the case of freshwater sediments, decarboxylation (i.e., loss of carbon-oxygen groups) of organic matter may lead to carbon dioxide generation followed by subsequent reduction to methane, or direct fermentation of the organic matter to methane. This may cycle as other sources of nutrients or other microbes interact in the subsurface or consume the products.

In the case of marine sediments, the pathways can be more complex due to the presence of two zones in the subsurface, one where sulphate is present and one where it has been consumed by sulphur microbial species (Figure 8). Here decarboxylation and other conversion mechanisms predominate in different zones.

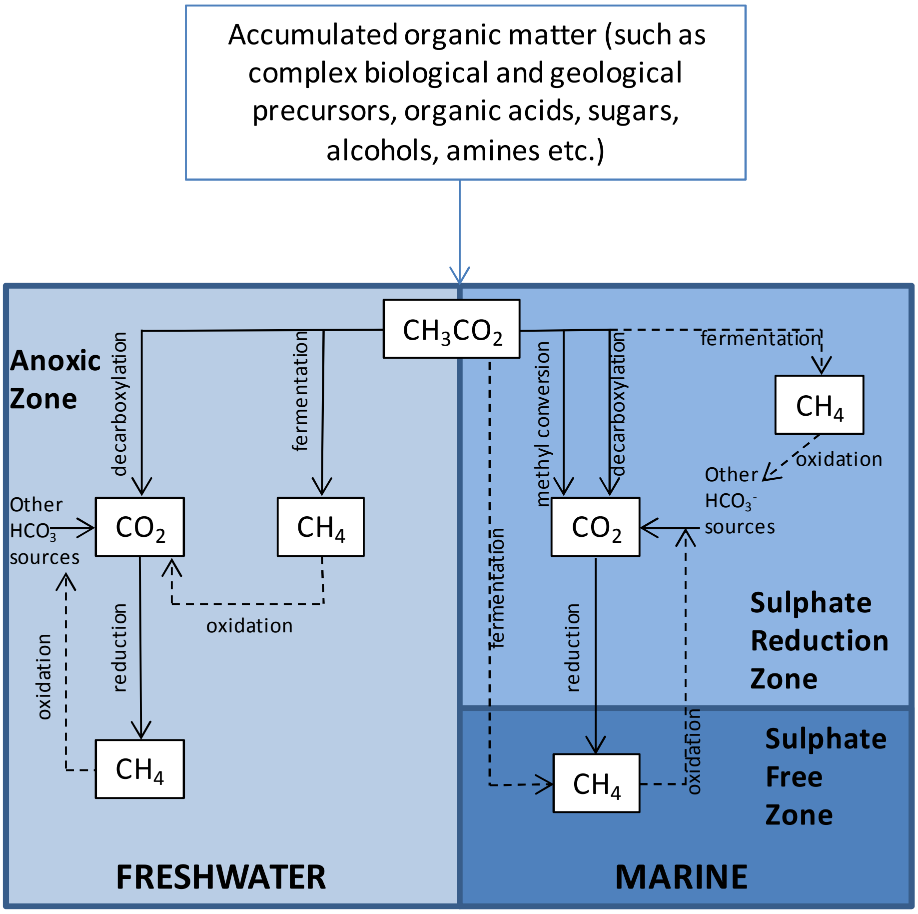


Figure 8 Schematic illustration of the pathways for the alteration of organic matter, which tends to be defined as a generic CH_3CO_2 or acetate molecule, during preservation and burial in fresh and marine water environments. Note that in freshwater environments the preservation of methane relies on a lack of oxygen in the subsurface (i.e., an anoxic zone), whereas the marine system is more complex. Figure adapted from Whiticar, 1999.

In marine sediments there is generally a sulphate reduction zone (Figure 8) where carbon dioxide may be generated during burial (i.e., an area within which sulphur reducing bacteria occupy. With increasing depth of burial and entry into the sulphate free zone, the microbial population changes (as the sulphate reducers have consumed all the sulphur materials) and can reduce the carbon dioxide to methane. If no further microbial alteration takes place, this methane can be trapped and buried deeper. The composition of methane to wetter hydrocarbons such as ethane and propane, together with the carbon isotope data are used to identify potential biogenic sources with methane with $\delta^{13}C$ of -60‰ or less being regarded as a microbial methane gas signature (Figure 9). However, biological sources of methane can be more varied than first anticipated (to be discussed in Sections 5 and 7.2).

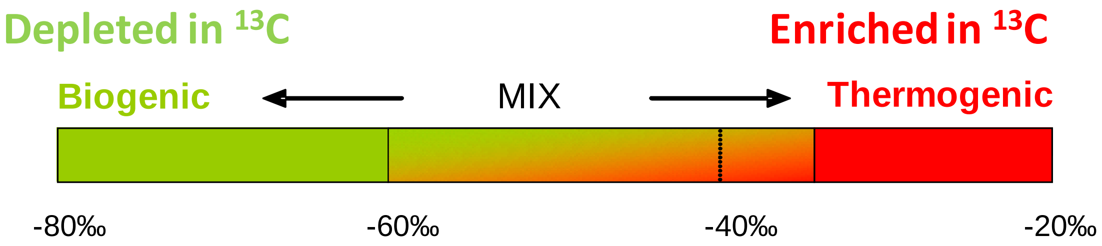


Figure 9 End member values for stable carbon isotopes of methane and the potential for mixing between these two sources in a reservoir. Geological information, such as burial history, type of organic matter deposited and potential for the introduction of later gas charges all have to be considered when evaluating the stable carbon isotopic data.

Assuming a degree of preservation, thermally matured organic matter (Section 3.2) can later become biodegraded by microbes as well. Following expulsion of oil or gas into shallower reservoir intervals, the hydrocarbons can become consumed and converted progressively into smaller chain molecules including methane. This often occurs at temperatures of less than 80°C as there has been a lack of “pasteurisation” of any microbes that may have been deposited in the system to begin with. Alternatively meteoric water from the surface can enter the formations later which is believed to be a potential transmitter of new microbes and nutrients into fields that are of deeper thermogenic origin. These fields are then “degraded” by consumption of some species leaving either very dry methane deposits or very heavy oils where the lighter components have been removed.

In both cases of microbial alteration, the chemistry and stable isotopic composition of the hydrocarbons, including methane can be altered significantly from the original source matter input signature. Carbon isotopes have for a long time been regarded as an important method for identifying the presence of microbial methane in particular with a $\delta^{13}C$ signature of less than -60‰ being taken as a standard maximum value (Figure 9; Schoell, 1980; Clayton, 1991; Smith and Pallasser, 1996; Whittaker, 1999; Faiz et al 2003).

Microbial alteration of hydrocarbons in coal seams has been a recognised feature of Australian coals and is well reviewed in Faiz and Hendry (2006). They note that Eastern Australian Basins contain gases that have undergone abundant microbial activity, especially in those seams shallower than 600m. The extent of microbial methane potentially contributes an order of magnitude higher production rates in those areas containing both biogenic and thermogenic sourced gases.

3.3 Coal Seam Gas as a Source of Methane

Coal seam gas (CSG) or coal bed methane (CBM) has been an emerging area of energy provision in Australia and globally, with activities starting in earnest in Australia in the late 1990s. The exploration and exploitation of this energy source is rapidly expanding to access coal seams that would otherwise be too deep to mine. CSG development is occurring all over the world where coal reserves remain. For some areas this “new” resource provides energy security and local gas to market that has previously been unavailable. In the case of NSW, it has been reported that only 5% of natural gas is local with the remainder imported from Victoria (http://www.energyaction.com.au/news/317-nsw-gas-supply.html;

http://www.energy.nsw.gov.au/__data/assets/pdf_file/0003/476544/Energy-Security-Summit-26092013-BCA.pdf). Relative to coal fired power plants, methane results in a cleaner burning fuel with lower carbon footprint than coal.

Initially coal seams were vented to improve mine safety but it was recognised at the turn of the previous century that methane from coal could be a useful resource. By recovering the methane through production methods, fugitive emissions from mines is reduced thus decreasing impact on climate change.

As is the case with the generation of petroleum or gaseous hydrocarbons from the subsurface, the composition and volume of gas from coal seams is impacted by the following:

- The elemental composition of the source organic matter (i.e., percentage carbon, hydrogen nitrogen, oxygen and sulphur [CHNOS]),
- The materials and matrix of the organic matter (what type of organic matter, woody or algal and percentage of clays, sand etc.) and,
- The level of thermal maturation of that organic matter.

Good overviews of coal seam gas are available and some are fairly recently published such as Moore (2012) and Strapoc et al, (2011).

Coals typically contain Type III or terrestrially derived organic matter which has low amounts of hydrogen. While coaly Type III organic matter can generate liquid hydrocarbons such as n-alkanes, coals tend to retain these materials rather than them being expelled into sandstones. Therefore as the coal is heated and buried more, the longer chain molecules are cracked thermally into smaller and smaller molecules, and results in methane generation. A greater abundance of oxygen or sulphur within the organic matter might also result in an increase in carbon dioxide or hydrogen sulphide production during maturation of the organic matter.

Composition of gases and higher hydrocarbons expelled can be influenced by the different source materials from coals (woody materials, leaf matter, bark, charcoal etc.). These macerals represent different biological materials (a maceral being an equivalent to a mineral identification for these organic components). They are studied to aid in the understanding of the quality of coals for mining or the potential for gas generation and production in coal seam gas exploitation. For example, vitrinite being the equivalent of woody fragments, inertinite is almost charcoal like material, poor in hydrogen. A general overview is provided in Strapoc et al, (2011) with reference to the Indiana University Atlas of Coal Macerals to provide more information and images (http://igs.indiana.edu/Coal/Macerals.cfm).

The composition of the organic matter together with the level of maturation is responsible for the mobilisation (or lack of) within sedimentary basins.

For different organic matter types, not only is the chemical composition different, the stable isotopic composition is different. So the ^{13}C of the starting material will vary depending on the origins of the organic matter, i.e., plant versus marine sourced organic matter, but the action of heating and maturation has an impact during thermal cracking as well. Examples of the carbon isotopes of some initial coals are presented in Table 9 to show the variability (or lack in some cases) depending on the organic matter type, the age or maturity of the samples.

The continuous challenge to understand the source of natural gas is to use the limited compositional and stable isotopic data available to deconvolute the impacts of origins of organic matter versus its journey along the maturation pathway with increasing burial depths and temperatures (Table 8).

Furthermore, secondary processes impact on the hydrocarbons and kerogen. A predominant process is microbial alteration, which can occur at more than one point on the pathway from deposition to deep burial as discussed above.

Table 9 Stable carbon isotopic composition of methane from different basins around the world.

