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Review article

Stable isotope geochemistry of coal bed and shale gas and related production waters: A review

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ABSTRACT

Coal bed and shale gas can be of thermogenic, microbial or of mixed origin with the distinction made primarily on the basis of the molecular and stable isotope compositions of the gases and production waters. Methane, ethane, carbon dioxide and nitrogen are the main constituents of coal bed and shale gases, with a general lack of C_{2+} hydrocarbon species in gases produced from shallow levels and more mature coals and shales. Evidence for the presence of microbial gas include $\delta^{13}C$–CH_4 values less than −50‰, covariation of the isotope compositions of gases and production water, carbon and hydrogen isotope fractionations consistent with microbial processes, and positive $\delta^{13}C$ values of dissolved inorganic carbon in production waters. The CO_2-reduction pathway is distinguished from acetate/methyl-type fermentation by somewhat lower $\delta^{13}C$–CH_4 and higher δD–CH_4, but can also have overlapping values depending on the openness of the microbial system and the extent of substrate depletion. Crossplots of $\delta^{13}C$–CH_4 versus $\delta^{13}C$–CO_2 and δD–CH_4 versus $\delta^{13}C$–H_2O may provide a better indication of the origin of the gases and the dominant metabolic pathway than the absolute carbon and hydrogen isotope compositions of methane. In the majority of cases, microbial coal bed and shale gases have carbon and hydrogen isotope fractionations close to those expected for CO_2 reduction. Primary thermogenic gases have $\delta^{13}C$–CH_4 values greater than −50‰, and $\delta^{13}C$ values that systematically increase from C_1 to C_4 and define a relatively straight line when plotted against reciprocal carbon number. Although coals and disseminated organic matter in shales represent a continuum as hydrocarbon source rocks, current data suggest a divergence between these two rock types at the high maturity end. In deep basin shale gas, reversals or rollovers in molecular and isotopic compositions are increasingly reported in what is effectively a closed shale system as opposed to the relative openness in coal measure environments. Detailed geochemical studies of coal bed and shale gas and related production waters are essential to determine not only gas origins but also the dominant methanogenic pathway in the case of microbial gases.

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1. Introduction

Unconventional gas resources including coal bed methane and shale gas are a growing part of the global energy mix, which has changed the economic and strategic picture for gas consuming and producing countries. Most notable are the USA, China and Australia that together have around half of currently recoverable unconventional gas resources (International Energy Agency, 2011). Other countries including Canada, India and Indonesia are also seeking to develop their CBM and shale gas resources. Commercial production of coal bed methane (CBM), also referred to as coal seam gas (CSG) or coal seam methane (CSM), commenced in the United States in the late 1980s and in Australia in the late 1990s, with the industry in both countries showing a remarkably similar pattern of development (Day, 2009). Exploration initially focused on mature coals with high contents of what was thought to be thermogenic gas (e.g., Black Warrior, San Juan and Bowen basins); however, CBM production was often hindered by low permeability and mineralisation in cleats and fractures that necessitated the development of cost effective horizontal drilling and completion techniques. CBM exploration then extended beyond the producing fields to lower rank coals and then to less mature coal basins where it was thought that higher permeability and greater coal thicknesses would compensate for lower gas contents (e.g., Illinois, Powder River and Surat basins). An argument ensued as to the origin of the gas, which was mostly methane with minor ethane and carbon dioxide at shallow depths (150 m to 600 m), notwithstanding the rank of the coal. Carbon isotope studies indicated that much of the gas was biogenic, with microbial methane generation linked to meteoric water ingress during uplift of the coal measures, and that methanogenesis is ongoing in shallow coal seams subject to meteoric recharge (e.g., Alberta Basin (Cheung et al., 2010; Harrison et al., 2006), Black Warrior Basin (Pashin, 2007), Bowen Basin (Kinnon et al., 2010; Smith and Pallasser, 1996), Illinois Basin (Gao et al., 2013; Schlegel et al., 2011; Strąpoć et al., 2007, 2008), Powder River Basin (Bates et al., 2011; Flores et al., 2008; Green et al., 2008; Rice et al., 2008), San Juan Basin (Scott et al., 1994; Zhou et al., 2005), Surat Basin (Draper and Boreham, 2006; Papendick et al., 2011); Sydney Basin (Faiz and Hendry, 2006; Faiz et al., 1999), and the Upper Silesian Basin (Kotarba, 2001; Kotarba and Pluta, 2009; Weniger et al., 2012)).

Reviews by Whiticar (1996, 1999), Clayton (1998), Faiz and Hendry (2006) and Strąpoć et al. (2011) summarize the evidence for the microbial origin of methane in low rank coals and the presence of secondary microbial gas at shallow levels in higher rank coals and provide an introduction to the use of compositional and isotopic parameters in the determination of the origin of CBM. However, the timing of methanogenesis, the controls on coal bioavailability and the processes for stepwise microbial degradation of coal to methane remain topics of considerable interest to researchers and industry in light of the possibility for stimulation of enhanced microbial methane generation in coal (Furmann et al., 2013; Penner et al., 2010; Scott, 1999).

Shale gas occurs in a range of organic-matter rich rock types with low permeability that historically limited gas extraction rates. Developments in horizontal drilling and multi-stage hydraulic fracturing through the 1980s to the present day have allowed commercial production rates from shale gas plays in a number of regions across North America (International Energy Agency, 2011). In like fashion to CBM, shale gas can be of thermogenic, microbial or of mixed origin with the distinction made primarily on the basis of the stable isotope compositions of the gases and co-produced waters (e.g., Antrim Shale, Michigan Basin (Brown, 2011; Martini et al., 1998, 2003), Barnett Shale, Fort Worth Basin (Jarvie et al., 2007; Rodriguez and Philip, 2010; Zumberge et al., 2012), Fayetteville Shale, Eastern Arkoma Basin (Zumberge et al., 2012), Marcellus Shale, Appalachian Basin (Jenden et al., 1993; Osborn and McIntosh, 2010); New Albany Shale, Illinois Basin (Gao et al., 2013; McIntosh et al., 2002; Schlegel et al., 2011; Strąpoć et al., 2010), and the Colorado Group, Western Canada Sedimentary Basin (Huang et al., 2011; Tilley and Muehlenbachs, 2013; Tilley et al., 2011)). These studies showed that the relative proportions of microbial and thermogenic gas are depth related such that deeper locations contain exclusively thermogenic gas, whereas shallower locations may contain a mixture of microbial and thermogenic methane. Although there are many studies of the gas and fluid geochemistry of CBM and shale gas plays, these have generally focused on a single reservoir type with a few exceptions (e.g., Schlegel et al., 2011). In this review, we provide an overview of the isotope systematics and hydrochemistry of CBM and shale gas occurrences and show that the microbial versus thermogenic origin of methane influences not only gas content and composition in coal and shale gas, but also the degree of saturation in shallower CBM fields.

2. Gas molecular and stable isotope compositions

2.1. Gas molecular compositions

The gas generation potential of an organic-rich source rock is a major factor in the formation of thermogenic gas and also has an influence on the composition of the gas generated at different maturity levels. Organic matter type and maturity are also important parameters in the formation of microbial gas, with lower rates of biomethane production expected at higher maturity levels (cf. Strąpoć et al., 2011). The classification of organic matter as Type I, II or III kerogen is based on H/C and O/C atomic ratios using the classic van Krevelen (1961) diagram or Hydrogen Index (HI) and Oxygen Index (OI) from Rock Eval pyrolysis (Peters, 1986). Type I kerogen is hydrogen rich (H/C > 1.5; HI > 600 mg hydrocarbons/g TOC) and generally forms from aquatic plants (algae) and/or planktons in marine or lacustrine environments. It is relatively uncommon in coals and shales and is not considered further in this review. Type II kerogen has intermediate hydrogen content, originates commonly from lipid rich components of higher plants and is the most abundant kerogen in organic-rich marine sediments. It is a major source of oil and gas, with primary and secondary cracking of kerogen and bitumen, respectively, considered to be an important factor in shale gas generation (e.g., Jarvie et al., 2007; Mahlstedt and Horsfield, 2012). Type III kerogen is comparatively hydrogen-poor with H/C < 1 and HI < 200 mg hydrocarbons/g TOC (Peters et al., 2005) and comprises the remains of land plants (vitrinite group macerals) in coals and coaly sediments. Experimental studies suggest that Type III kerogen generates gas and condensates rather than oil although the heterogeneous nature of kerogen in coal means that some coals have significant hydrocarbon generation potential (e.g., Boreham and Powell, 1993; Clayton, 1993; Mahlstedt and Horsfield, 2012; Newman et al., 1997; Powell and Boreham, 1991; Powell et al., 1991).

The compositions of production gases from CBM and shale gas fields are quite similar, notwithstanding the differing hydrocarbon generation potential of the coal and shale host that are both source and reservoir for the gases. Methane, ethane, carbon dioxide and nitrogen are the

main constituents, with a general lack of C_{2+} hydrocarbon species in gases produced from shallow levels and more mature coals and shales (e.g., Burruss and Laughrey, 2010; Draper and Boreham, 2006; Faiz and Hendry, 2006; Faiz et al., 1999; Flores et al., 2008; Kinnon et al., 2010; Osborn and McIntosh, 2010; Strąpoć et al., 2008; Xia et al., 2013; Zumberge et al., 2012). The hydrocarbon composition of coal bed and shale gas can be quantified in a number of different ways such that it is important to define exactly what is meant by gas dryness or wetness. Even though ethane to butane are gases at ambient conditions, common usage of gas dryness also includes associated liquid hydrocarbons; a dry gas being defined as having a $\%C_1/\Sigma C_n$ (approximated by $\%C_1/\Sigma C_1 - C_5$) ratio >97–98% (Tissot and Welte, 1984 page 199), while the ratio $C_1/(C_2 + C_3)$ is >50 (Bernard et al., 1976; Hunt, 1996 page 195; Whiticar, 1999). The ratio of methane to the sum of ethane and propane ($C_1/(C_2 + C_3)$) is used to compare gas dryness with the $\delta^{13}C$–CH_4 of natural gas (Fig. 1) (e.g., Bernard et al., 1978; Faber and Stahl, 1984; Strąpoć et al., 2008, 2011; Whiticar, 1996, 1999), whereas other authors use the terms gas dryness or dry gas index (DGI) for the ratio of methane to the sum of C_2 to C_5 hydrocarbons ($C_1/(C_2 + C_3 + C_4 + C_5)$) (e.g., Cody and Hutcheon, 1994; Draper and Boreham, 2006). On the other hand, gas wetness is defined most commonly as the ratio of the sum of the C_2 to C_5 hydrocarbons to the sum of the C_1 to C_5 hydrocarbons $(C_2 + C_3 + C_4 + C_5)/(C_1 + C_2 + C_3 + C_4 + C_5)$, which may be reported as a percentage (e.g., Jenden et al., 1993; Zumberge et al., 2012). Because production gases from many CBM and some shale gas fields are relatively dry, the ratio of methane to the sum of ethane and propane ($C_1/(C_2 + C_3)$) is widely used to distinguish between microbial and thermogenic gases. Ratios greater than 1000 and less than 100 (wet gases commonly associated with oil tend to show $C_1/(C_2 + C_3) < 50$) are considered to be definitive for microbial and thermogenic gas, respectively when used in combination with methane carbon isotope composition (Fig. 1) (e.g., Bernard et al., 1978; Faiz and Hendry, 2006; Flores et al., 2008; Osborn and McIntosh, 2010; Smith and Pallasser, 1996; Strąpoć et al., 2008, 2011; Whiticar, 1996, 1999).