Country	Basin/Location	Other info	Material	Depth (m)	Vitrinite reflectance Ro%	$\delta^{13}C$ coal range	Average	stdev	Number of samples	Reference
Poland	Upper Silesian Coal Basin		Coal/kerogen	214-658 m below sea level	0.59-1.5		-23.9	0.3	13	Kotarba & Clayton, 2003
Poland	Lower Silesian Coal Basin		Coal/kerogen	263-397 m below SL	0.97-4.22		-23.8	0.4	69	Kotarba & Clayton, 2003
Poland	Lublin Coal Basin		Coal/kerogen	690-713 m below SL	0.66-0.68	-23.2 and -23.4			2	Kotarba & Clayton, 2003
Poland	Upper Silesian Coal Basin		Carbonaceous shale/kerogen		0.59-1.52		-23.6	0.5	28	Kotarba & Clayton, 2003
Poland	Lower Silesian Coal Basin		Carbonaceous shale/kerogen		0.97-4.22		-23.2	0.3	10	Kotarba & Clayton, 2003
Australia		Permian	Bituminous coal				-24.4	1.4		Smith et al, 1982
USA		Pennsylvanian, U. Carboniferous	Bituminous coal and anthracite				-23.9	0.4		Mastalerz & Schimmelmann, 2002
Germany	Saar District	Upper Carboniferous	High volatile bituminous				-24.4	1.4		Colombo et al 1970
Germany	Lower Rhine and Aachen districts	Upper Carboniferous medium to high volatile bituminous					-23.9	0.4		Colombo et al 1970
USA	Mahogany Shale, Green River Fm	Utah, Eocene	Type I Kerogen, 15.23% TOC				-30.33		1	Ruble et al, 1995
USA	Clavert Bluff Fm, Wilcox Gp	Texas, Pliocene	Type III Lignite, 58.0% TOC				-26.42			Breyer, 1997

3.4 Examples of Interpreting the Source of Gases

Once data is acquired from a gas sample (Section 3.1), there are a number of different interpretation models or templates that can be used to characterise a gas. The example used to illustrate this approach here uses data from the Southern Sydney Basin (SSB) from Faiz et al., (2003) and references therein. In that paper specifically, data have been plotted in a variety of ways in which to show the lateral and vertical distribution of methane, ethane and carbon dioxide in the SSB to better understand the high producing or "sweetspot" intervals.

It must be noted that there are many interpretive models, some which can be more suited to oil exploration, some to natural gas exploration or coal seam gas exploration. Furthermore, they might be specific to certain regions or geological basins. Interpretive models are often built on empirical data from geographic regions, and not necessarily applicable to other locations. Hence most organic geochemists will try several models to verify the interpretation.

Shown earlier (Figure 4) was a cross plot of the gas dryness for samples from the SSB. This showed a simple relationship with depth and degree of biodegradation. Figure 5 showed an equivalent cross plot for the carbon isotopes of methane versus depth and illustrates that there may be more than one methane gas source in the area. This can be related to Figure 9 where the end member biogenic (δ^{13}C -60 to -80‰) and end member coal derived thermogenic gas (δ^{13}C -35 to -20‰) can mix to produce gases that are isotopically mixed and around the δ^{13}C -45 to -40‰).

As there are few wetter hydrocarbons in the SSB area much of the interpretive work has been done solely on the carbon isotopes of methane and gas dryness. As such, an interpretive model of Clayton (1991), defining certain relationships between the gas composition and isotopes, has been applied to some of the data to try to observe any differences between the coal seam gas samples, ascribe the gas to a particular source and attempt to understand secondary processes (Figure 10).

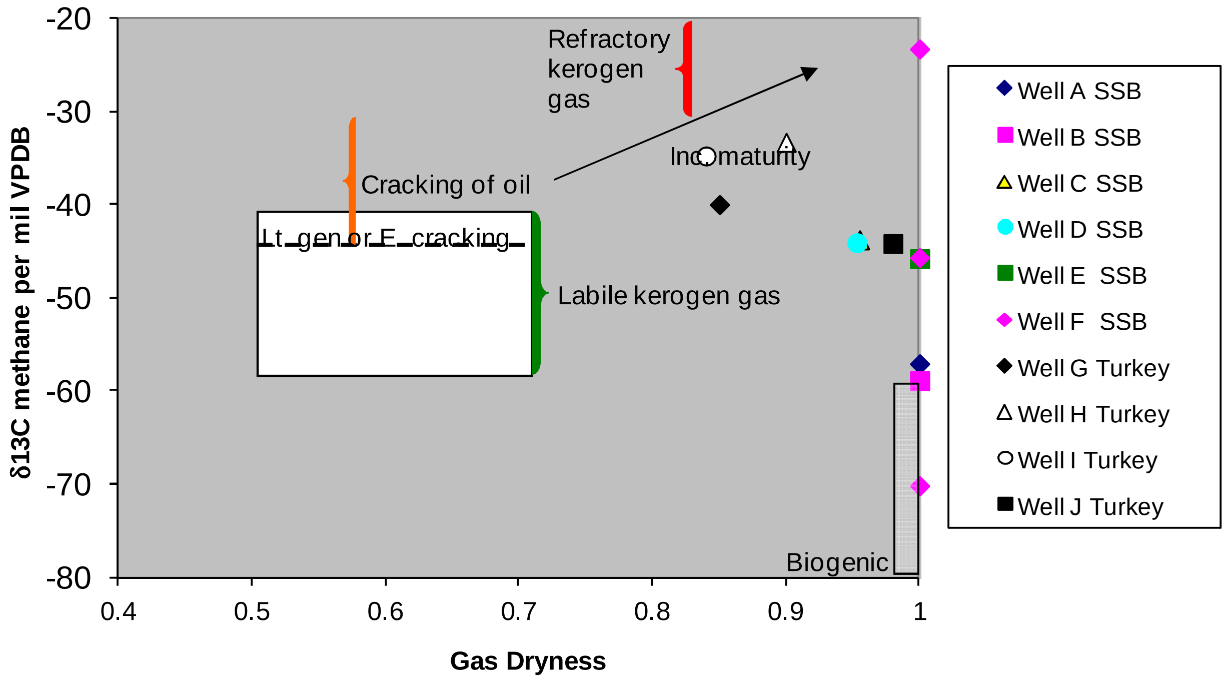


Figure 10 Example of a cross-plot of gas dryness versus stable carbon isotopic composition of methane gas. Even with only this limited data, models have been generated that can provide information on the likely source and secondary effects on a gas. Figure modified after Clayton (1991) with real data from the southern Sydney basin and from Gurgey et al (2005) for illustration to show how other natural gas samples from a marine source might compare with samples from a coaly type III source. Refractory kerogen (i.e., sedimentary organic matter) tends not

to generate hydrocarbons at all, labile kerogen is oil producing, Lt gen or E cracking = late generation or early cracking.

There are a number of other models and plots that can be used to understand the source of the gas and the degree to which biogenic alteration or generation has contributed to the overall gas concentrations in a natural gas or coal seam gas field. Some focus closely on the biogenic versus thermogenic gas mixing and the mechanism of biodegradation (Bernard et al., 1978; Clayton, 1991; Whiticar, 1996; 1999; Smith and Pallasser, 1996; Clayton, 1998; Gurgey et al, 2005).

Figure 11 shows the example of an interpretive plot of gas composition (a modified form of gas dryness on the Y-axis) and again carbon isotopes of methane on the X-axis (where PDB is quoted – an earlier calibrant that has similar values to the modern V-PDB calibrant). The figure is a modification of a number of papers (Bernard et al, 1978; Whiticar, 1996; Gurgey et al, 2005). The figure attempts to differentiate bacterial methane where the dryness is high and carbon isotopes are depleted in ^{13}C, versus thermogenic gas which is wetter and more enriched in ^{13}C. Furthermore, the plot attempts to show what mixing of the two types might result in, and whether the gas generated microbially is from oxidation or fermentation type reactions. The purpose of this differentiation, as mentioned in Faiz et al, (2003) is to identify the highest producing intervals in a coal seam gas field to focus drilling activities and maximise production.

A good summary of some of the main interpretive models used generally is presented in Gurgey et al, (2005) where a variety of models are used to determine the source of gases in natural gas and condensates in the Thrace Basin, Turkey (Figure 10). While the data from Turkey may not be relevant, the model presentations are used to show the range in application and how they are used.

Patience (2003) also used a variety of models to evaluate the contribution of different sources of organic matter to gas found in the Norwegian North Sea, where both marine and terrestrial (coaly) organic matter is present and can generate gas. He summarised that the models used to define the source of natural gases were in need of major revision, as significant alteration of the stable carbon isotopic composition of the gas took place post-expulsion or where low expulsion efficiencies were encountered.

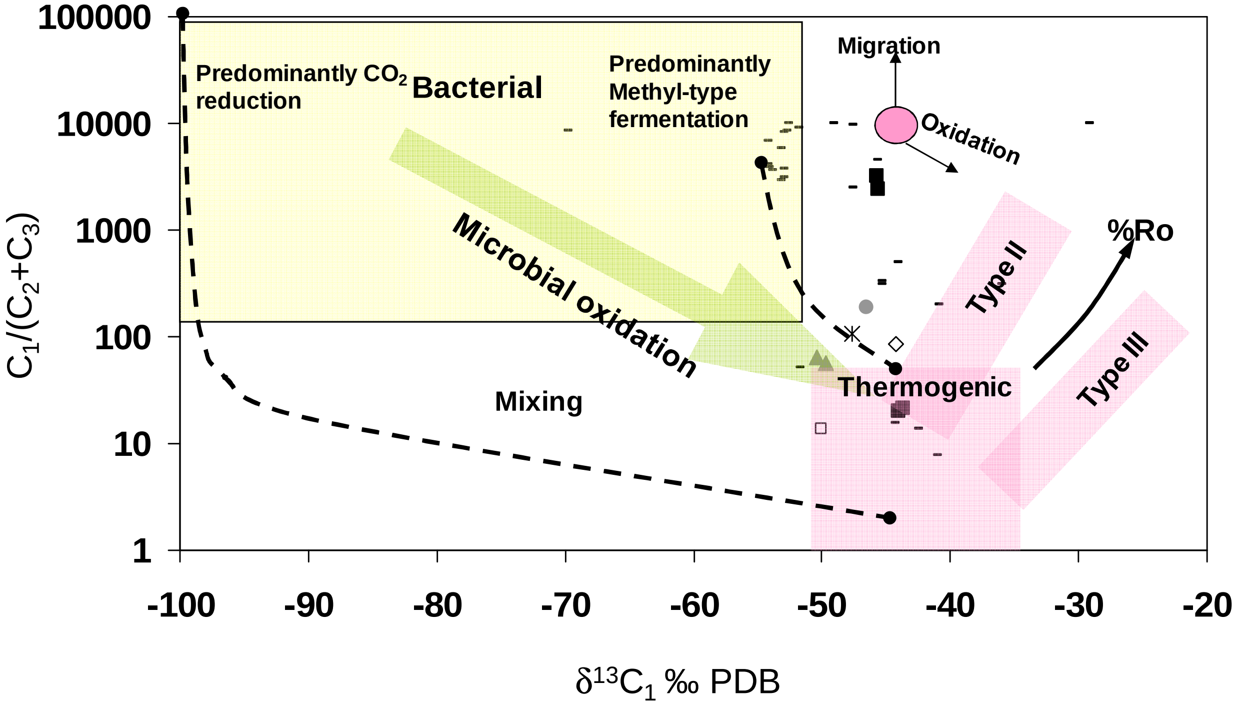


Figure 11 Modified plot showing data from the southern Sydney Basin (unpublished) to illustrate where some of the results fit on the modified Bernard interpretive model which cross plots carbon isotopes of methane against gas dryness. The SSB data show a range from thermogenically derived gas from the deep burial of the coals but some of the gas had come from fermentation reactions to produce biogenic methane. A fuller description of the interpretation of data from the SSB can be found in Faiz et al, 2003.

3.5 Use of Interpretive Models

Clearly these interpretive models (and other models not shown here) have great value in understanding the source of the gases. These models are effective in understanding where the methane has been derived from and can be used to great effect in exploration for gas and oil. This approach has been used to some extent to understand the origin of gas from samples taken from bore waters collected from sites around NSW to determine the potential for commercial gas extraction (e.g., Pallasser and Stalker, 2001; Figure 12).

Not all models will suit a particular geographic or geological region so it is often best to try several different models with the range of data available. Not all the models will agree but there may well be sufficient commonality in the interpretation to provide a degree of confidence that indicates the likely source of the gas present.

An emerging issue is the fact that some of these models may be broadly applicable, however, with advances in understanding the microbial effects on coals and gas, there may be the need for major revision of these models (Section 5 and 7.2) as microbes appear to produce a larger range in the carbon isotopic composition of methane than first thought.

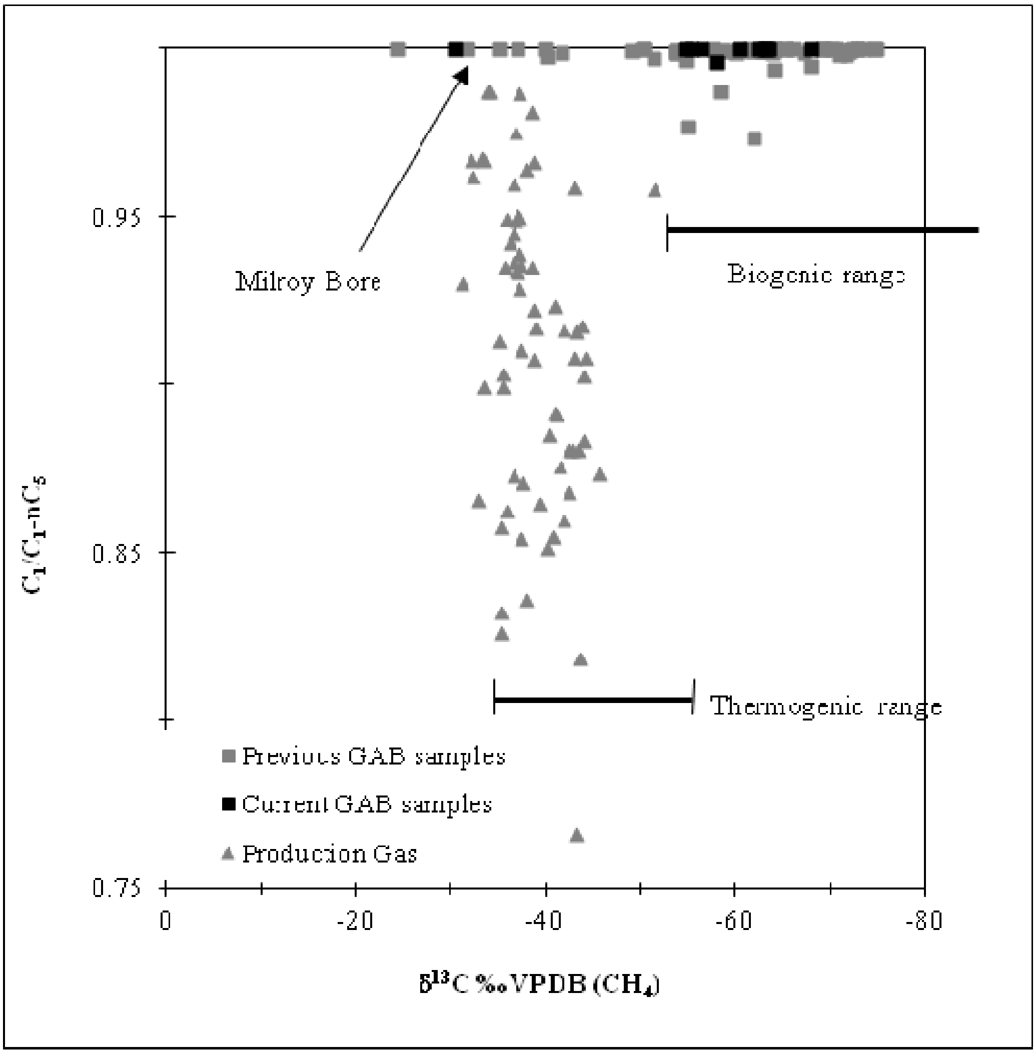


Figure 12 Examples of the data generated by measuring the gas composition (providing gas dryness data on the Y-axis) and methane carbon isotopes of methane. These are samples of gases dissolved in borewaters collected from the Goondiwindi district (NSW), supplied by NSW DPI, where bore waters were used as an exploration tool to identify presence of thermogenic methane which is regarded as evidence of a potential gas field that could be produced. Many of the samples are from different locations in the Great Artesian Basin (GAB) From Pallasser and Stalker, 2001.

4 Coal Seam Gas Production versus Conventional Gas Production

Engineering challenges to produce coal seam gas are one of the major focuses on extracting methane currently. This is because the production of methane from coal seams is quite different from the conventional extraction of methane and higher hydrocarbons from subsurface formations (usually sandstones and carbonate reservoirs). An excellent overview can be found by Halliburton (2008).

4.1 Conventional Recovery

In the case of conventional hydrocarbon recovery, one must first consider that the commercial hydrocarbon discoveries are not found in the same location as the source organic matter from which the hydrocarbons were generated. Instead, the hydrocarbons are generated within the source rock (which may be of terrestrial, lacustrine or marine source as described above). Only if the source rock is sufficiently rich in total organic matter (TOC) will the hydrocarbons reach a threshold pressure which allows them to be expelled from the source rock. From the source rock, this more buoyant fluid will tend to migrate upwards, wetting a migration pathway for the other hydrocarbons being generated to follow.

If geological timing coincides appropriately, the maturation, expulsion and migration of the hydrocarbons will be sufficiently aligned with the development of a trapping interval (zone where the hydrocarbons are contained) with sealing unit (shale or impermeable mudstone) to contain the hydrocarbons from buoyantly migrating upwards. The trapping interval is typically a sandstone or carbonate reservoir with sufficient porosity, permeability and closure above, to retain the hydrocarbons. Because the hydrocarbons are no longer in association with the organic-rich source materials there is far lower impact of adsorption processes on the recovery of the hydrocarbons with conventional hydrocarbon recovery.

The hydrocarbons are often at significant depth and therefore pressure, and in some cases the fields may be overpressurised in the initial phases of production and require limited efforts to recover the hydrocarbons. However as the field pressure declines, pumping of the fluids to surface is increasingly important.

Field developments may occur to infill with further wells to maximise recovery, and detailed 3D models are developed to aid in the recovery of the hydrocarbons. The number of wells used to produce a field over its lifetime will be strongly dependant on the structure of the field and presence of isolated compartments, each of which requires its own well to produce the fluids. Pressure support may be encouraged, or even enhanced recovery processes may be employed, for example carbon dioxide injection for the sweeping and pressure support of hydrocarbon recovery of large fields with an abundance of residual oil.

4.2 Coal Seam Gas Recovery

In contrast to conventional recovery, coal seam gas production requires a different approach. This is due to a number of differences between the storage or reservoir intervals for conventional versus coal seam gas. These include:

- The different trapping or gas storage mechanism of the hydrocarbons in the coal.
- Differences in the rock properties between sandstone/carbonate reservoirs versus the coal matrix as a reservoir.
- How the gas physically moves through the respective reservoirs to be transported to a well.
- The difference in rates at which the gas is recovered for coal versus conventional recovery.

- The approaches to dealing with water recovery and disposal at different times in the lifetime of an asset.
- Density of wells per square kilometre.
- Gas composition differences. Coal seam gas is often much drier than conventional hydrocarbon gas, but there may be increased amounts of nitrogen and very high concentrations of carbon dioxide in some areas.

The coal matrix allows adsorption of the gas onto the coal post-generation and retains much of the hydrocarbons such that they tend not to migrate out of the organic-rich matrix. There is however in some cases evidence of the expulsion of hydrocarbons from the coal seams into adjacent sandstone intervals but they are rarely observed (Philp and Gilbert, 1986; Ahmed et al 2009).

Early efforts to extract methane from coal have had a strong focus on mine safety due to the relatively low explosive limit of methane. However there has been minor utilisation of methane from coal seams reported as early as the 1920s in the US before the recognition that mine drainage by drilling wells was an appropriate step before mining the coal (Halliburton Report, 2008).

4.2.1 GAS COMPOSITION

The gases can have quite different compositions between conventional and unconventional gases. Some examples have been discussed in more detail in Section 3. Conventional hydrocarbon deposits may be richer in higher hydrocarbons (ethane, propane, butanes etc.) and can contain dissolved within them more waxy components or aromatic species dissolved up in them as gas condensates. Conventional resources in the past tended not to have too much in the way of non-hydrocarbon gases, such as carbon dioxide or nitrogen. However, as exploration extent continues, some fields have been discovered and exploited that may contain of the order of 10-20% carbon dioxide, such as the Sleipner Field in the Norwegian North Sea or the Gorgon Gas Field in the North West Shelf of Australia. These fields have or will undergo carbon dioxide removal and storage underground to reduce emissions of greenhouse gases. Sleipner has been safely conducting this method of storage since 1996. There are fields that are very high in methane concentration and these are often the result of biogenic alteration of conventional resources. Fields such as Troll in the Norwegian North Sea contain vast reserves of natural gas that appear to have come from biodegradation of oil accumulations (Larter and di Primio, 2005).

Coal seam gas composition varies due not only to the source of the gas, but also the desorption process. This causes changes in composition over time as methane is preferentially desorbed before ethane or other higher hydrocarbon gases. There can also be far larger quantities of non-hydrocarbon gases such as carbon dioxide or nitrogen. In the example of the Southern Sydney Basin, some wells may have only carbon dioxide present (Faiz et al, 2003), or mixtures with significant dilution by carbon dioxide, controlled in most cases by the structural location of the seam being extracted. Those wells that have intersected coal seams at the top of geological structures appear to have trapped the high concentrations of carbon dioxide. Over time, the relative abundance of methane versus carbon dioxide will change due to the chemical behaviour of each of the species and this may need to be taken into account during production, transportation and sale of the gas.

4.2.2 STORAGE OR TRAPPING MECHANISM

The way in which the gas is trapped in the different rock formations also makes for different methods for the recovery of gas to be employed. In conventional recovery, the gas sits in pore space between the sand grains or in fractures within carbonate reservoirs. It exists as a free gas and is more easily recovered with fewer wells in place. Gas may also be dissolved in the oil phase in some reservoirs and separates out on recovery at the surface due to the large pressure drops on production.

By contrast, gas is adsorbed within the coal matrix as well as potentially being retained as free gas in naturally occurring fractures and cleats within the coal. Because the surface area is of such a great extent in coals, large amounts of gas can be stored within the coal seam. The coal is desorbed when the local pressure drops allowing the gas to be released from the coal. Pressure reduction tends to be due to the production of water also present in the coal.

The profile of gas recovered varies greatly between the conventional and coal seam gas production. Coal seams have been noted to continue to produce slowly for many decades whereas conventional fields will decline in a more pronounced manner over time due to pressure decline.

4.2.3 WATER PRODUCTION

During conventional recovery of hydrocarbons the associated water profile tends to start with very little water present and increase towards later in the production phase of a field. Methods can be introduced to reduce the water production and limit water coning (where it is drawn preferentially towards the well bore). This may be done by blocking higher permeability intervals and drawing on lower permeability intervals where the hydrocarbons have not yet been recovered.

With coal seam gas recovery, water production is at its highest during the initial phases of recovery. Removal of water is essential to reduce the formation pressures to allow the gas desorption to take place. Volumes of water produced from coal seam gas wells can be very high, and as they occur at the onset of production, it results in a significant up-front cost for water treatments and/or disposal. Rates of water production often decline exponentially and reach a steady state. In some cases the water production is not as high, typically in areas where underground coal mining has occurred and water disposal has already occurred. Some other instances do occur where water is less abundant such as in the Southern Sydney Basin.

Water treatments can range from setting up evaporation ponds, reinjection of fluids in nearby formations or even use in desalination plants in more arid regions have been investigated. Not all of these options are still available in various jurisdictions in Australia.