In the subsurface, wet gas is generally generated through the thermal decomposition of organic matter (kerogen) or destruction of bitumen or oil, with the preservation deadline for wet gas generally assumed to be around 250–300°C and $R_o = 2.5$–4% (Burruss and Laughrey, 2010; Hunt, 1996), although for humic coals approximately 18% of residual methane (enriched in ^{13}C) generation potential remains above $R_o > 6\%$ (Chen et al., 2011). However, both biogenic and

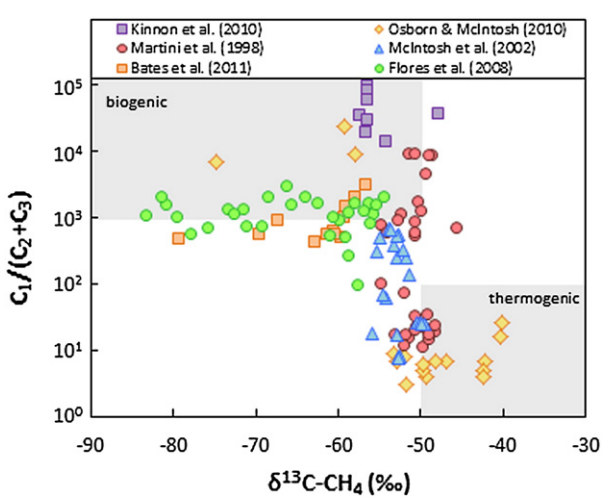

Fig. 1. Gas dryness ($C_1/(C_2 + C_3)$) versus $\delta^{13}C$–CH_4 for northern Bowen Basin CBM wells (Kinnon et al., 2010). Also shown are gas samples from the Powder River Basin (Bates et al., 2011; Flores et al., 2008), the Antrim and New Albany shales (Martini et al., 1998; McIntosh et al., 2002), and organic-rich shales of the northern Appalachian Basin (Osborn and McIntosh, 2010).

abiogenic processes also produce C_{2+} hydrocarbons. The former is a low temperature (generally <80 °C; Head et al., 2003 and references therein) process producing a dry gas sometimes with trace amounts of wet gas dominated by ethane (Hinrichs et al., 2006; Oremland et al., 1988; Sassen and Curiale, 2006), while the latter can abiogenically produce heavier wet gas components though at much higher temperatures involving mineral catalysis (Sherwood Lollar et al., 2002, 2008; Tang and Xia, 2011; Zumberge et al., 2012). While each process has a distinctive isotopic signature (see below), quantitatively, both processes are dwarfed by the thermogenic origin for wet gases. There is greater potential for a contribution of all the three processes to a shale gas occurrence, while for coal seam gas an abiogenic origin for wet gases is less likely due to a reduced mineral content and the requirement for much higher maturities (i.e., semi-anthracite rank and above).

Source and maturity have a primary control on the wetness of a gas (Tissot and Welte, 1984), while secondary processes such as biodegradation (Boreham et al., 2001b; Head et al., 2003; James and Burns, 1984; Milkov, 2011; Pallasser, 2000), expulsion and migration fractionation (Lorant et al., 1998; Prinzhofer and Huc, 1995) and absorption/desorption (Friedrich and Jüntgen, 1972; Rice, 1993; Snowdon, 2001; Xia and Tang, 2012) have varying influence on molecular and isotopic compositions. For thermogenic coal seam gas, wet gas contents up to 20 vol.% are common with extremes to 70 vol.% (Rice, 1993). Wet gas-dominated shale gas begins at very low levels of maturity ($R_o = 0.45\%$) increasing consistently to 80 ± 10 vol.% wet gas within the oil window (Jarvie et al., 2007; Price and Schoell, 1995; Snowdon, 2001). High wet gas contents are consistent with artificial pyrolysis experiments on shales (Hill et al., 2003 and references therein). Reconciliation between laboratory and field data for the composition of gas at the time of generation has elevated the need for alternate mechanisms for gas generation (e.g., transition metal catalysed; Mango et al., 2010) in order to explain the differences between wet gas-rich laboratory pyrolysis gases and methane-enriched reservoired natural gas (Snowdon, 2001). In coals and shales, wet gas components (and liquids) are preferentially sorbed onto the organic matrix within the source rock, resulting in a higher wet gas content compared to the expelled gas and genetically related conventional natural gas. Moreover, the higher clay mineral content in shales can increase the gas content in artificial pyrolysis studies when compared to kerogen (Hill et al., 2003). There is generally a strong relationship between gas wetness and coal maturity (rank), with dry gas at low and high maturity and wetter gas at intermediate maturity levels. However, the peak gas wetness varies between 0.6 and 1.35% R_o (Rice, 1993) and temperature of 100–150°C (Price and Schoell, 1995), encompassing the conventional oil window and is related to coal composition (Boreham and Powell, 1993) with perhydrous coals (H-rich Type II/III) generating a greater proportion of C_{2+} hydrocarbons over a wider maturity range than Type III humic coal (Boreham and Powell, 1993; Rice, 1993). A bias towards C_{2+} maxima in coals at higher maturity is likely related to the retention of liquid hydrocarbon coupled to the onset of oil to wet gas cracking. Rice (1993) noted a possible tendency towards wetter gases from Cretaceous–Cenozoic coals compared to Paleozoic coal, with the former generally more H-rich, most likely reflecting a floral evolutionary trend.

Wet gas content is initially controlled by primary generation from kerogen, while at higher maturities, both primary generation from the residual kerogen and secondary cracking of liquid hydrocarbons occur, with significant overlap of these two processes (Behar et al., 1992, 1995; Hill et al., 2003), and finally wet gas cracking. In oil pyrolysis experiments, wet gas generation begins around R_o 1.0%, with maxima in wet gas contents observed at vitrinite reflectance of 2–2.3% after which cracking of the wet gas components themselves begins. Although coals and disseminated organic matter (in shales) are thought to represent a continuum as source rocks for hydrocarbons (Powell and Boreham, 1991), current data suggest a divergence between these two rock types at the high maturity end. In shale gas, rollovers and reversals in composition are increasingly being found in what is effectively

a closed shale system (Tilley and Muehlenbachs, 2013; Tilley et al., 2011; Zeng et al., 2011; Zumberge et al., 2012) as opposed to the relative openness in coal measure environments. For example, the *iso*-butane/*n*-butane ratio in Barnett and Fayetteville shale gas maximise at around ~5 vol.% wet gas content, corresponding to a R_o = ~1.5%, with an accelerated decrease below 2 vol.% wet gas (i.e., a dry gas). This compositional change is a reflection of cracking of the wet gases, sometimes leading to overpressuring and increased rates of shale gas production as is the case in the Barnett Shale (Jarvie et al., 2007; Zumberge et al., 2012).

It has been variously suggested that carbon dioxide is more or less abundant in microbial versus thermogenic gases. For example, Martini et al. (1996) documented microbial gas accumulations in an organic-rich shale with high concentrations of ^{13}C-enriched carbon dioxide, and Scott et al. (1994) reported that carbon dioxide concentrations greater than 10 vol.% in the San Juan Basin were restricted to the CBM production 'fairway' where produced gas is also very dry. Because the microbial communities that degrade coal to methane both produce and consume carbon dioxide, some variation in the concentration of carbon dioxide is to be expected even with microbial gases. On the other hand, it is well known that the carbon dioxide content of shale gases increases with maturity in many settings, although this thermogenic input is unlikely to result in CO_2 contents > 5 vol.%. This is true for the Barnett and Fayetteville shales; however, the wide range of carbon dioxide carbon isotope compositions suggests that the carbon dioxide has multiple origins (Zumberge et al., 2012). Similar studies in the eastern Australian basins where coals locally contain more than 90 vol.% carbon dioxide show that coal bed and natural gases with carbon dioxide contents greater than 10 vol.% exhibit a narrow range of $\delta^{13}C$–CO_2 values between −3 and −10‰, and are derived largely from inorganic sources (Fig. 2) (Boreham et al., 2001b; Draper and Boreham, 2006; Golding et al., 2013; Smith and Pallasser, 1996), varyingly sourced from mantle and carbonate decomposition based on associations with helium-3 to helium-4 ratios (Watson et al., 2004).

Nitrogen is one of the most common non-hydrocarbon gases in CBM and shale gas after carbon dioxide although published studies rarely go beyond reporting the observed ranges in concentration (e.g., Burruss and Laughrey, 2010; Flores et al., 2008; Golding et al., 2009; Kotarba and Pluta, 2009; Osborn and McIntosh, 2010; Whiticar, 1996). In the case of gases desorbed from coal and shales, it is necessary to correct the nitrogen concentrations based on the oxygen present to take account of atmospheric nitrogen in the canister headspace and desorption system. Some of the oxygen initially present may have been consumed by reaction with the coal such that the reported levels of nitrogen in desorbed gases are often an overestimate of that originally adsorbed in the coal (H. Jin et al., 2010). What we know from published studies of natural gases and their source rocks is that the nitrogen content of gases often correlates with the thermal maturity of the source rocks, with nitrogen mostly produced by the thermal decomposition of organic matter and high ammonium clays (e.g., Jurisch and Krooss, 2008; Krooss et al., 1995; Liu et al., 2012; Zhu et al., 2000). In other cases, high concentrations of nitrogen are interpreted to be related to mantle or igneous sources because of the tectonic setting and/or helium isotope systematics of the gases (Boreham et al., 2001b; Liu et al., 2012).

The molecular composition of coal seam and shale gas typically varies laterally and vertically in sedimentary basins. In many basins, the $C_1/(C_2 + C_3)$ ratio that is a sensitive indicator of the origin of the gases decreases with depth and towards basin depocentres, with most authors relating these trends to the deeper generation of thermogenic wet gases (Rice, 1993) and at the shallower depths late stage microbial gas in areas subject to meteoric recharge (e.g., Appalachian Basin (Osborn and McIntosh, 2010), Bowen Basin (Kinnon et al., 2010; this study), Illinois Basin (Strąpoć et al., 2008), Michigan Basin (Martini et al., 1998, 2003), Powder River Basin (Flores et al., 2008), Sydney Basin (Faiz and Hendry, 2006; Faiz et al., 1999, 2007), Upper Silesian Basin (Kotarba and Pluta, 2009)). For example, the C_{2+} hydrocarbon species are virtually absent down to depths of 400 to 600 m in coals of the northern Bowen Basin and the Sydney Basin and increase rapidly at greater depths (Fig. 3) (Faiz et al., 1999; Kinnon et al., 2010; this study). However, this increase in gas wetness at depths greater than 600 m in the northern Bowen and Sydney basins frequently coincides with a plateau or even decrease in total gas content (Faiz et al., 1999, 2007; Kinnon et al., 2010). Individual wells in the Walloon Subgroup of the Surat Basin where the gas is dominantly of microbial origin based on the work of Draper and Boreham (2006) also commonly show a positively parabolic trend in gas content with depth; however, in this case, gas content maxima coincide with a sandstone unit that separates the upper and lower coal measures regardless of depth (Hamilton et al., 2012).