4.2.4 ROCK PROPERTIES

There are significant behavioural differences between the rock properties of a sandstone versus an organic-rich coal. Sandstone intervals that act as hydrocarbon reservoirs often have relatively high porosities (20-30%) and permeabilities from 0.5 to several darcy (darcy is the unit of permeability where a rock with 1D or 1 darcy allows 1cm^3/s flow). Often quartz dominated, they have specific physical properties but are robust and strong intervals in many cases. Some fields may well be less consolidated and result in issues with sand production over time.

Coals have much higher organic matter contents which impacts on their rock strength and behaviour to some extent. The rank or maturity of the coal has an impact on its strength as well and often the higher rank coals are very friable and brittle. The coals are typically very low permeability in the solid part of the matrix, with natural cleats and fractures facilitating desorption of the gas to some extent. Gas can be flowed readily from wells without any additional treatments. However in some cases, because of particularly low permeability, stimulation of gas production can be causing by fracturing parts of the formation to induce gas desorption.

4.2.5 IDENTIFYING AND QUANTIFYING THE PRESENCE OF GAS DURING EXPLORATION

Because of the way in which the gas is trapped in coals, it is not easily possible to identify that a coal seam contains abundant gas using standard well logging tools. During conventional hydrocarbon exploration, well logging tools, measurements of gas dissolving out of drilling muds, or even observed gas kicks during drilling provide major indicators of the presence of methane and higher hydrocarbons. Observations can be made to estimate the flow rates and potential resource size from some flow tests and well logging analysis.

In the case of coal seam gas, the methane and higher hydrocarbons often remain retained in the coal when a well is drilled and so the main method of determining whether a seam contains sufficient methane is to core the interval and measure the gas desorbing from that core sample at the surface. Surface facilities are designed to quickly insert the coal core into gas tight canisters and the volume of gas released under specific temperature and pressure conditions are used to work out the gas content of a given seam. The gas content is dependent on a number of factors including the coal rank, ash content of the coal (i.e. minerals present relative to organic matter), burial history (uplift can cause release of some of the gas), or subsequent recharge from biogenic processes nearer the surface, the chemical composition or source of the organic matter and temperature. All this information is used to quantify the gas composition and gas content of the core for assessing field development.

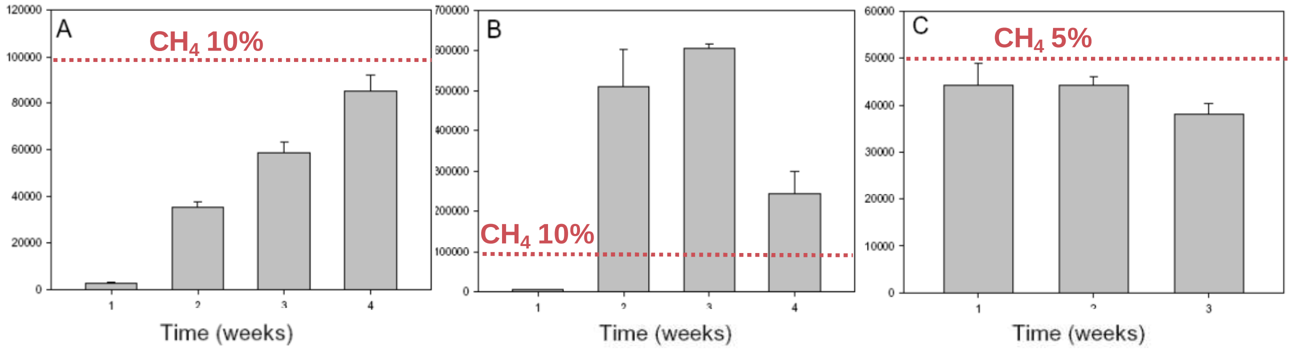
5 Methane as a Potentially Renewable Resource

There is growing interest in evaluating the potential of methane as a renewable resource. This is in part due to the understanding that methane resources do in many cases have significant contribution from biogenic rather than thermogenic generation mechanisms as discussed earlier (Faiz and Hendry, 2006). Early work has occurred that has begun to investigate the mechanism of carbon dioxide reduction to methane or fermentation processes that might produce methane.

An excellent overview of microbial alteration of coals for coal bed methane is presented by Strapoc et al., (2011) who have used a variety of tools to evaluate the behaviour of various microbes and their contribution to the generation of coal seam gas. Detailed studies are being undertaken to evaluate the rates at which methane might be generated by microbes and numerous methods, phylogenetic sequencing which involves the study of the evolutionary relationships that might be observed between groups of organisms by conducting molecular sequencing including rRNA (ribosomal ribonucleic acid) and DNA (deoxyribonucleic acid) analyses (Strapoc et al, 2011 and references therein). Their generalised observations suggest that the rate-limiting step(s) towards the production of methane by bacteria or methanogenic archaea is/are generally not yet well understood.

Batch reactor or similar experiments have been undertaken at various laboratories (including CSIRO; Tran-Dinh et al, 2012) in order to demonstrate that methane can be generated from a culture of coal and microbes from coal producing areas (e.g., Stalker et al, 2009b). Results from coals from NSW indicated that methane could be generated from coal samples. However the concern, as Strapoc et al (2011) point out, is that in the presence of other media or nutrients, care must be taken to correct for any additional carbon pools added during these experiments or an overestimation of the amount of methane generated from the coal itself will occur. Therefore in tests where no additional carbon sources were added, 5% methane (or 50,000ppm) was generated in one test (Figure 13). The stable carbon isotopes were also measured and found to be far more enriched in ^{13}C than had been expected based on the interpretive models discussed in Section 3. Instead, carbon isotopic compositions of these microbially generated gases were much more similar to the coal substrate (i.e., the material used for the basis of the experiment) with values ranging from $\delta^{13}C$ -33 to -47 ‰ (Figure 14). This work and other observations implies that the standard "rule of thumb" regarding the use of carbon isotopes as a simple diagnostic of biogenic versus thermogenic gas may not be as robust as previously assumed.

Much of the expectation that coal can either be naturally or artificially stimulated to produce a virtually renewable source of methane stems from observations in nature. In the case of the southern Sydney Basin the results collected over the years on gases from that region have resulted in the following model being generated (Figure 15). Faiz et al (2003) showed that there was abundant stimulus of new methane generation occurring in the southern Sydney Basin. Initially the Permian age coals were deeply buried and underwent thermal maturation, resulting in the generation of methane, ethane and wetter hydrocarbons with $\delta^{13}C$ -25 to -40‰. Later, this area underwent a period of uplift and erosion, resulting in a loss of the overlying rocks. These rocks had previously applied significant pressure, retaining the gas. The loss of this overburden reduced confining pressures, allowing much of the thermogenic gas to be lost. Modern observations of the gas composition and isotopes in the area shows that the stable carbon isotopic compositions of methane across the basin (values lower than $\delta^{13}C$ -60‰) indicate re-charge of methanearound the shallower edges or margins of the basin with biogenic gas. Coal seams that originally contained thermogenic methane have become re-saturated with methane. The question is whether this process can be stimulated, at relevant rates, to provide ongoing methane via the introduction of microbes and nutrients. Furthermore, could carbon dioxide be used as a part of this process, being one of the two major pathways for generating methane microbially as discussed earlier?



0.25 g Coal
Yeast Medium
<5% H_2

0.25 g Coal
Yeast Medium
80% H_2
20% CO_2

0.25 g Coal
Carbon-free Medium
<5% H_2

Figure 13 Results from batch tests of coal samples that had been inoculated with microbes from a coal district. Y-axis is ppm methane generated. Note that the Y-axis scales vary for each of the above graphs, but the percentage methane generated is clearly labelled for comparative purposes. From Stalker et al., (2009b).

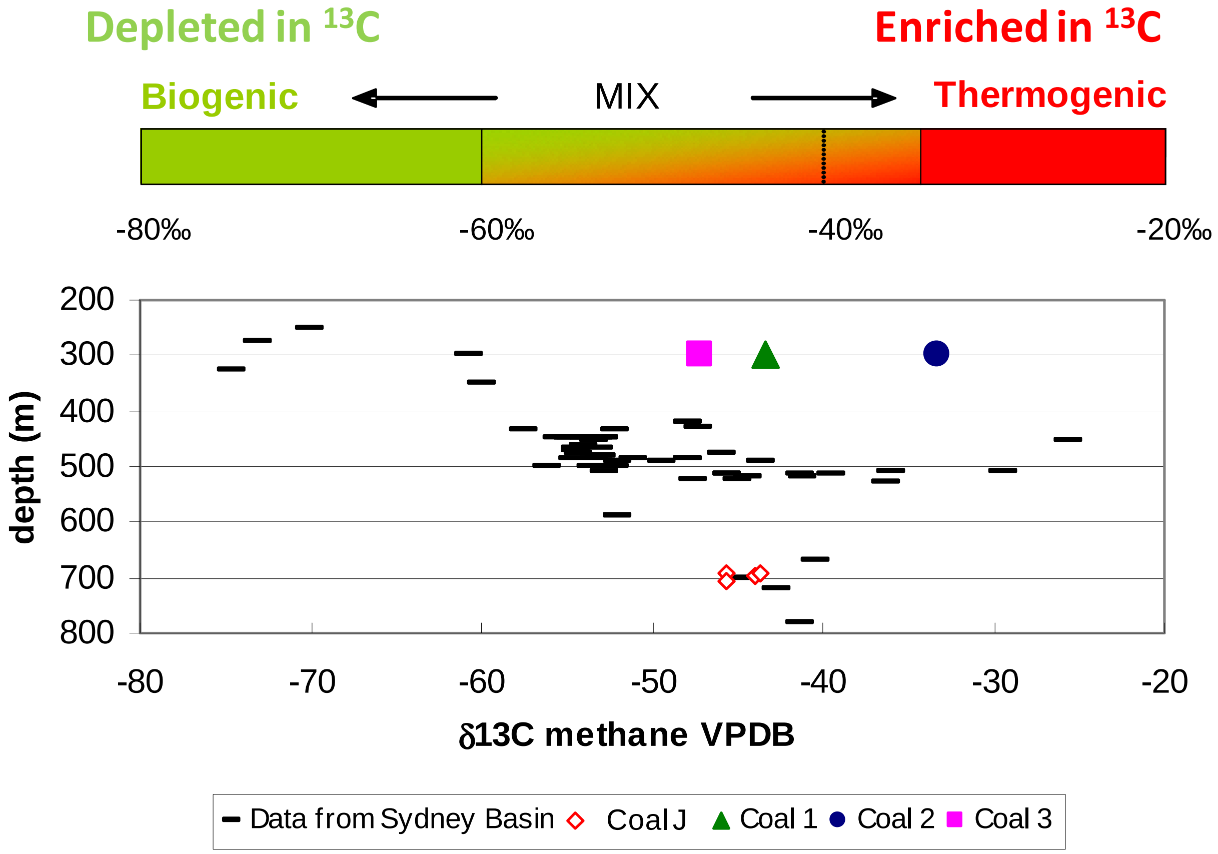


Figure 14 Carbon isotopes of methane generated from batch experiments to demonstrate ability of microbes to generate methane directly from coal. From Stalker et al., (2009b).