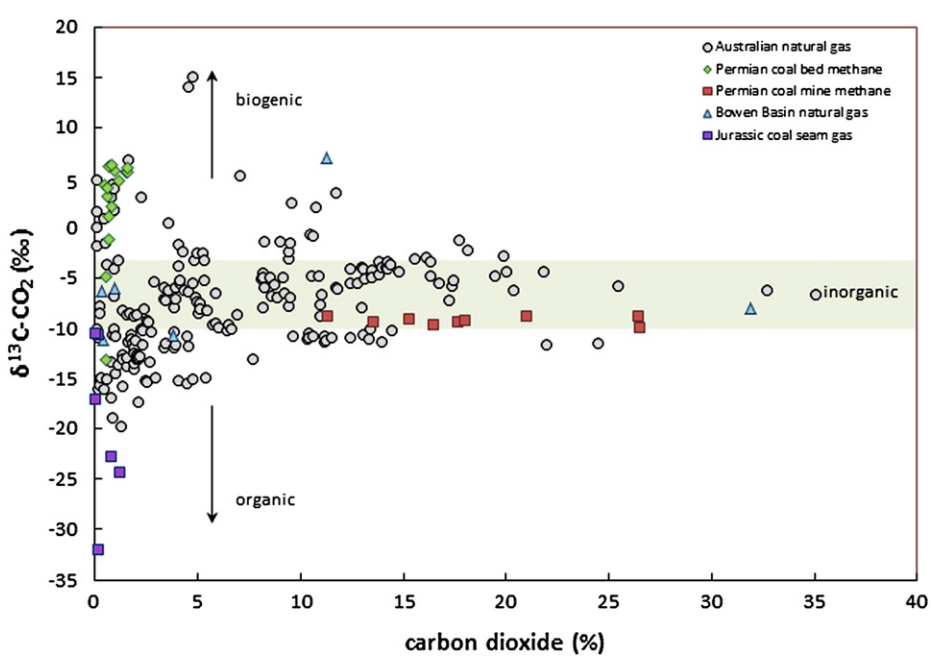

Fig. 2. Carbon isotopic composition of CO_2 versus molecular percentage of Australian coal bed and coal mine methane and natural gas (Boreham et al., 2001b; Golding et al., 2013; Kinnon et al., 2010). Note: biogenic = influenced by microbial activity; inorganic = mainly from igneous input; organic = from thermal decomposition of organic matter.

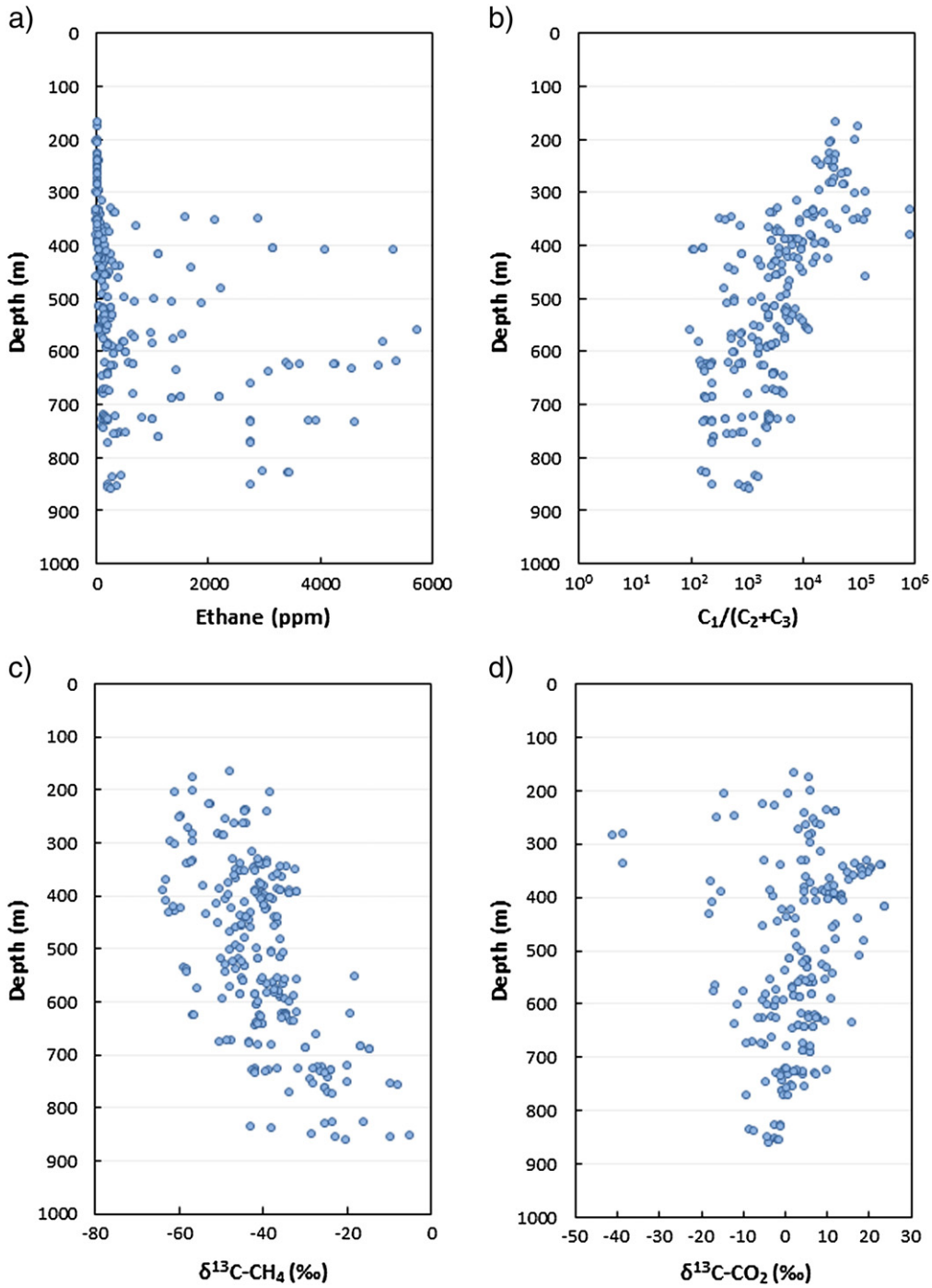

Fig. 3. Trends with depth in molecular and isotopic compositions of CBM pilot and production wells from the northern Bowen Basin. (a) Depth versus ethane concentration. (b) Depth versus gas dryness ($C_1/(C_2 + C_3)$). (c) Depth versus $\delta^{13}C$–CH_4. (d) Depth versus $\delta^{13}C$–CO_2.

More generally, the production behaviour of CBM and shale gas fields shows an interesting correlation with gas composition, particularly the ethane content and the gas dryness/wetness. Zumberge et al. (2012) showed that gas production rates from Barnett Shale gas wells after six months of production were inversely correlated with gas wetness values, with highest production rates achieved below gas wetness values of some 5 vol.%. These authors conclude that high gas production rates from the Barnett Shale were related to overpressure caused by wet gas cracking. A number of studies in the USA and Australia have shown that CBM production rates are highest at intermediate levels in areas where the gases are dry and of mixed or microbial origin (e.g., Bowen Basin (Kinnon et al., 2010), San Juan Basin (Scott et al., 1994; Zhou et al., 2005), Sydney Basin (Faiz et al., 1999, 2007)). Gas saturation levels in these high production 'fairways' are higher than in areas where wet thermogenic gas predominates and the higher permeability that allowed meteoric water recharge also favours high gas production.

2.2. Methane carbon and hydrogen isotopes

The carbon and hydrogen isotopic compositions of methane and associated gases in combination with molecular composition are used to establish gas origin, particularly the relative role of thermal and microbial processes and the microbial methane generation pathway (e.g., Berner and Faber, 1988; Chung et al., 1988; Schoell, 1980; Strąpoć

et al., 2007, 2008; Whiticar, 1999; Whiticar et al., 1986). Schoell (1980) showed that the different types of methane have characteristic carbon and hydrogen isotope compositions, which varied also with source rock type and maturity in the case of thermogenic methane. Whiticar et al. (1986) extended this work to include the effect of methane generation pathway on the molecular and isotopic compositions of microbial gases (Fig. 4). Primary thermogenic gases have methane carbon isotope compositions greater than −50‰ and commonly fall on parallel trends that extrapolate to the isotope composition of the source material on a Schoell style plot of methane δD versus $\delta^{13}C$ (e.g., Burruss and Laughrey, 2010; Osborn and McIntosh, 2010; Schoell, 1980). Microbial gases typically have methane carbon isotope compositions less than −50‰ for acetate fermentation/methyl utilisation and less than −60‰ for the carbon dioxide reduction pathway (Strąpoć et al., 2011; Whiticar, 1996, 1999; Whiticar et al., 1986). The CO_2-reduction pathway is distinguished from acetate fermentation/methyl utilisation by its somewhat lower $\delta^{13}C$–CH_4 and higher δD–CH_4 on a Whiticar style plot of methane δD versus $\delta^{13}C$ (Fig. 4) (Smith et al., 1992; Whiticar, 1996, 1999; Whiticar et al., 1986). Mixing between microbial and thermogenic gases may produce intermediate methane carbon isotope compositions between −50 and −60‰ that could also reflect secondary processes like water stripping or cracking of bitumen and liquid hydrocarbons (Boreham et al., 1998, 2001a; Faiz and Hendry, 2006; Flores et al., 2008; Golding et al., 1999; Kinnon et al., 2010; Whiticar, 1996, 1999; Xia et al., 2013). Another process that could also produce intermediate and arguably thermogenic methane carbon isotope compositions where the methane is actually of microbial origin is substrate depletion in a partially closed system (cf. Whiticar, 1999). In this context, Schlegel et al. (2011) found that Pennsylvanian coals and the New Albany Shale of the Illinois Basin had correlated methane and carbon isotope compositions and a fractionation indicative of CO_2 reduction, but had $\delta^{13}C$–CH_4 values as high as −47.1‰. These authors concluded that the less negative $\delta^{13}C$–CH_4, $\delta^{13}C$–CO_2 and $\delta^{13}C$-DIC values of deeper samples resulted from progressive depletion of the carbon reservoir, most likely linked to the residence time of groundwater. On the other hand, mixing of overmature dry gas or abiogenic methane with thermogenic gas results in ^{13}C enrichments in methane with carbon isotope composition up to +7‰ (Jenden et al., 1993; Prinzhofer et al., 2011).

A range of discrimination diagrams developed initially for classification of natural gases including the Schoell and Whiticar plots discussed above have been applied to determining the origin of CBM and shale gas. One of the most widely used is the Bernard diagram (modified after Bernard et al., 1978 and Faber and Stahl, 1984), which compares the molecular ratio of $C_1/(C_2 + C_3)$ with $\delta^{13}C$–CH_4 (Fig. 1) to distinguish between dry microbial and wet thermogenic gases. There are various forms of the Bernard plot depending on the type of gases being assessed and some variation in the fields used for microbial and thermogenic gases, with different workers using <15 to <100 for the upper boundary of the wet thermogenic gas field and >1000 for the lower boundary of the dry microbial gas field (e.g., Osborn and McIntosh, 2010; Kotarba and Pluta, 2009; Martini et al., 1998: Strąpoć et al., 2008; Whiticar, 1996). These different boundaries for the thermogenic gas field largely reflect the effect of coal thermal maturity on the gas molecular and isotopic compositions.

Strąpoć et al. (2011) have recently modelled the combined effect of coal thermal maturity and methanogenic pathway on gas molecular and isotopic compositions as well as mixing between thermogenic and microbial gases and presented this in several different ways (Fig. 5). Mixing lines provide an indication of the relative proportions of thermogenic and microbial gas. On the Bernard plot (Fig. 5a), exclusively microbial gas contains essentially no ethane and propane and shows a range of $\delta^{13}C$–CH_4 values reflecting the methanogenic pathway. On the other hand, the gas dryness and $\delta^{13}C$–CH_4 values of exclusively thermogenic gas vary with coal thermal maturity (Fig. 5a). A second diagram compares the molecular ratio of $C_1/(C_2 + C_3)$ with the carbon isotope difference between carbon dioxide and methane defined as $\Delta^{13}C_{CO2-CH4}$ (Fig. 5b), which is another indicator of the thermogenic versus microbial origin of gases and the methanogenic pathway (Smith and Pallasser, 1996; Strąpoć et al., 2007, 2011). Coal seam and shale gases from a number of sedimentary basins generally fall within the appropriate fields on these diagrams based on our understanding of the origins of the gases (Fig. 5). Nevertheless, there is considerable scatter and the same gases fall in somewhat different parts of the two gas origin and mixing diagrams, which likely reflects a range of primary and secondary processes such as substrate depletion in a partially closed microbial system and post-mature gas cracking in a closed thermogenic system. The latter is discussed in more detail in a subsequent section.

The carbon isotope composition of coal bed methane often varies vertically and in some cases laterally in sedimentary basins in tandem with ethane content and gas wetness (Fig. 3), with most authors

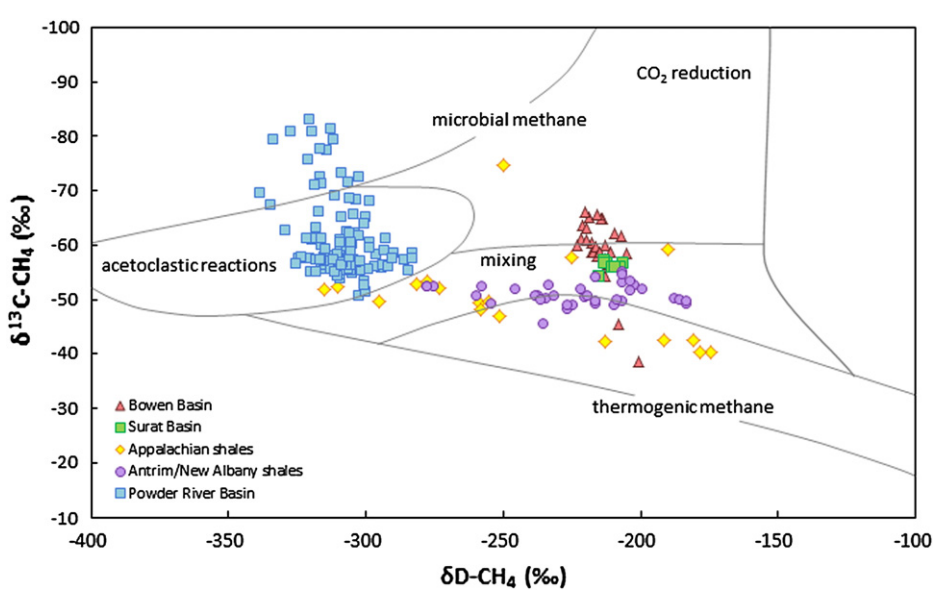

Fig. 4. Methane $\delta^{13}C$ versus δD for coal bed and coal mine methane from the Bowen and Surat basins (Moranbah Gas Project (Kinnon et al., 2010); Oaky Creek (Golding et al., 2013); Avon Downs 1, Berwyndale 1, McNulty 2, Moura 29, Peat 20, Pinelands 3 and Wee Warra 1 (Draper and Boreham, 2006)). Also shown are gas samples from the Powder River Basin (Bates et al., 2011; Flores et al., 2008), the Antrim and New Albany shales (Martini et al., 1998; McIntosh et al., 2002), and organic-rich shales of the northern Appalachian Basin (Osborn and McIntosh, 2010).

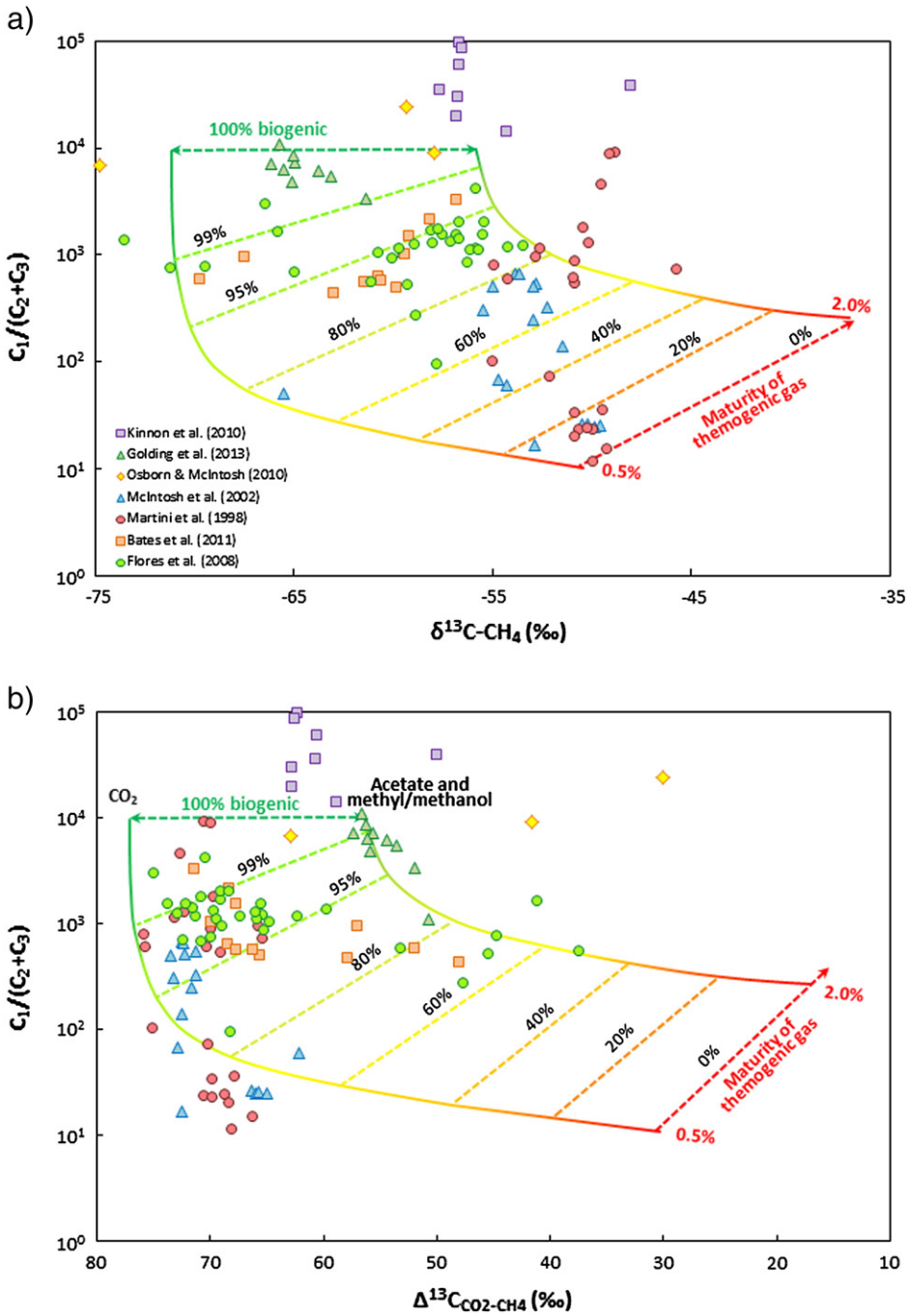

Fig. 5. Gas origin and mixing diagrams after Strąpoć et al. (2011) where mixing lines show the effect of source maturity and biogenic pathway. Data shown are for the Bowen Basin (Golding et al., 2013; Kinnon et al., 2010), the Powder River Basin (Bates et al., 2011; Flores et al., 2008), the Michigan and Illinois basins (Martini et al., 1998; McIntosh et al., 2002) and the northern Appalachian Basin (Osborn and McIntosh, 2010). (a) Gas dryness ($C_1/(C_2 + C_3)$) versus $\delta^{13}C$–CH_4. (b) Gas dryness ($C_1/(C_2 + C_3)$) versus $\Delta^{13}C_{CO2-CH4}$.

relating these trends to mixing between shallow microbial gas ($\delta^{13}C$–CH_4 values < −50‰) and deeper thermogenic gas ($\delta^{13}C$–CH_4 values > −50‰), and/or variations in the microbial pathways employed in gas generation (e.g., Bowen Basin (Kinnon et al., 2010; this study), Powder River Basin (Flores et al., 2008; Rice et al., 2008), Sydney Basin (Faiz and Hendry, 2006; Faiz et al., 1999)). In coals of the northern Bowen Basin, methane carbon isotope compositions become less negative with depth and highest gas production occurs at intermediate levels where the gas is of mixed origins (Fig. 3) (Kinnon et al., 2010; this study). The higher gas production is a function of saturation and permeability. Similar trends in $\delta^{13}C$–CH_4 values are observed in the Sydney Basin where gas contents plateau or decrease at depths greater than 600 m (Faiz et al., 1999, 2007).

The hydrogen isotope composition of microbial methane is determined by the hydrogen isotope composition of the associated formation water and the methanogenic pathway, with the CO_2-reduction pathway separate from the acetate fermentation/methyl-type utilisation pathways on a Whiticar style plot of methane δD versus $\delta^{13}C$ (Fig. 4). The hydrogen isotope fractionation during CO_2-reduction has been shown to be consistent around 160‰ (Whiticar, 1999), such that the hydrogen isotope composition of the methane is related to the associated formation water by the following equation.

$$\delta D_{CH4} = \delta D_{H2O} - 160(\pm 10)‰ \quad (1)$$

This equation predicts that methane formed via the CO_2-reduction pathway from intermediate latitude formation water with a δD–H_2O value in the range −40 to −80‰ would have a δD–CH_4 value of −200 to −240‰ (±10‰), which falls within the appropriate field on the Whiticar plot (Fig. 4). On the other hand, methane formed via the CO_2-reduction pathway from high latitude or altitude waters with δD–H_2O values significantly less than −80‰ falls in the mixed origins or bacterial fermentation field on the Whiticar plot. For example, Fort Union Formation waters from the Powder River Basin have δD–H_2O values from −121 to −167‰ (Rice et al., 2008) that indicate δD–CH_4 values of −281 to −327‰. The actual measured δD–CH_4 values are −283 to −328‰, with only a few sample pairs falling outside the range in values expected for CO_2-reduction when account is taken of the δD values of the associated formation water (Rice et al., 2008). What this means is that the Whiticar plot of methane δD versus $\delta^{13}C$ is useful for distinguishing the major sources of methane but should be treated with caution when it comes to determining the methane generation pathway where high latitude or altitude formation waters are involved. In this circumstance, it is essential to determine the δD values of the associated formation water as the hydrogen isotope difference between the methane and water (Fig. 6) is a better indicator of the dominant methane generation pathway.