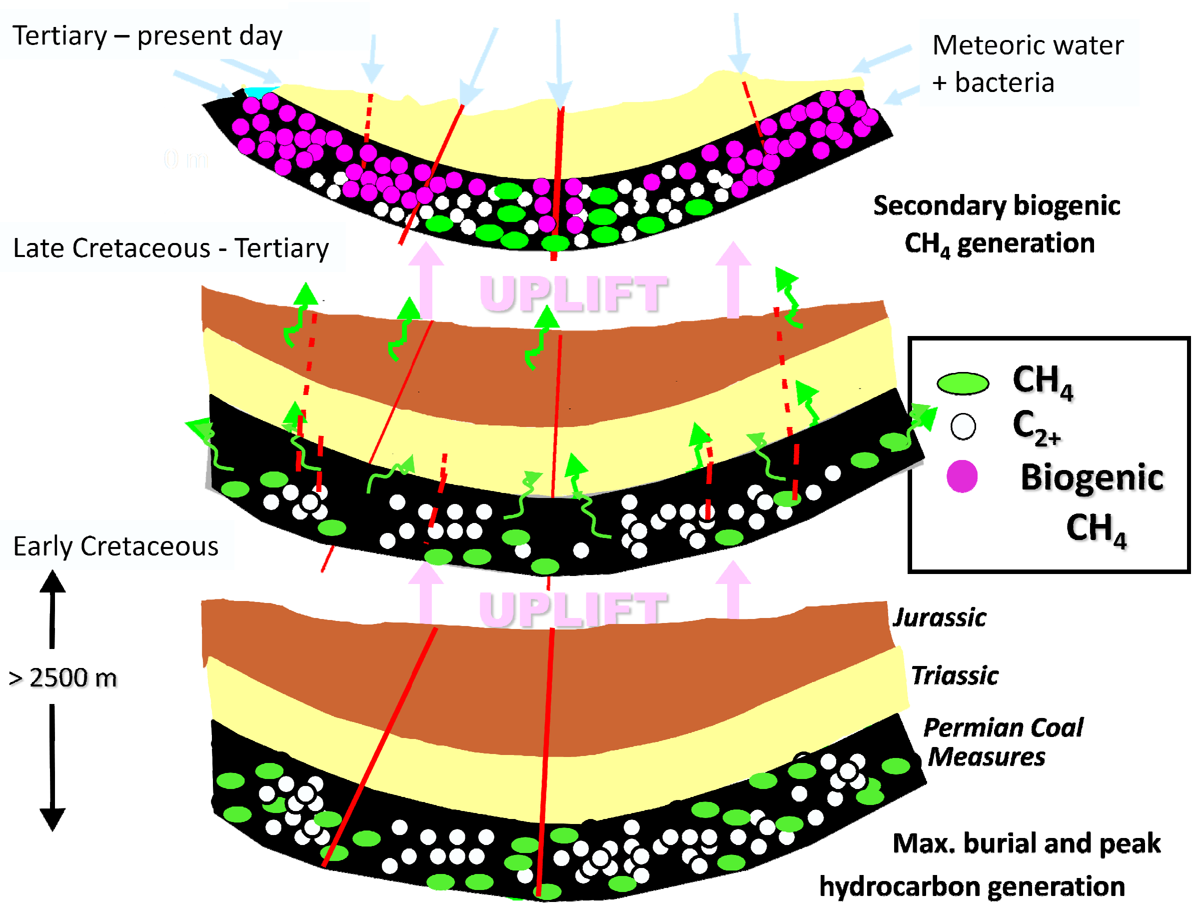


Figure 15 Schematic of the evolution of the southern Sydney Basin and how it became re-charged with methane post-uplift. The lower image from the Early Cretaceous shows the in situ thermogenic production of gas containing methane and wet hydrocarbons from the coals at depth. The middle image shows partial loss of the thermogenic gas during loss of overburden. The upper image illustrates the recharge of methane in the coal seams from the introduction of microbes and nutrients so that coals today in the Southern Sydney Basin have similar gas contents to that in the Cretaceous. Note the increase in faulting (red lines and dashes) as the structures evolve over time. From Faiz et al, (2003). The figure was generated for a number of in-house presentations.

One example of where this is being conducted is in Colorado, USA where Luca Technologies (http://lucatechnologies.com/) have engaged in pilot tests to produce natural gas from the use of microorganisms from coal, oil and carbonaceous shales to produce methane. Their focus is on the rate of bioconversion and identifying the rate limiting steps in the process. Luca has developed this activity at a scale that has allowed the production and sale of gas. This gas was being delivered to customers via existing gas infrastructure. Their activities have extended to over 500 field level applications including many existing wells with natural gas, oil and coal bed methane reserves already exploited.

In the case of coal seam gas Luca have developed a proprietary Restoration Process to stimulate microbial methane production by the application of specific nutrients, resulting in commercial volumes of natural gas to be generated at rates fitting with gas production.

Research conducted on the stimulation of methanogens in incubation tests using coal as the sole substrate have been summarised in Strapoc et al, (2011). Here it is noted that many of the tests demonstrated slow rates of methane production on the order of months to years to obtain accurate data on the conversion rates. The addition of stimulants and nutrients may provide potential improvements, as has been described by Luca. Nutrients tested include ammonia, phosphate, yeast extract, tryptone, milk, agar, trace metals and vitamins (e.g., Jin et al, 2007; Pfeiffer et al, 2010).

Alternatively specific consortia of microbes may enhance coal conversion to methane, such as the testing performed at CSIRO or work by Jin et al, 2007. However, little overall information on field trials, beyond the suggestion by many authors (see Faiz et al, 2003; Faiz and Hendry, 2006; Strapoc et al, 2011 and references therein) that subsurface enhancement of microbial methane is possible has been documented other than the information provided by Luca. Therefore it is so far difficult to assess how far this approach has come, due to the proprietary nature of the work, and further research may be required.

6 Monitoring of Methane and other Chemical Species

It is proposed here that there is abundant information in the public domain that can aid in the monitoring of methane and other chemical species to aid in management of coal seam gas production. There are existing regulations, legislation and requirements in different states and territories to deal with a variety of aspects associated with coal seam gas production. These include licensing arrangements under various acts (e.g. Petroleum and Geothermal), EPA Regulations, self regulation by various industry partners and so forth. How the monitoring of the movement of methane and associated chemical species is done may in some cases be quite prescriptive, but in other cases less so.

There are however a variety of other information carefully constructed to manage the monitoring of carbon dioxide in the subsurface (and the mobilisation of associated species) for enabling the monitoring and verification of carbon storage in carbon capture and storage (CCS) projects. By reviewing some of this information, it is hoped that perspectives from CCS monitoring might add value to existing activities and protocols in the coal seam gas industry. In addition there are other sources of information on monitoring fugitive emissions (Day et al, 2012) and other monitoring needs such as for water management (Cook et al, 2013).

6.1 Baseline Monitoring

Fundamentally however, the most critical activity for any project proponent is to obtain a solid suite of baseline data. The baseline data set is critical in the first instance to provide some of the information that aids in the risk evaluations that are necessary to identify what ongoing monitoring should take place. In the case of some localities such as at Barrow Island in WA, the karst (limestone) surface layers provide caves for stygofauna (i.e., any fauna that live in groundwater or aquifer systems such as caves underground) to exist. It is also a Class A Nature Reserve (conservation of flora and fauna) with many special species in residence. Here there has to be a good understanding of what is important to monitor for baseline versus what is important to monitor for environmental impact. Measuring trace metals in groundwater (to address a risk of carbon dioxide mobilising these through mineral dissolution) is not the method for evaluating whether the stygofauna will be impacted, however counts of stygofauna may provide information on environmental impact. Therefore the design of a robust baseline and ongoing monitoring plan is complex and challenging in many instances and has to be sensibly related back to regulations.

Baseline and ongoing monitoring can also be used to understand the evolution of the environment which may be affected by climate change. If projects are going to go over decades, there will be observable impact on the sites even in the absence of industrial activity, and data need to be acquired to demonstrate that changes are not necessarily due to project activities.

6.2 Monitoring and Verification

There are a number of different ways in which the CCS industry might refer to monitoring strategies. These include monitoring and verification (M&V), measurement, monitoring and verification (MM&V) and monitoring, verification and accounting (MVA). Whichever nomenclature is used, in essence the goal is to monitor presence or absence of the material (carbon dioxide in the CCS industry, but could be equally applied to methane emissions from coal seam gas), measure the amount of gas being emitted/leaked/released so that it can be quantified or accounted for. In the case of the EU Storage Directive, if emissions stored are credited under the Emissions Trading Scheme, then it is similarly expected that there is a corresponding debit for any leakage of carbon dioxide (Wartmann et al;. 2009).

Verification allows for the fact that there are many different sources of the same gas and attribution has to be well understood before any penalties or tax credits are sought. In order to verify the source of the gas, there is typically an extensive "baseline survey" conducted to characterise the area prior to any (new) activity. The baseline surveys are often integrated with the ongoing M&V programs and these programs are reported by the operator of a site, but can be verified by third party regulators. There is an expectation in various regulatory guidelines that not only should other third parties be able to reach the same conclusions based on the survey data reported but that the operator should be constantly striving for new approaches to improve the measurement and monitoring over time. This may also include improving efficiencies and reducing costs, reducing error in measurements and so forth.

Because of the financial implications for storage of carbon dioxide, as well as a series of similar issues in the public acceptance of CCS, reviewing M&V strategies used at pilot and commercial scale CCS operations with a view to deployment at coal seam gas operations is highly relevant to the coal seam methane industry. Common tools and approaches that have been evaluated for economic benefits are critical in the CCS space and may provide low cost monitoring solutions for methane monitoring.

As well as the EU Directive, there are a number of other regulatory papers that have varying degrees of prescriptiveness. One that has been found to be very difficult to engage with has been the US EPA regulation on the drilling of Class VI Injection Wells for CCS (http://water.epa.gov/type/groundwater/uic/class6/gsclass6wells.cfm). While the regulations may be highly relevant for the commercial scale operation of injection of carbon dioxide underground in the order of 1 million tonnes carbon dioxide per annum, small scale pilot test activities have so far been subject to the same regulation, stifling research to advance the activities. Furthermore, there is confusion as this regulation is not applied to the case of enhanced oil recovery (EOR) where carbon dioxide injection is the method of enhanced recovery.

To inform the development of such regulations, legislation, and related monitoring and operations, a number of studies have been conducted. Some have utilised pilot, commercial or EOR activities to test sampling methods and timing, the nature of the data types collected and what information arises from the different data types. Some projects have focused on the use of 4D seismic surveys, microseismic studies, pressure monitoring, geochemical analyses, other geophysical methods, atmospheric, soil gas and groundwater monitoring to evaluate the containment security of CCS sites. These methods are equally well suited to identifying mobilisation of different species associated with methane extraction. These studies include the IEA GHG Weyburn-Midale carbon dioxide Storage and Monitoring Project in Canada, Statoil's Sleipner and Snoehvit CCS Projects in Norway, BP's In Salah, Algeria, Chevron's Gorgon Project and the CO2CRC Otway Project in Australia to name but a few. Some of the monitoring tools have been reviewed in Stalker et al, (2012) including sensors for monitoring hydrocarbons and methane.

Other projects have focused on the actual potential tools that may be deployable for the monitoring of gas and substances mobilised by that gas. In the case of carbon dioxide, it may dissolve minerals in the storage formation and could potentially release heavy metal species that could be mobilised in to shallower intervals including potable aquifers in the worst case scenario. Carbon dioxide also acts as an effective solvent of organic contaminants and therefore BTEX and similar compounds are often checked as a part of the baseline monitoring to inform the project proponents of likely substances at risk of mobilisation. There are many tools that can be used to conduct monitoring and the zones that can be monitored, at least in the case of CCS, these include the atmosphere, near surface at the soil interface, shallow subsurface, zones above the containment seal that stops the migration of hydrocarbons or carbon dioxide out of its storage reservoir and the storage or reservoir interval can be measured directly as well (Figure 16).

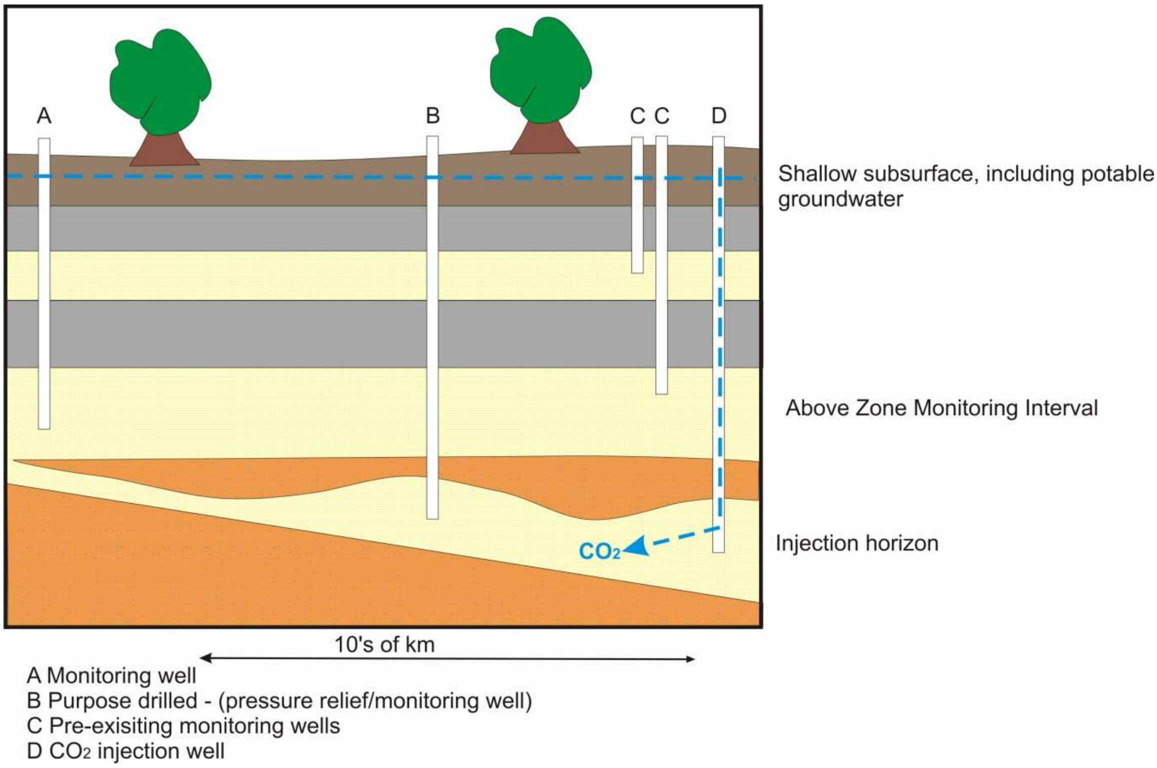


Figure 16 Schematic of the monitoring intervals considered for evaluation of suitable tools for monitoring substances mobilised by carbon dioxide. This approach could be modified for monitoring of methane and other substances mobilised during coal seam gas extraction. From Stalker et al, (2012).

6.3 Coal Seam Gas Monitoring Context

There is increasingly more information and research being conducted in the CCS space that could be swiftly applied to the coal seam gas industry to provide good frameworks for monitoring strategies that could facilitate discussions with landowners and communities on the impacts of coal seam gas extraction. This could be reviewed and provided to enable a more transparent mechanism for reporting the impacts and degree of those impacts going forward.

However, change is already underway in the manner in which some monitoring is being conducted. At the recent International Association of Hydrogeologists Congress in Perth in September 2013 a number of examples of groundwater monitoring studies were presented which take similar approaches to groundwater monitoring as have been employed at CCS sites, including extensive baseline monitoring and ongoing monitoring and reporting. It is important that the data and information are transparent and easily accessible to provide full value to the projects and these data provide a meeting point between project proponents and the local community where projects occur.

These studies focused heavily on the issue of groundwater monitoring for contaminants such as BTEX or for changes in salinity of waters. Few considered any dissolved gases in the groundwaters.

Methane as a greenhouse gas needs to have fairly stringent controls on emissions if it is to continue to be regarded as a better energy source and less of an emitter than coal fired power plant equivalents. Therefore understanding emissions relating to plant operations, pipelines and bores is critical. In the case of coal seam gas, it is the well heads that might require the most concentrated monitoring in terms of gas release and the well heads could be routinely monitored with hand held instruments or be instrumented with sensors that can regularly gauge the relative abundance of a range of gases in order to assess the integrity of the well.

Well integrity is important in both CCS and coal seam gas activities so that gases injected or produced are not introduced into other aquifer intervals. Wells can be instrumented with behind casing tools, fibre optics and other sensors or samplers that enable regular monitoring of gases or liquids in the wells and the potential for well bore compromise. Many of these tools already exist in the oil and gas industry, and while expensive, it is possible that lower cost options could be designed that do not have to operate in such high pressure and temperature regimes in the coal seam gas environment.

Acceptable levels of leakage of gas from well heads will have been partly informed by discussions of how high an emission source may be before there is a net loss in benefit. In the case of CCS there is a point at which if losses from a storage site over a time period exceed the emissions generated to bury that carbon dioxide, there is a net increase in emissions (Leuning et al, 2008 and references therein). In the case of methane, with a GWP of 21, this is multiplied and therefore any leakage from well heads need to be correspondingly smaller for the impact of emissions to be minimised. Regular monitoring of well heads may need to be a consideration to manage the accounting of this source of methane.

6.4 Modelling and Monitoring

In most cases in CCS, there are extensive modelling activities associated with the monitoring of a site. This approach attempts to deal with the risk profile developed for the project, that is, the identification and ranking of the cases that may see either leakage of gas to surface, impacts on groundwater from heavy metal mobilisation and so on. This approach can be applied to any baseline and other ongoing monitoring scenarios, whether it be for CCS or coal seam gas production.

The process may commence with the identification of the area of interest and its geometry. In the case of CCS this might be to identify the geometry of a carbon dioxide plume in the storage interval and its movement over a 1000 year period laterally and vertically. In coal seam gas activities it may relate to the likely footprint of the coal seams or acreage that may be produced.

Using a risk based approach, models can be generated that can address the impacts of “worst case scenarios” to see how obvious a leak of carbon dioxide (or methane) might be relative to regulation limits. Modelling of carbon dioxide (or methane) from a point emission source, such as a fault or well head is often conducted with respect to being able to identify and quantify leakage a the surface (Jenkins et al, 2012) so that monitoring methods can be validated and minimum leakage volumes that are visible by these methods can be ascertained. Understanding background concentrations of the compound of interest is therefore critical.

These surface leakage scenarios can be used to evaluate methane losses from well heads and similar equipment and expertise can be used to better monitor leakage from these instances. Hydrodynamics, fault seal analysis and other modelling techniques can be used to better identify and rank the risks for different scenarios prior to monitoring. Data from the monitoring is then used to evaluate the veracity of the models and this can be used by regulators to confirm that a project proponent understands and can predict the behaviour of the system they are working in over long periods of time.

This approach is central to the EU Directive on CCS and may be considered to supply some information on a potential workflow for modelling and monitoring methane movement and other substances that might be mobilised or altered during the production of methane and associated waters.

7 Knowledge Gaps and Research Underway

Three examples of knowledge gaps are identified here and discussed below. They relate to monitoring methane release from the subsurface (or a well), understanding the potential for renewable methane resources and the role of carbon isotopes in identifying the source and secondary effects on exploring for natural gas. This list of knowledge gaps is by no means exhaustive, but in fact illustrates that even when there is a large body of literature on certain subjects (i.e. that of the use of stable carbon isotopes to understand the source of methane) there are still new observations and ideas occurring due to our better understanding of related topics (namely the role of microbes and how they metabolise different stable isotopes).

7.1 Identifying and Quantitating Methane Leakage from the Subsurface – The Ginninderra Shallow Release Site, Canberra

One of the major issues in CCS activities is the ability to measure the change to the atmosphere if carbon dioxide leaks to surface. This is where the main impact is on carbon dioxide through its increase in concentration and impact on climate change. Being able to identify a leak at surface and quantitate that leak has been a focus of soil gas and atmospheric researchers through the CO2CRC (Cooperative Research Centre for Greenhouse Gas Technologies) and CSIRO in recent years (Leuning et al, 2008; Jenkins et al, 2012). In collaboration with Geoscience Australia, these three parties have developed a field test site, Ginninderra, near Canberra, ACT. This field site has been designed based on the ZERT (Zero Emissions Research and Technology) test site in Montana, USA (Spangler et al, 2009) where a 100 m horizontally drilled well, set at a few metres below the soil surface has been prepared. This well has a series of packers that isolate zones along the well and is able to pump carbon dioxide (or other gases) along that well. By using and testing a variety of sensors and tools, scientists are able to attempt to find a leak along that interval, and that leak is of a known concentration. Tracer chemicals can be added to the gas to use other mechanisms for identifying and quantitating the leakage. Crops are sown prior to testing to observe die back both on the ground and using hyperspectral data from aerial surveys. The package of techniques can be compared and evaluated for sensitivity, ease of use, cost of equipment, manpower, modelling and so forth.

In discussions with the staff running the Ginninderra test site, it is proposed that rather than a carbon dioxide test, the site could also be used to do a methane test to evaluate monitoring equipment and sensitivity of that equipment to a methane leak. As methane is present in the atmosphere at much lower amounts than carbon dioxide, it is expected that this site may be able to identify low concentration leaks and the results could be used to apply to surveys in active working areas where there are wells, or indeed to conduct baseline surveys in prospective areas for new coal seam gas production. Tests could include different ratios of carbon dioxide to methane and different rates of release, use of tracers and so forth. At the present time this site has not included extensive ground water monitoring, but this could be investigated as an option in the future.

Results would be able to provide some information on expected levels of release being detected at a well head for example, versus natural leakage from a fault to surface and better inform models for future monitoring.

7.2 Isotopes are Not as Good as We Thought for Source Identification

One of the most active and abundant areas of research in the understanding of methane generation has come about in recent times with the increasing use of stable carbon isotopes to act as a means of identifying the source of methane. The use of empirical data over the years to generate various interpretive models has relied heavily on the observations that have suggested that biogenic or microbial methane typically ranges in carbon isotope values from between δ^{13}C -60 to -90‰. Increasingly it is being observed that this is not such a reliable indicator as data sets grow and new research in stimulating the generation of methane from microorganisms takes off (see results discussed in Section 5). There are other possible sources of methane that produce carbon isotopic values in this range; early generating methane from coals or terrestrial organic matter are being identified that have very depleted signatures that may fit in the range traditionally believed to fit microbial methane. More work will be ongoing in the CSIRO laboratories to understand methane generation from coal and carbonaceous substrates that will include stable isotopic analysis of the various carbon sources. Addition of isotopically labelled compounds will allow the tracking of the biochemical changes taking place to allow for a better understanding of the processes of methane generation and alteration of coal, oils and other carbon-rich materials, partly in an effort that relates to the third research example, renewable methane.

7.3 Rate Limiting Steps to use Carbonaceous Materials to Produce Renewable Methane

As described in Section 5, there is increasing research into the assessment of methane as a potentially renewable source of energy. Luca Technologies have already developed proprietary methods (http://lucatechnologies.com/) that have been demonstrated in the US to provide gas to market. By using existing wells and high carbon source materials, the wells have been stimulated to produce more methane then transported by existing gas infrastructure pipelines etc. Unfortunately this company has very recently gone into administration (http://wyomingpublicmedia.org/post/luca-technologies-files-bankruptcy). This is most likely due to the major fall in gas price in the US with the increase in unconventional gas production and a general glut of gas.

While there is the information provided on the Luca website and patent applications, little detail is presented in the literature (summarised in Strapoc et al, 2011). Clearly there are aspects of IP protection that account for the limited publicly available information available, and suggest that there is still opportunity to encourage further research in this area. Existing projects in enhanced microbial coal seam gas research have been underway at CSIRO since the mid-2000s, but so far there is little in the way of large scale laboratory batch experiments, pilot or demonstration scale field projects or indeed reporting of many lab results in the literature. The work could be compared with existing activities in biogas, landfill gas and other projects that utilise simpler carbon rich materials to produce methane on smaller scales and see how they compare with the use of coaly or carbonaceous materials.