The hydrogen isotope fractionation associated with acetate and methyl-type fermentation is less well defined although it is significantly larger than CO_2-reduction (Whiticar, 1996, 1999; Whiticar et al., 1986). In contrast with CO_2-reduction where 100% of the hydrogen is derived from the associated formation water, only a fraction of the hydrogen for acetate and methyl-type fermentation is derived from the associated formation water (Whiticar, 1996, 1999; Whiticar et al., 1986). However, some studies suggest that enzyme-mediated hydrogen isotope exchange between methyl–hydrogen and water–hydrogen during acetate fermentation in freshwater environments can increase the δD–CH_4 values so they may be similar to methane formed by CO_2-reduction (De Graf et al., 1996; Waldron et al., 1999). In this context, Waldron et al. (1999) determined the following relationship between the δD–CH_4 and δD–H_2O in shallow freshwater environments that may be representative of acetate fermentation processes in sulphate-poor systems.

$$\delta D_{CH4} = 0.675 * \delta D_{H2O} - 284(\pm 6)‰ \quad (2)$$

This equation predicts that methane formed predominantly via the acetate fermentation pathway from intermediate latitude formation water with a δD–H_2O value in the range −40 to −80‰ would have a δD–CH_4 value of −311 to −351‰ (±6‰), which falls within the appropriate field on the Whiticar plot (Fig. 4). Methane formed via the acetate fermentation pathway from high latitude or altitude waters with δD–H_2O values significantly less than −80‰ also has a δD–CH_4 value that falls in the bacterial fermentation field on the Whiticar plot. This shows that the compositional fields on a Whiticar plot of methane δD versus $\delta^{13}C$ can be used with caution together with δD–H_2O of associated formation water to determine the dominant microbial methane generation pathway.

The measured $\Delta D_{CH4-H2O}$ for produced gas and associated production waters commonly fall in the range 150 to 170‰, which indicates the CO_2-reduction pathway is more widely applicable than acetate and methyl-type fermentation in the formation of microbial CBM and shale gas (e.g., Bowen Basin (Golding et al., 2013; Kinnon et al., 2010), Illinois Basin (McIntosh et al., 2002; Strąpoć et al., 2007), Michigan Basin (Martini et al., 1998, 2003), and the Powder River Basin (Bates et al., 2011; Flores et al., 2008; Rice et al., 2008)). In some cases the results plot immediately below the theoretical CO_2-reduction equilibrium line on a δD–CH_4 versus δD–H_2O diagram (Fig. 6), which may indicate mixing with thermogenic gases or secondary effects like methane oxidation (McIntosh et al., 2002; Schlegel et al., 2011).

In both coal seam and shale gas, the methane is found in a free and adsorbed state; the former, with almost no pore water complexities, being the most easily produced through the natural or stimulated fracture system, which is most significant for shale gas where free gas is predominant. Tang and Xia (2011) have utilised the increase in the heavier isotopes (^{13}C and D) of methane during shale gas production as a decision making tool for optimising the timing of re-stimulation of a fracture system.

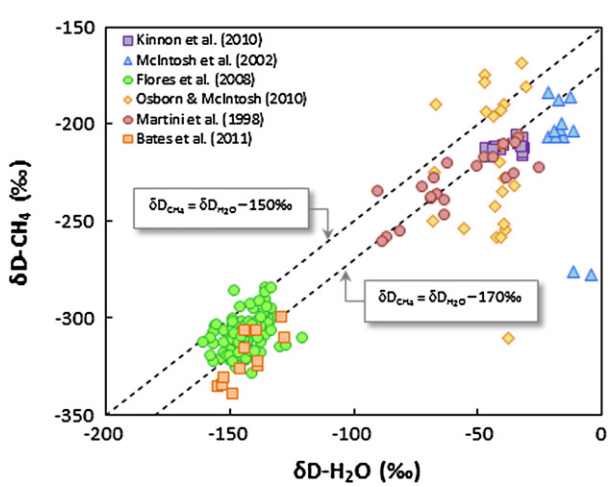

Fig. 6. δD–CH_4 versus δD–H_2O of CBM and associated production water from the Bowen Basin; data shown are from Kinnon et al. (2010). Also shown are the values for formation water and gas samples from the Powder River Basin (Bates et al., 2011; Flores et al., 2008), the Antrim and New Albany shales (Martini et al., 1998; McIntosh et al., 2002) and organic-rich shales of the northern Appalachian Basin (Osborn and McIntosh, 2010). Most samples define a linear trend close to the CO_2-reduction fractionation line.

2.3. Wet gas carbon and hydrogen isotopes

The carbon isotope values of the gaseous hydrocarbons in thermogenic natural gas generally become less negative (enriched in ^{13}C) with increasing carbon number, in accord with theoretical predictions (Chung et al., 1988; James, 1983; Rooney et al., 1995; Tang et al., 2000). The Chung et al. (1988) model relies on the isotopic discrimination occurring at the site of bond cleavage (kinetic isotope effect). This kinetic isotope effect is vividly expressed in methane where the maximum carbon isotopic fractionation occurs compared to the precursor kerogen. For the wet gas components derived from the same source as methane (single source), there should be a linear relationship between the carbon isotope composition of the hydrocarbon gas components and the reciprocal of their carbon number. A plot of $\delta^{13}C$ against the reciprocal of the carbon number (natural gas plot of Chung et al., 1988) approximates a straight line when the gas is generated from a single source, attenuated with maturity by a change in slope (Fig. 7). Such a relationship is seen for the Permian-sourced unaltered natural gases from the Bowen and Surat basins, Queensland (Boreham, 1995). Extrapolation to a large carbon number (1/n ~ 0) predicts the $\delta^{13}C$ value of the source kerogen, which in this case is within the measured range of the potential Permian coal and shale source rocks (Boreham et al., 2001b). Similar relationships are seen with the hydrogen isotopes of the gaseous hydrocarbons (Boreham et al., 2008; Burruss and Laughrey, 2010; Prinzhofer and Huc, 1995; Schoell, 2011).

The Chung et al. (1988) model simplistically assumes that the carbon isotope ratios of individual carbon atoms of the gas-producing precursors (kerogen, bitumen or oil) are isotopically homogeneous. With increasing maturity, gas becomes increasingly enriched in ^{13}C in a predictable proportional manner (James, 1983; Schoell, 1983). Molecular mechanistic models suggest that carbon isotopic separation between methane and each higher homologue decreases with increasing maturity (temperature). This forms the basis for maturity estimates for natural gas generation (James, 1983, 1990). These trends are further supported by empirical relationships within large datasets (Schoell,

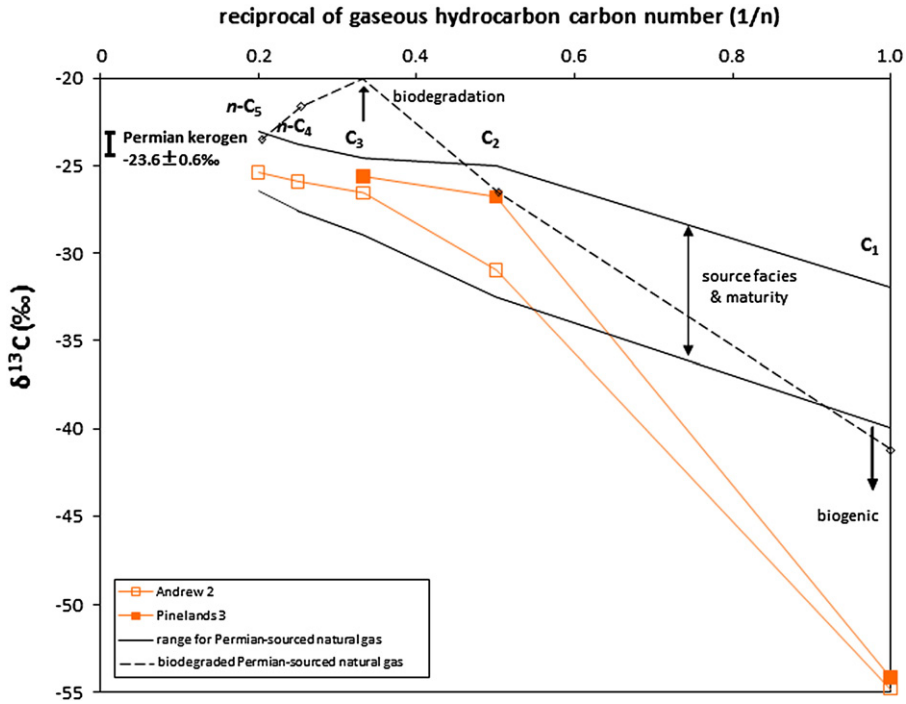

Fig. 7. Reciprocal of carbon number (1/n) versus $\delta^{13}C_n$ (Chung et al., 1988) for Surat Basin CBM (Andrew 2 and Pinelands 3; Draper and Boreham, 2006) and Bowen Basin-sourced natural gases (Boreham, 1995; Boreham et al., 2001b).

1983). However, others have developed alternative models to explain differences between methane and ethane being either constant or increasing with maturity (Clayton, 1991; Faber, 1987). Unfortunately, these models suffer from the disadvantage of either incorrectly assuming that the petroleum generation process is reversible or only using the average carbon isotopic compositions of kerogen as surrogates for the gaseous precursors. The combined kinetic and Rayleigh distillation models considered above have distinct advantages but are both complex and mostly sample specific. Curve-fit models (based on kinetic concepts) that relate carbon isotopic ratios to source rock maturities also have their advantages (Berner and Faber, 1996).

Deviations from a straight line in the natural gas plot can be attributed to multiple source inputs and alteration processes. For example, biodegradation (aerobic, anaerobic, bacterial sulphate reduction) of the wet gases is selective towards the lighter isotope whereby the residual wet gas components become selectively enriched in ^{13}C (Fig. 7) (Boreham et al., 2001b, 2008; Head et al., 2003; James and Burns, 1984; Milkov, 2011; Pallasser, 2000) and D (Boreham et al., 2008; Milkov, 2011), with the hydrogen isotopes showing up to a 10-fold wider isotopic alteration range compared to carbon isotopes (Boreham et al., 2008; Milkov, 2011). Mixing of dry gas with a wet gas will selectively alter the isotopic composition of methane (mixed signal) while leaving the isotopic composition of the wet gases relatively unaltered. Such is observed with the Permian coal seam gases from the Bowen Basin where late stage secondary microbial methane (dry gas) overprints the in-place thermogenic wet gas (Draper and Boreham, 2006). Thus, the carbon isotopes of methane are highly depleted in ^{13}C reflecting the major secondary microbial input while the minor thermogenic wet gas components are unaltered and within the range of the carbon isotopic composition of the natural gas, which had previously generated and migrated from the same Permian source to the natural gases (Fig. 7) (Draper and Boreham, 2006). This biogenic–thermogenic mixing trend for the Permian CBM is also seen in Fig. 8 where those (few) coal seam gases with the lowest $C_1/(C_2 + C_3)$ ratios show heavier methane.

A trend that is opposite to microbial overprint on a thermogenic gas is post-genetic alteration by gas leakage, principally biassed towards methane, which can have a dramatic effect and should be recognised by an increase in gas wetness, and isotopically heavier methane and to a lesser extent heavier ethane (Pernaton et al., 1996), resulting in decreasing value of $\Delta^{13}C_{C1-C2}$ (Prinzhofer and Huc, 1995). Continued leakage will result in the methane becoming isotopically heavier (isotopic reversal) than the wet gas components. It would be difficult to distinguish this process from that of an admixture of two thermogenic gases, one dry and overmature with the isotopically heaviest methane and the other wetter and much less mature (Burruss and Laughrey, 2010; Prinzhofer and Huc., 1995; Tilley et al., 2011) where deconvolution of the alteration mechanism is aided by integration of the geochemistry with the geological setting (Tilley and Muehlenbachs, 2013).

2.4. Isotopic rollovers and reversals in shale gas systems

With the recent exploration and production successes in shale gas, it has been demonstrated that isotopic rollover and reversal are more commonplace than previously realised, with fully reversed $\delta^{13}C$ and δD methane > $\delta^{13}C$ and δD ethane > $\delta^{13}C$ and δD propane observed in overmature shales gases such as those from the Fayetteville play (Fig. 9) (Burruss and Laughrey, 2010; Laughrey, 2011; Tilley and Muehlenbachs, 2013; Tilley et al., 2011; Xia et al., 2013; Zeng et al., 2011; Zumberge et al., 2012). Although these shale gases are dry ($C_1/(C_2 + C_3) > 50$; Fig. 8), the non-oil-associated gases (NAG) from the northern Appalachian Basin have a lower C_2/C_3 content compared to those dry gases from the Fort Worth and Arkoma basins (Fig. 8). Previous models for hydrocarbon gas generation appear inadequate to fully explain the isotopic reversals recently observed. Only now are unified models being proposed involving modelled isotopic fractionation associated with primary gas generation from kerogen, and secondary gas generation from kerogen and decomposition of liquid hydrocarbons and wet gases (Tilley and Muehlenbachs, 2013; Xia et al., 2013). Furthermore, isotopic rollover precedes full isotopic reversal but the maturity levels when, or if, the latter occurs is governed by other factors such as access to water and the permeability history (open versus closed system) of the host rock (Tilley and Muehlenbachs, 2013).

Unconventional natural gases from Silurian and Ordovician reservoirs in the northern Appalachian Basin show isotopic reversals in

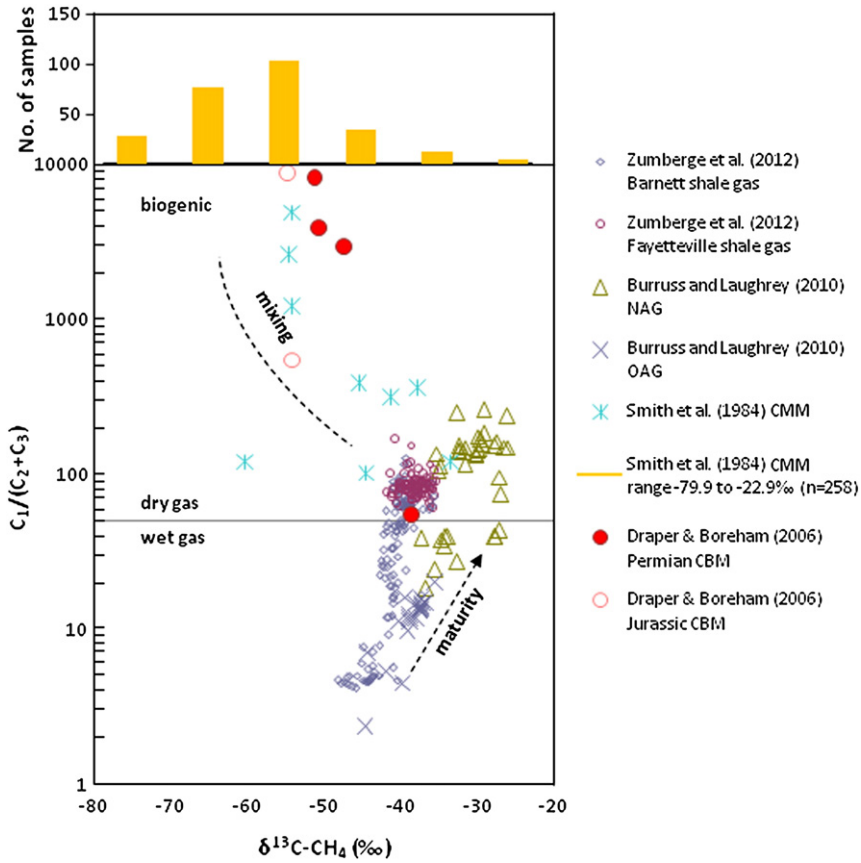

Fig. 8. Gas dryness ($C_1/(C_2 + C_3)$) versus $\delta^{13}C$–CH_4 for deep basin shale gases (northern Appalachian Basin non-associated gas 'NAG' and oil associated gas 'OAG' data (Burruss and Laughrey, 2010), Barnett and Fayetteville formations (Zumberge et al., 2012)). Also shown are values for CBM from the Bowen and Surat basins (Draper and Boreham, 2006); bar chart at top is data from Smith et al. (1984) for eastern Australian coal mines.

carbon and hydrogen of the wet gases that, in part, rely on conventional Rayleigh fractionation and kinetic isotope effects acting on isotopically depleted wet gas precursors, i.e., the residual wet gases become differentially enriched in ^{13}C (Burruss and Laughrey, 2010; Laughrey, 2011). However, the proposed mechanism does not involve a pure thermal pyrolysis; rather the isotopic reversals likely result from redox

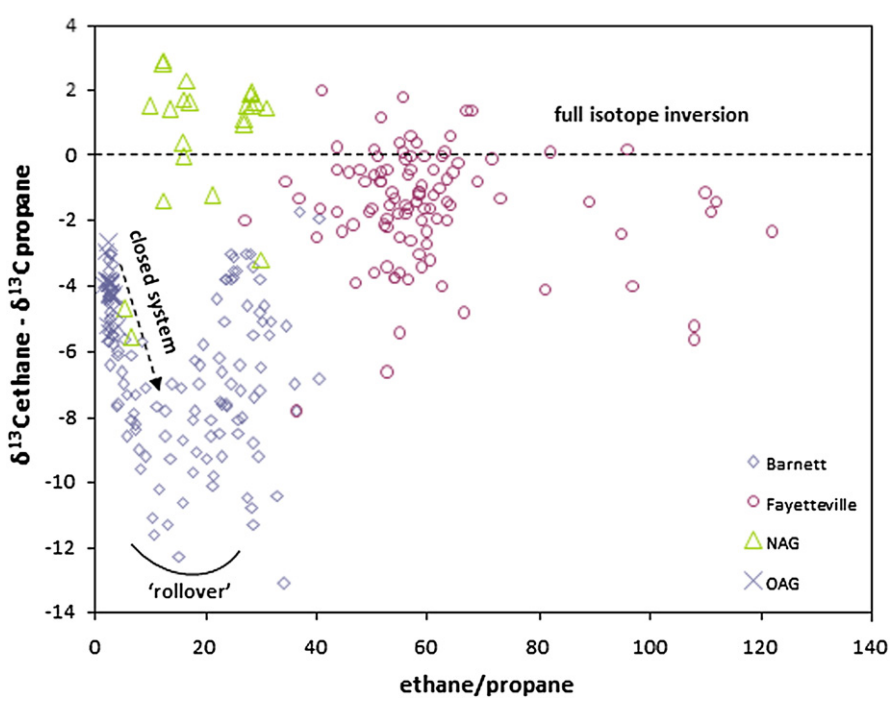

Fig. 9. $\delta^{13}C$ ethane minus $\delta^{13}C$ propane versus ethane mol% to propane mol% ratio for shale gases. Data from Burruss and Laughrey (2010) and Zumberge et al. (2012)

reactions with transitional metals and water during late stage catagenesis (Burruss and Laughrey, 2010).

The degree of openness of the gas system also appears to be a critical factor in the development of isotopic reversals. In the natural gases from the Permian–Triassic, mixed clastic-carbonate reservoirs of the Western Canada Sedimentary Basin (WCSB), Tilley et al. (2011) attributed the isotopic reversals to mature shale gas generation ($R_o > 2.2\%$) in a closed system, which was subsequently released and migrated to the more classical reservoir rocks as a result of later tectonics. Here the thermal destruction of kerogen, wet gas and bitumen at high thermal maturity combine to generate isotopically heavy methane and isotopically lighter ethane, broadly consistent with carbon isotopic trends observed in closed-system pyrolysis of oil (Hill et al., 2003) and model compounds (Y.B. Jin et al., 2010); however, laboratory pyrolysis experiments are yet to demonstrate full isotopic reversals. The fact that high maturity Devonian gases of the WCSB are not isotopically reversed is attributed to ongoing escape of the shale gas from the source rock in a more open system (Tilley et al., 2011). For full carbon isotope reversals in gases from the Singliao Basin China, Zeng et al. (2011) suggest that post-mature in-situ gas cracking (closed system) and the accompanying overpressuring combined to transform methane to wet gases with ^{13}C enrichment in methane and progressive ^{13}C depletion in the wet gases.

Where isotopic reversals are observed, additional mechanisms are also considered to be operative. Abiotic processes involving mineral catalysis and polymerisation leads to complex isotopic reversals. However, the enrichment in ^{13}C of these gaseous hydrocarbons (Dai et al., 2011; Sherwood Lollar et al., 2002, 2006, 2008) compared to those shale gases featured in Fig. 9 is assumed to be a distinguishing mechanistic characteristic of abiogenic gas; further distinguished by progressive enrichment in D with increasing carbon number (Sherwood Lollar et al., 2008). In the shale gases from the Mississippian Barnett and Fayetteville formations, carbon isotopic rollover in ethane is observed at lower thermal maturities ($R_o \sim 1.5\%$) and a gas wetness around 5 vol.% (Zumberge et al., 2012). At this maturity, around 90% of the source rock kerogen has been converted to gas and oil for the Type II organic matter, and oil to gas cracking has begun (Jarvie et al., 2007). Indeed, only 1% oil cracking in a closed system can create enough pressure to fracture the rock fabric (Gaarenstroom et al., 1993). Fully reversed dry shale gases, wherein propane is lighter than ethane (Fig. 9) and ethane lighter than methane, occur at much higher maturities where abiotic catalytic processes, possibly with the aid of transition metals, are thought to occur involving reactions of water with methane to produce isotopically light CO_2 and H_2 (or induce hydrogen-isotopic exchange with formation water resulting in D-depleted methane with a methane D-isotope reversal; Burruss and Laughrey, 2010), which then react to form ^{13}C-depleted ethane and propane (Tang and Xia, 2011; Zumberge et al., 2012). Whether such isotopic reversals occur in deep coal seams that remain at comparable high temperatures is yet to be demonstrated as presently these extreme geological settings are not of economic interest. However, partial reversals ($\delta^{13}C_1 > \delta^{13}C_2$) are seen in high maturity coal-formed gases in the Ordos Basin, China (Hu et al., 2008; Xia et al., 2013).