Reproducing some of the work done overseas with Australian coals may also produce some challenges as the source materials for some of the Australian coals and shales can be quite different to those in the northern hemisphere in particular. Therefore there is abundant further work that could be encouraged in this space to evaluate whether this approach is feasible to generate a virtually renewable source of methane in the future.

8 Conclusions

It is hoped that this review of aspects of methane in the context of its presence in coal seams provides some suitable background information on its physical and chemical properties and abundance in nature. There remains many unknowns about how to identify biogenic versus thermogenic gas still, but work continues in this space. There may be the need to develop interpretive tools that are specific to the coals of Australia due to some of the more unusual plant materials present in this continent rather than using models built on empirical data from overseas. But often there are only a few pieces of data relating to the composition of the gas (there may only be methane in the sample taken) and their stable isotopic composition (^{13}C and ^{2}H). So the amount of data, if analysing the gas alone, is limited and restricts our understanding of the source of the gas. Therefore full, comprehensive studies of related geological data are critically important.

The differences between recovery methods in conventional and unconventional production are great from the perspective of production history, reservoir properties and so forth, however many of the methods to understand and characterise the resources and geology remain common to both industries.

There has been increasing research activity in understanding how biogenic methane is formed and whether the rates can be stimulated to such an extent that commercial scale renewable methane gas could be generated. The joining of coal geology with microbial research is growing and in one case a pilot study has been partially successful in the US. More work is underway at different laboratories, but so far results and reporting seems limited.

Increasingly important is the need to provide transparent monitoring approaches both for water production and handling but also for the impact of methane emissions during methane gas production and handling. There are many established protocols for baseline and ongoing monitoring of gases (especially carbon dioxide) and products mobilised during the injection or recovery of gases that can be drawn on to develop good monitoring plans. These have been discussed in the light of the similar activities underway in carbon capture and storage.

Thus there are many knowledge gaps that remain but some may be regarded as exciting new prospects, such as understanding the rate limiting steps towards generating methane in a renewable manner via microbial stimulation. Other research activities could inform our monitoring strategies better by conducting field trials to quantitate leaks during testing with horizontal wells and controlled release experiments.

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Appendix A MSDS for Methane

CHEMGOLD III SHORT MATERIAL SAFETY DATA SHEET (MSDS) FOR METHANE.

Chemgold III short Material Safety Data Sheet (MSDS) for methane.

Section 1 - CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME

methane

SYNONYMS

CH4, "fire damp", "marsh gas", "methyl hydride", "natural gas"

PROPER SHIPPING NAME

METHANE, COMPRESSED or NATURAL GAS, COMPRESSED with high methane content

PRODUCT USE

Operators should be trained in procedures for safe use of this material. Constituent of illuminating and cooking gas. Base raw material for many chemicals, in the manufacture of hydrogen, methanol, methyl chloride, methylene chloride, hydrogen cyanide, ammonia, acetylene, formaldehyde, in organic syntheses.

SUPPLIER

Company: BOC Gases Ltd

Address:

10 Julius Avenue

North Ryde

NSW, 2113

Australia

Telephone: +61 2 8874 4400

Telephone: +61 131 262

Emergency Tel: **1800 653 572 (A/H) (Australia only)**

Fax: +61 2 9886 9000

Email: Chris.Sherry@boc.com

Website: https://pgw100.portal.gases.boc.com/scripts/wgate/zcpwp_b2c/!?~

Company: A-Gas (Australia) Pty Ltd

Address:

9-11 Oxford Road

Laverton North

VIC, 3026

Australia

Telephone: +61 3 9368 9222

Emergency Tel: **+61 1800 024 973 (TOLL)**

Fax: +61 3 9368 9233

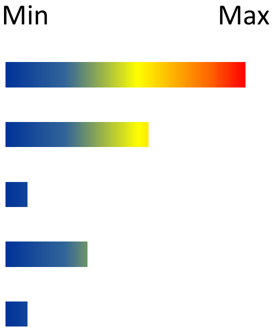
Website: www.agas.com

Section 2 - HAZARDS IDENTIFICATION

STATEMENT OF HAZARDOUS NATURE

DANGEROUS GOODS. NON-HAZARDOUS SUBSTANCE. According to NOHSC Criteria, and ADG Code.

CHEMWATCH HAZARD RATINGS



Flammability:	4	Min/Nil=0
Toxicity:	2	Low=1
Body Contact:	0	Moderate=2
Reactivity:	1	High=3
Chronic:	0	Extreme=4

RISK	SAFETY
• Extremely flammable.	• Keep away from sources of ignition. No smoking.
• Risk of explosion if heated under confinement.	• Do not breathe gas/ fumes/ vapour/ spray.
• Inhalation may produce health damage*.	• Avoid contact with skin.
* (limited evidence).	• Use only in well ventilated areas.
	• Keep container in a well ventilated place.
	• Keep container tightly closed.
	• This material and its container must be disposed of as hazardous waste.

Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

NAME	CAS RN	%
methane	74-82-8	>98

Section 4 - FIRST AID MEASURES

SWALLOWED

- Not considered a normal route of entry.

EYE

- If product comes in contact with eyes remove the patient from gas source or contaminated area.
- Take the patient to the nearest eye wash, shower or other source of clean water.

- Open the eyelid(s) wide to allow the material to evaporate.
- Gently rinse the affected eye(s) with clean, cool water for at least 15 minutes. Have the patient lie or sit down and tilt the head back. Hold the eyelid(s) open and pour water slowly over the eyeball(s) at the inner corners, letting the water run out of the outer corners.

SKIN

■ If skin or hair contact occurs:

- Flush skin and hair with running water (and soap if available).
- Seek medical attention in event of irritation.

INHALED

- Following exposure to gas, remove the patient from the gas source or contaminated area.
- NOTE: Personal Protective Equipment (PPE), including positive pressure self-contained breathing apparatus may be required to assure the safety of the rescuer.
- Prostheses such as false teeth, which may block the airway, should be removed, where possible, prior to initiating first aid procedures.
- If the patient is not breathing spontaneously, administer rescue breathing.

NOTES TO PHYSICIAN

for gas exposures:

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BASIC TREATMENT

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- Establish a patent airway with suction where necessary.
- Watch for signs of respiratory insufficiency and assist ventilation as necessary.
- Administer oxygen by non-rebreather mask at 10 to 15 l/min.
- Monitor and treat, where necessary, for pulmonary oedema .

Section 5 - FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA

DO NOT EXTINGUISH BURNING GAS UNLESS LEAK CAN BE STOPPED SAFELY:
OTHERWISE: LEAVE GAS TO BURN.
FOR SMALL FIRE:

- Dry chemical, CO2 or water spray to extinguish gas (only if absolutely necessary and safe to do so).
- DO NOT use water jets.

FOR LARGE FIRE:

- Cool cylinder by direct flooding quantities of water onto upper surface until well after fire is out.
- DO NOT direct water at source of leak or venting safety devices as icing may occur.

FIRE FIGHTING

FOR FIRES INVOLVING MANY GAS CYLINDERS:

- To stop the flow of gas, specifically trained personnel may inert the atmosphere to reduce oxygen levels thus allowing the capping of leaking container(s).
- Reduce the rate of flow and inject an inert gas, if possible, before completely stopping the flow to prevent flashback.
- DO NOT extinguish the fire until the supply is shut off otherwise an explosive re-ignition may occur.
- If the fire is extinguished and the flow of gas continues, used increased ventilation to prevent build-up, of explosive atmosphere.

GENERAL

- Alert Fire Brigade and tell them location and nature of hazard.
- May be violently or explosively reactive.
- Wear breathing apparatus plus protective gloves.
- Consider evacuation

FIRE/EXPLOSION HAZARD

- HIGHLY FLAMMABLE: will be easily ignited by heat, sparks or flames.
- Will form explosive mixtures with air
- Fire exposed containers may vent contents through pressure relief valves thereby increasing fire intensity and/ or vapour concentration.
- Vapours may travel to source of ignition and flash back.

Combustion products include: carbon monoxide (CO), carbon dioxide (CO2), other pyrolysis products typical of burning organic material.

FIRE INCOMPATIBILITY

- Avoid contamination with oxidising agents i.e. nitrates, oxidising acids, chlorine bleaches, pool chlorine etc. as ignition may result

HAZCHEM

2SE

Section 6 - ACCIDENTAL RELEASE MEASURES

MINOR SPILLS

- Avoid breathing vapour and any contact with liquid or gas. Protective equipment including respirator should be used.
- DO NOT enter confined spaces where gas may have accumulated.
- Shut off all sources of possible ignition and increase ventilation.
- Clear area of personnel.

MAJOR SPILLS

- Clear area of all unprotected personnel and move upwind.

- Alert Emergency Authority and advise them of the location and nature of hazard.
- May be violently or explosively reactive.
- Wear full body clothing with breathing apparatus.

- Remove leaking cylinders to a safe place.
- Fit vent pipes. Release pressure under safe, controlled conditions
- Burn issuing gas at vent pipes.

- DO NOT exert excessive pressure on valve; DO NOT attempt to operate damaged valve.

Personal Protective Equipment advice is contained in Section 8 of the MSDS.

Section 7 - HANDLING AND STORAGE

PROCEDURE FOR HANDLING

■ Radon and its radioactive decay products are hazardous if inhaled or ingested.

- Consider use in closed pressurised systems, fitted with temperature, pressure and safety relief valves which are vented for safe dispersal.
- The tubing network design connecting gas cylinders to the delivery system should include appropriate pressure indicators and vacuum or suction lines.
- Fully-welded types of pressure gauges, where the bourdon tube sensing element is welded to the gauge body, are recommended.
- Before connecting gas cylinders, ensure manifold is mechanically secure and does not containing another gas. Before disconnecting gas cylinder, isolate supply line segment proximal to cylinder, remove trapped gas in supply line with aid of vacuum pump

- Avoid generation of static electricity. Earth all lines and equipment.

- DO NOT transfer gas from one cylinder to another.

SUITABLE CONTAINER

- Cylinder:
- Ensure the use of equipment rated for cylinder pressure.
- Ensure the use of compatible materials of construction.
- Valve protection cap to be in place until cylinder is secured, connected.

STORAGE INCOMPATIBILITY
Methane:

- reacts violently with oxidizing agents such as chlorine, bromine pentafluoride, oxygen trifluoride and nitrogen trifluoride in the presence of catalysts or sources of ignition.
- contact with chlorine dioxide causes spontaneous explosion.
- contact with liquid fluorine causes spontaneous explosion, even at very low temperatures (-19 deg.C).

A mixture of liquid methane and liquid oxygen is an explosive.

- Explosion hazard may follow contact with incompatible materials
- Avoid reaction with oxidising agents

PACKAGING MATERIAL INCOMPATIBILITIES

Chemical Name	Container Type
	"Carbon Steel", EPDM, "Natural rubber", Silicone

STORAGE REQUIREMENTS

- Store in an upright position.
- Outside or detached storage is preferred.
- Cylinders should be stored in a purpose-built compound with good ventilation, preferably in the open.
- Such compounds should be sited and built in accordance with statutory requirements.
- The storage compound should be kept clear and access restricted to authorised personnel only.
- Cylinders stored in the open should be protected against rust and extremes of weather.

Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

EXPOSURE CONTROLS

The following materials had no OELs on our records

- methane: CAS:74-82-8

MATERIAL DATA

METHANE:

PERSONAL PROTECTION

EYE

- Safety glasses with side shields
- Chemical goggles.
- Contact lenses may pose a special hazard; soft contact lenses may absorb and concentrate irritants. A written policy document, describing the wearing of lens or restrictions on use, should be created for each workplace or task. This should include a review of lens absorption and adsorption for the class of chemicals in use and an account of injury experience. Medical and first-aid personnel should be trained in their removal and suitable equipment should be readily available. In the event of chemical exposure, begin

eye irrigation immediately and remove contact lens as soon as practicable. Lens should be removed at the first signs of eye redness or irritation - lens should be removed in a clean environment only after workers have washed hands thoroughly. [CDC NIOSH Current Intelligence Bulletin 59], [AS/NZS 1336 or national equivalent]

HANDS/FEET

- When handling sealed and suitably insulated cylinders wear cloth or leather gloves.

OTHER

- The clothing worn by process operators insulated from earth may develop static charges far higher (up to 100 times) than the minimum ignition energies for various flammable gas-air mixtures. This holds true for a wide range of clothing materials including cotton.
- Avoid dangerous levels of charge by ensuring a low resistivity of the surface material worn outermost.

BRETHERICK: Handbook of Reactive Chemical Hazards.

- Protective overalls, closely fitted at neck and wrist.
- Eye-wash unit.

IN CONFINED SPACES:

- Non-sparking protective boots
- Static-free clothing.

- Some plastic personal protective equipment (PPE) (e.g. gloves, aprons, overshoes) are not recommended as they may produce static electricity.
- For large scale or continuous use wear tight-weave non-static clothing (no metallic fasteners, cuffs or pockets), non sparking safety footwear.

ENGINEERING CONTROLS

■ Engineering controls are used to remove a hazard or place a barrier between the worker and the hazard. Well-designed engineering controls can be highly effective in protecting workers and will typically be independent of worker interactions to provide this high level of protection.
The basic types of engineering controls are:
Process controls which involve changing the way a job activity or process is done to reduce the risk.
Enclosure and/or isolation of emission source which keeps a selected hazard "physically" away from the worker and ventilation that strategically "adds" and "removes" air in the work environment.

Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE

Colourless, odourless and tasteless gas. Gas has no odour detection level; unless mercaptan odorant is deliberately added. Gas is less dense than air. Burns with a pale, faintly luminous flame. Very slightly soluble in water 3.3 mg of gas/100ml water @ 20 deg.C. Soluble in alcohol, ether, hydrocarbon and other organic solvents. Packed as a gas under pressure. Sudden release of pressure or leakage may result in generation of a large volume of highly flammable/ explosive gas.

Critical temperature: -82.1 deg. C. Critical pressure: 4640 kPa.

PHYSICAL PROPERTIES

Gas.
Does not mix with water.
Floats on water.

State	Compressed gas	Molecular Weight	16.04
Melting Range (°C)	-182	Viscosity	Not Applicable
Boiling Range (°C)	-162	Solubility in water (g/L)	Immiscible
Flash Point (°C)	-218	pH (1% solution)	Not applicable.
Decomposition Temp (°C)	Not Applicable	pH (as supplied)	Not applicable
Autoignition Temp (°C)	540-595	Vapour Pressure (kPa)	Not applicable.
Upper Explosive Limit (%)	15.0	Specific Gravity (water=1)	0.422 as liquid
Lower Explosive Limit (%)	5.0	Relative Vapour Density (air=1)	0.55
Volatile Component (%vol)	100	Evaporation Rate	Not applicable
Gas group	IIA		

Section 10 - CHEMICAL STABILITY

CONDITIONS CONTRIBUTING TO INSTABILITY

- Presence of incompatible materials.
- Product is considered stable.
- Hazardous polymerisation will not occur.

- Presence of elevated temperatures.

- Presence of heat source and ignition source

For incompatible materials - refer to Section 7 - Handling and Storage.

Section 11 - TOXICOLOGICAL INFORMATION

POTENTIAL HEALTH EFFECTS

ACUTE HEALTH EFFECTS

SWALLOWED

■ Not normally a hazard due to physical form of product.
Considered an unlikely route of entry in commercial/industrial environments.

EYE

■ Although the material is not thought to be an irritant (as classified by EC Directives), direct contact with the eye may produce transient discomfort characterised by tearing or conjunctival redness (as with windburn).
Not considered to be a risk because of the extreme volatility of the gas.

SKIN

■ The material is not thought to produce adverse health effects or skin irritation following contact (as classified by EC Directives using animal models). Nevertheless, good hygiene practice requires that exposure be kept to a minimum and that suitable gloves be used in an occupational setting. Open cuts, abraded or irritated skin should not be exposed to this material.
Entry into the blood-stream, through, for example, cuts, abrasions or lesions, may produce systemic injury with harmful effects. Examine the skin prior to the use of the material and ensure that any external damage is suitably protected.

INHALED

■ The material is not thought to produce respiratory irritation (as classified by EC Directives using animal models). Nevertheless inhalation of the material, especially for prolonged periods, may produce respiratory discomfort and occasionally, distress.
Inhalation of vapours or aerosols (mists, fumes), generated by the material during the course of normal handling, may be damaging to the health of the individual.
Inhalation of non-toxic gases may cause:

- CNS effects: headache, confusion, dizziness, stupor, seizures and coma;
- respiratory: shortness of breath and rapid breathing;
- cardiovascular: collapse and irregular heart beats;
- gastrointestinal: mucous membrane irritation, nausea and vomiting.

The paraffin gases are practically not harmful at low doses. Higher doses may produce reversible brain and nerve depression and irritation.

CHRONIC HEALTH EFFECTS

■ Long-term exposure to the product is not thought to produce chronic effects adverse to the health (as classified by EC Directives using animal models); nevertheless exposure by all routes should be minimised as a matter of course.
Principal route of occupational exposure to the gas is by inhalation.

TOXICITY AND IRRITATION

■ No significant acute toxicological data identified in literature search.

Section 12 - ECOLOGICAL INFORMATION

This material and its container must be disposed of as hazardous waste.

Ecotoxicity

Ingredient	Persistence: Water/Soil	Persistence: Air	Bioaccumulation	Mobility
methane	No Data Available	No Data Available	LOW	No Data Available

Section 13 - DISPOSAL CONSIDERATIONS

- Evaporate or incinerate residue at an approved site.
- Return empty containers to supplier.
- Ensure damaged or non-returnable cylinders are gas-free before disposal.

Section 14 - TRANSPORTATION INFORMATION

Labels Required: FLAMMABLE GAS

HAZCHEM:

2SE (ADG7)

ADG7:

Class or Division:	2.1	Subsidiary Risk1:	None
UN No.:	1971	Packing Group:	None
Special Provision:	None	Limited Quantity:	0
Portable Tanks & Bulk Containers - Instruction:	None	Portable Tanks & Bulk Containers - Special Provision:	None
Packagings & IBCs - Packing Instruction:	P200	Packagings & IBCs - Special Packing Provision:	None

Name and Description: METHANE, COMPRESSED or NATURAL GAS, COMPRESSED with high methane content

Air Transport IATA:

ICAO/IATA Class:	2.1	ICAO/IATA Subrisk:	None
UN/ID Number:	1971	Packing Group:	-
Special provisions:	A1		
Cargo Only			
Packing Instructions:	200	Maximum Qty/Pack:	150 kg
Passenger and Cargo		Passenger and Cargo	
Packing Instructions:	Forbidden	Maximum Qty/Pack:	Forbidden
Passenger and Cargo Limited Quantity		Passenger and Cargo Limited Quantity	
Packing Instructions:	Forbidden	Maximum Qty/Pack:	Forbidden

Shipping name: METHANE, COMPRESSED or NATURAL GAS, COMPRESSED with high methane content

Maritime Transport IMDG:

IMDG Class:	2.1	IMDG Subrisk:	None
UN Number:	1971	Packing Group:	None
EMS Number:	F-D,S-U	Special provisions:	None
Limited Quantities:	0		

Shipping name:METHANE, COMPRESSED or NATURAL GAS, COMPRESSED with high methane content

Section 15 - REGULATORY INFORMATION

Indications of Danger :

F+	Extremely flammable

POISONS SCHEDULE

None

REGULATIONS

methane (CAS: 74-82-8) is found on the following regulatory lists;

"Australia - Queensland Work Health and Safety Regulation - Hazardous chemicals at major hazard facilities (and their threshold quantity)", "Australia - Tasmania - Work Health and Safety Regulations 2012 - Hazardous Chemicals at Major Hazard Facilities (and their Threshold Quantity) - Table 15.1", "Australia FAISD Handbook - First Aid Instructions, Warning Statements, and General Safety Precautions", "Australia Hazardous Substances Information System - Consolidated Lists", "Australia High Volume Industrial Chemical List (HVICL)", "Australia Inventory of Chemical Substances (AICS)", "Australia Standard for the Uniform Scheduling of Medicines and Poisons (SUSMP) - Appendix E (Part 2)", "Australia Standard for the Uniform Scheduling of Medicines and Poisons (SUSMP) - Schedule 5", "Australia Work Health and Safety Regulations 2011 - Hazardous chemicals at major hazard facilities and their threshold quantity", "FisherTransport Information", "International Council of Chemical Associations (ICCA) - High Production Volume List", "OECD List of High Production Volume (HPV) Chemicals", "Sigma-AldrichTransport Information"

Section 16 - OTHER INFORMATION

■ Classification of the preparation and its individual components has drawn on official and authoritative sources as well as independent review by the Chemwatch Classification committee using available literature references.
A list of reference resources used to assist the committee may be found at:
www.chemwatch.net/references.

■ The (M)SDS is a Hazard Communication tool and should be used to assist in the Risk Assessment. Many factors determine whether the reported Hazards are Risks in the workplace or other settings.

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Appendix B Terms of Reference

SCHEDULE E

TERMS OF REFERENCE FOR THE BACKGROUND PAPER ON METHANE

To deliver a Background Paper to the Office of the NSW Chief Scientist and Engineer (OCSE) providing information and a discussion about methane, the main gas in coal seam gas (CSG) production, including sources and environmental impacts.

1. The Background Paper should be 50 pages maximum length (excluding appendices). The Background Paper must be delivered electronically in Word format; be fully referenced and contain suggestions for further reading for those interested in gaining a more detailed understanding of the subject.

2. The purpose of the background paper is to provide an overview of methane, including sources and environmental impacts and how they can be addressed. The paper will identify issues associated with methane and how they are or can be addressed.

3. The Background Paper should include discussion of the following:
    a. Methane
        i. Definition – include a description of the chemical and physical characteristics and properties
        ii. What are the uses of methane
        iii. Sources of methane (including biological and geological) and how is it produced (including biogenic and thermogenic).
        iv. Intensity as a greenhouse gas (as compared to other gases)
    b. Other gases associated with CSG production and conventional gas production (comparison of gas constituents from conventional and coal seam gas production)
    c. What are best practice methods for monitoring methane associated with coal seams?
    d. What are the knowledge gaps/unknowns/research questions in relation to the impact of methane?
    e. Any other comment you believe relevant to the understanding or management of these issues.

4. The Background Paper should be developed having regard to the following:
    a) Under Terms of Reference 6 of the Review (Schedule D), a series of information papers will be commissioned about the CSG industry; which are aimed at informing the Review and a wide audience, both general and technical. These information papers are likely to be publicly released and may appear on the website of the Chief Scientist and Engineer.
    b) Each Review information paper will draw on multiple sources of information, including background papers which may be sourced from different experts.

c) The Review information papers are likely to include extracts from the expert background papers, including the Background Paper delivered under this contract. In some cases, a background paper may be appended to a Review information paper in part or full, and therefore may be publicly released and may appear on the website of the Chief Scientist and Engineer.

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