2.5. Carbon dioxide carbon isotope compositions

The likely sources for CO_2 in coals and shales depend on burial and uplift history and may include dissolved CO_2 from the atmosphere and soil gas, microbial degradation of organic substrates, thermal maturation of kerogen, thermal decomposition of carbonates and magmatic/mantle degassing (Dai et al., 1996; Wycherley et al., 1999). The CO_2 concentration in CBM and shale gas is quite variable and reflects these multiple sources and the pathways employed in the microbial degradation of coal to methane. One way to evaluate the origin of the CO_2 is to look at the relationship between concentration and carbon isotopic composition (Boreham et al., 2001b). Gases with CO_2 contents > 10 vol.% mostly have $\delta^{13}C$ values between −3 and −10‰ and are predominantly of magmatic/mantle origin (Fig. 2). Gases with CO_2 contents < 10 vol.% display a wide range of $\delta^{13}C$ values. Thermogenic CO_2 sourced from coal or organic matter in shales is variably depleted in ^{13}C as is soil gas, whereas isotopically heavy CO_2 (>−3‰) is residual after methanogenesis or the dissolution product of limestone (Fig. 2). Gases with CO_2 contents < 10 vol.% and carbon isotope compositions in the inorganic range between −3 and −10‰ are most likely mixtures or thermogenic CO_2 affected by microbial degradation.

The relative proportions of different gases generated by thermal degradation of organic matter depend on temperature and the type of organic matter. Significant CO_2 is produced through the catagenesis and metagenesis of humic or coaly (Type III kerogen) source rocks, whereas only minor CO_2 is generated from sapropelic (Type I/II kerogen) source rocks (Hunt, 1996). Notwithstanding somewhat lower yields, gaseous hydrous pyrolysis products from marine Type II source rocks are dominated by CO_2 at the lowest maturity levels (Andresen et al., 1995). In laboratory simulations of organic maturation of coal, CO_2 exhibits a relatively small range in carbon isotope composition during closed system pyrolysis that overlaps the organic source isotopic composition (Boreham et al., 1998). On the other hand, CO_2 from open system pyrolysis of coal is variably enriched in ^{13}C exhibiting maximum $\delta^{13}C$ values at some 700°C (Boreham et al., 1998; Gaschnitz et al., 2001). Both these studies showed that CO_2 generated at the lowest pyrolysis temperatures was enriched by only a few per mil relative to the bulk coal, whereas CO_2 generated at the highest pyrolysis temperatures was enriched by up to 17‰ relative to coals with bulk $\delta^{13}C$ values of −24.6 to −23.7‰. Hence, the $\delta^{13}C$ values of CO_2 generated during coalification should fall mainly in the range −20 to −10‰.

In the case of microbial methane, covariance of the $\delta^{13}C$ values of methane and carbon dioxide is expected where methanogens utilise the CO_2-reduction pathway. Moreover, microbial consortia of methanotrophs and methanogens both produce and consume methane and carbon dioxide, with the carbon isotope fractionation between the two species determined largely by the methanogenic pathway (cf. Whiticar, 1999). The $\Delta^{13}C_{CO2-CH4}$ values associated with carbonate reduction range from 49‰ to over 100‰ although the most commonly observed values lie between 60‰ and 80‰ (e.g., Jenden and Kaplan, 1986; Whiticar, 1999; Whiticar et al., 1986). The $\Delta^{13}C_{CO2-CH4}$ values for acetate fermentation and methanogenesis utilising methylated substrates are somewhat lower, with typical values between 40‰ and 55‰ (Whiticar, 1999). A plot of carbon dioxide $\delta^{13}C$ versus methane $\delta^{13}C$ values shows the carbon isotope fractionation lines for the various methanogenic pathways (Fig. 10), where $\alpha CO_2–CH_4 = (1000 + \delta^{13}C–$

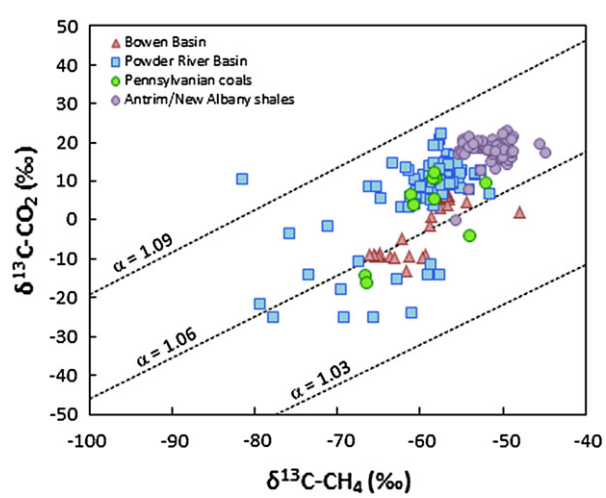

Fig. 10. $\delta^{13}C–CO_2$ versus $\delta^{13}C–CH_4$ for coal bed and coal mine methane from the Bowen Basin (Golding et al., 2013; Kinnon et al., 2010). Also shown are gas samples from the Powder River Basin (Bates et al., 2011; Flores et al., 2008), Pennsylvanian coals (Schlegel et al., 2011), and the Antrim and New Albany shales (Martini et al., 1998; McIntosh et al., 2002; Schlegel et al., 2011).

CO_2) / (1000 + $\delta^{13}C$–CH_4). Values from 1.06 to 1.09 are characteristic of CO_2 reduction, whereas acetate and methyl-type fermentation result in α values from 1.03 to 1.06. Microbial gases from subsurface settings tend to have a similar carbon isotope fractionation between methane and carbon dioxide even when the methane and carbon dioxide $\delta^{13}C$ values shift in response to progressive depletion of the substrate (e.g., Schlegel et al., 2011; Whiticar, 1999) (Fig. 10). This suggests that the carbon isotope fractionation between carbon dioxide and methane may be a better discriminant between gases of microbial and thermogenic origin than the $\delta^{13}C$ and δD value of the methane, particularly in the absence of hydrogen isotope data for the associated formation water. Flores et al. (2008) used the basin wide distribution of the carbon and hydrogen isotope fractionation factors (αCO_2–CH_4 and αCH_4–H_2O) to show that both methyl-type fermentation and CO_2 reduction were implicated in gas generation in the Powder River Basin although microbial CO_2 reduction was the dominant metabolic pathway.

3. Co-produced water chemistry and stable isotope compositions

3.1. Hydrochemistry

Coal measures commonly behave as fractured aquifers confined by less permeable units and may be local to regional sources of water for agriculture and stock if at shallow depth. Extraction of CBM requires pumping of water from the coal measures to reduce the pressure that keeps the methane adsorbed to the coal. Water production decreases with time as gas production increases but is highly variable even within the same CBM field (e.g., Kinnon et al., 2010). These co-produced waters are typically sodium–bicarbonate or sodium–bicarbonate–chloride waters, with very low sulphate concentrations and a relatively wide range of total dissolved solids (TDS values) (cf. Van Voast, 2003). CBM production waters associated with high gas production are characterised by low concentrations of calcium and magnesium and higher concentrations of sodium, with high alkalinity and dissolved inorganic carbon (DIC) values where the gases are interpreted to be of microbial or mixed origin on the basis of the methane and water stable isotope compositions (e.g., Alberta Basin (Cheung et al., 2009; Harrison et al., 2006), Bowen Basin (Draper and Boreham, 2006; Kinnon et al., 2010), Pennsylvanian coals (Schlegel et al., 2011), and the Powder River Basin (Bates et al., 2011; Rice et al., 2008)). In contrast, waters from areas of thermogenic gas production have lower alkalinity values and DIC concentrations as well as higher amounts of C_{2+} hydrocarbons (e.g., Pennsylvanian coals (Schlegel et al., 2011)). These differences suggest that the hydrochemistry of CBM production waters is determined in significant part by the extent of methanogenesis, which will be inhibited by high chloride and sulphate concentrations (Lovley and Klug, 1982). In this context, CBM production water TDS and salinity values in many of the major CBM producing basins are lower at shallower levels in the vicinity of recharge zones, and typically increase with depth and distance from the zones where recharge occurs (e.g., Bates et al., 2011; Cheung et al., 2009; Draper and Boreham, 2006; Kinnon et al., 2010; Rice et al., 2008).

Significant volumes of formation water of variable salinity are also produced from relatively shallow gas wells in the Antrim and New Albany shales of the Michigan and Illinois basins where the shale gas is interpreted to be of mixed microbial and thermogenic origin (Martini et al., 1998; McIntosh et al., 2002). The chloride content increases rapidly in these basins away from the inferred zones of freshwater recharge and produced waters from thermogenic shale gas plays such as the Marcellus Formation of the northern Appalachian Basin have variable but high TDS (e.g., 20,000 to > 200,000 mg/L; Chapman et al., 2012). Major ion chemistry and chloride to bromide relationships help to identify sources of solutes in formation waters and indicate that waters from the Antrim and New Albany shales have a complex history related to episodes of glacial meltwater recharge, with the most saline waters having Ca/Mg ratios similar to basinal brines in adjacent formations (Martini et al., 1998; McIntosh et al., 2002; Osborn and McIntosh, 2010). Chloride versus bromide trends for the Appalachian Basin formation waters also provide evidence for mixing between salines brines and meteoric water, most likely recent precipitation (Osborn and McIntosh, 2010). However, chloride is the dominant anion in these waters, with the majority of samples having concentrations greater than 2000 mmol/L that is known to inhibit methanogenesis (Osborn and McIntosh, 2010).

The Ca/Mg ratio and alkalinity of subsurface waters including coal bed and shale gas production waters largely reflect reactions involving carbonate dissolution and precipitation and the extent of methanogenesis. Production waters from the Antrim and New Albany shales exhibit a range of alkalinity values that are positively correlated with the carbon isotope composition of DIC, whereas brines from thermogenic shale gas plays in the Appalachian Basin have generally lower alkalinity values that do not covary with the carbon isotope composition of DIC (Martini et al., 1998; McIntosh et al., 2002; Osborn and McIntosh, 2010). The trend of increasing alkalinity with increasing $\delta^{13}C$-DIC values is a good indication of microbial methanogenesis that has been observed in organic-rich gas reservoirs worldwide and will be discussed further in a subsequent section (Rice and Claypool, 1981; Schlegel et al., 2011). The Ca/Mg ratio and calcium and magnesium concentrations of coal bed and shale gas production waters are also an indicator of the extent of microbial activity as alkalinity increases in response to methanogenesis or for that matter sulphate reduction may lead to the precipitation of calcite and to a less extent dolomite (cf. Van Voast, 2003). In this context, production waters from the Antrim and New Albany shales both show decreasing Ca/Mg ratios with increasing alkalinity despite other differences in their hydrochemistry (McIntosh et al., 2002).

3.2. Water oxygen and hydrogen isotopes

The oxygen and hydrogen isotope compositions of formation waters in sedimentary basins are quite variable in composition but typically define trends to the right of the Global Meteoric Water Line (GMWL) (Fig. 11) (Clayton et al., 1966). On the other hand, production waters from high gas producing CBM wells typically plot along and to the left of the GMWL (Fig. 11) (e.g., Bowen Basin (Kinnon et al., 2010), Powder River Basin (Bates et al., 2011; Rice et al., 2008), and the San Juan Basin (Snyder et al., 2003)). A number of processes shift meteoric water compositions to the right of the GMWL including evaporation, fluid–rock interaction under high temperature conditions and mixing with seawater or basinal brines (Clayton et al., 1966; Sheppard, 1986; Taylor, 1997). Groundwaters with isotopic compositions to the left of the meteoric water line are relatively uncommon and, in the case of CBM production waters, may have been modified by methanogenesis wherein methanogens preferentially utilise water-derived hydrogen leaving the residual groundwater enriched in deuterium (cf. Whiticar, 1999). Other processes that can shift water isotopic compositions to the left of the GMWL are water–rock interaction under low temperature conditions (Kloppmann et al., 2002) and open system CO_2 exsolution from CO_2-rich groundwater (Cartwright et al., 2002). The precipitation of carbonates and clays in cleats in the coal and the alteration of feldspars and lithics in interburden sandstones would produce groundwaters depleted in ^{18}O and enriched in D (Kinnon et al., 2010; Solano-Acosta et al., 2008). Carbonate precipitation in particular may be a result of increasing alkalinity accompanying methanogenesis that would produce carbonates with high $\delta^{13}C$ values (>0‰) as have been observed in some coal seams and the Antrim Shale (e.g., Budai et al., 2002; Dawson et al., 2012; Golding et al., 2013; Kanduč et al., 2012; Pitman et al., 2003; Solano-Acosta et al., 2008). Open system CO_2 exsolution is a less likely process in view of the hydrology of coal measures that are usually confined by less permeable units and recharged locally and/or from the basin margin. As previously discussed, covariance of the δD values of produced water and methane is to be expected where methanogens utilise either the acetate fermentation or CO_2-reduction pathway (Fig. 6).

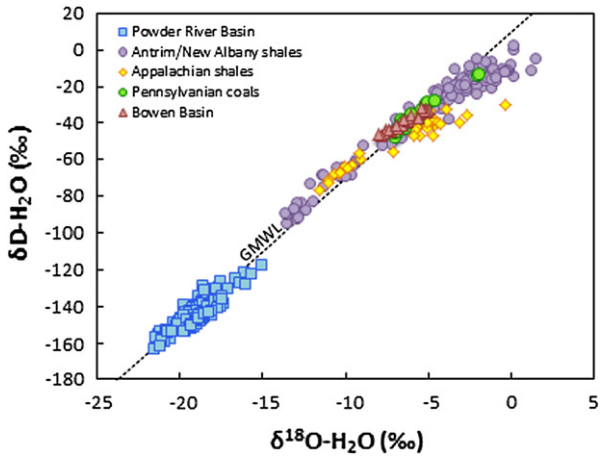

Fig. 11. δD versus $\delta^{18}O$ of CBM production waters from the Bowen Basin; data shown are from Kinnon et al. (2010). Also shown are the values for formation waters from the Powder River Basin (Bates et al., 2011; Flores et al., 2008), Pennsylvanian coals (Schlegel et al., 2011), the Antrim and New Albany shales from the Michigan and Illinois basins, respectively (Martini et al., 1998; McIntosh et al., 2002; Schlegel et al., 2011) and organic-rich shales of the northern Appalachian Basin (Osborn and McIntosh, 2010).

Oxygen and hydrogen isotope compositions of waters from shale gas fields plot along the GMWL or to the right on mixing lines between deep basin brines and meteoric water (Fig. 11) (Michigan and Illinois basins (McIntosh et al., 2002; Martini et al., 1998; Schlegel et al., 2011), and the northern Appalachian Basin (Osborn and McIntosh, 2010)). In this context, production waters from shale gas plays in the Michigan and Illinois basins that are interpreted to be of microbial or mixed origin have oxygen and hydrogen isotope compositions that are more negative than modern meteoric water and most likely reflect Pleistocene glacial melt water dilution of basin brines (Martini et al., 1998; McIntosh et al., 2002). Compared with the Michigan and Illinois basins, water production from the Marcellus Shale and other Devonian organic-rich shales in the northern Appalachian Basin is much lower, and the brines plot to the right of the GMWL and exhibit a mixing trend with modern meteoric water (Osborn and McIntosh, 2010). The molecular and isotopic compositions of gases in these organic-rich shales indicate that the gas is dominantly of thermogenic origin, which is consistent also with the lack of correlation between the hydrogen isotope compositions of the methane and associated formation water (Osborn and McIntosh, 2010).

CBM and shale gas fields commonly show production water chemical concentration gradients with depth and in some cases distance from the basin margin that are interpreted to reflect meteoric recharge and fluid migration (e.g., Antrim and New Albany shales (McIntosh et al., 2002; Martini et al., 1998; Schlegel et al., 2011), Bowen Basin (Kinnon et al., 2010), Pennsylvanian coals (Schlegel et al., 2011), and the Powder River Basin (Bates et al., 2011; Rice et al., 2008)). The oxygen and hydrogen isotope compositions of production waters also provide evidence of mixing between meteoric water and more saline formation waters across a range of scales. In most cases the water isotope and salinity patterns are consistent with inferred groundwater flow paths that are supported also by limited age dating of waters using the ^{3}H, ^{14}C, ^{129}I and ^{36}Cl isotope systems (e.g., Bates et al., 2011; Martini et al., 1998; Snyder et al., 2003). Lighter hydrogen and oxygen isotope compositions of production water than is typical of modern meteoric water are observed in some basins and interpreted to reflect somewhat older waters representative of a cooler or even glacial climate (e.g., Antrim and New Albany shales (McIntosh et al., 2002; Martini et al., 1998), Bowen Basin (Kinnon et al., 2010), and the Powder River Basin (Bates et al., 2011; Rice et al., 2008)).

3.3. Dissolved inorganic carbon isotopes

The two main sources of dissolved inorganic carbon (DIC) in groundwaters are dissolution of carbonates and the breakdown of organic matter that typically produces negative $\delta^{13}C$-DIC values $< -10‰$, with the actual value determined by the relative contributions from the different sources and the type of organic matter (Carothers and Kharaka, 1980; Clark and Fritz, 1997; Osborn and McIntosh, 2010; Sharma and Baggett, 2011; Sharma and Frost, 2008; Whiticar et al., 1986). Positive $\delta^{13}C$-DIC values occur mainly where methanogenesis in organic-rich systems such as coals and shales produces isotopically light CH_4 and residual CO_2 enriched in ^{13}C through the biodegradation of organic substrates (e.g., Alberta Basin (Harrison et al., 2006), Antrim and New Albany shales (Martini et al., 1998; McIntosh et al., 2002; Schlegel et al., 2011), Pennsylvanian coals (Schlegel et al., 2011), and the Powder River Basin (Scott et al., 1994; Sharma and Baggett, 2011; Sharma and Frost, 2008)). Production waters associated with CBM and shale gas interpreted to be of microbial or mixed origin on the basis of the stable isotope systematics of the gases also may exhibit a trend of increasing $\delta^{13}C$-DIC values with increasing alkalinity (e.g., Antrim and New Albany shales (McIntosh et al., 2002; Martini et al., 1998), Pennsylvanian coals (Schlegel et al., 2011), and the Powder River Basin (Bates et al., 2011)), whereas there is little correlation between these parameters where the gases are of thermogenic origin (e.g., organic-rich shales of northern Appalachian Basin (Osborn and McIntosh, 2010)). The extent of fractionation depends on the degree of openness of the system and is influenced by the residence time of groundwater, with larger microbial gas deposits in the Illinois Basin exhibiting the most positive $\delta^{13}C$-DIC, $\delta^{13}C$–CO_2 and $\delta^{13}C$–CH_4 values (Schlegel et al., 2011). In this context, Sharma and Baggett (2011) have used the positive $\delta^{13}C$-DIC values of production water in the Powder River Basin to trace seepage of produced waters from surface impoundments. This was based on the difference in the carbon isotope composition of the produced water ($\delta^{13}C$-DIC range of 12 to 22‰), which is very different to the carbon isotope composition of surface and shallow groundwater ($\delta^{13}C$-DIC range of -14 to $-10‰$) in the region.

4. Summary

4.1. CBM and shale gas origins of methane

The chemical and stable isotope compositions of CBM and related production waters confirm the microbial origins of methane in low maturity coals and the presence of secondary microbial methane at shallow depths in many higher maturity uplifted coals. The relative proportions of microbial and thermogenic shale gas are also depth related in the majority of basins, with exclusively thermogenic gas at deeper levels and a mixture of microbial and thermogenic methane at shallower levels close to basin margins. Diagnostic geochemical parameters include the ratio of methane to the sum of ethane and propane ($C_1/(C_2 + C_3)$), also termed gas dryness (Bernard et al., 1978; Faber and Stahl, 1984), the carbon and hydrogen isotope composition of CH_4 ($\delta^{13}C$–CH_4 and δD–CH_4) (Schoell, 1980: Whiticar, 1996; Whiticar et al., 1986), the carbon isotope difference between CO_2 and CH_4 ($\Delta^{13}C_{CO2-CH4}$) (Smith and Pallasser, 1996; Strąpoć et al., 2007, 2011), and the hydrogen isotope difference between CH_4 and co-produced formation water ($\Delta D_{CH4-H2O}$) (Martini et al., 1998; Schoell, 1980; Whiticar et al., 1986). Production gases from most CBM and shale gas fields are relatively dry, with ($C_1/(C_2 + C_3)$) ratios greater than 1000 and less than 100 typical for microbial and thermogenic gas, respectively. Other evidence for the presence of microbial gas may include $\delta^{13}C$–CH_4 values less than $-50‰$, covariation of the carbon isotope compositions of CH_4 and CO_2 and the hydrogen isotope compositions of CH_4 and production water, $\Delta^{13}C_{CO2-CH4}$ and $\Delta D_{CH4-H2O}$ fractionations consistent with CO_2 reduction or acetate/methyl-type fermentation processes, and positive $\delta^{13}C$-DIC values of production waters that increase with increasing alkalinity. Thermogenic gases on the other hand will have $\delta^{13}C$–CH_4 values greater than $-50‰$, and the hydrogen isotope composition of thermogenic CH_4 depends in part on the hydrogen isotope composition of the organic source. Thermogenic CO_2 also has more negative $\delta^{13}C$ values than CO_2 generated by acetate

fermentation or residual after CO_2 reduction, and $\delta^{13}C$-DIC values of production waters may be variable but do not become more positive with increasing alkalinity. In many cases, the groundwaters associated with thermogenic CBM and shale gas have chloride and/or sulphate levels that are inhibitory to methanogenesis.

Mixing between microbial and thermogenic gases shifts the $\delta^{13}C$–CH_4 values to more negative values and is accompanied by an increase in the methane to ethane and propane ratios. A shift in the δD–CH_4 values to more negative values would also occur wherever acetate fermentation is the dominant metabolic pathway, and accompany CO_2 reduction in basins at high latitude or altitude where the formation water is depleted in D and ^{18}O. Deviations from a straight line in the natural gas plot are also expected where there is mixing between late stage secondary microbial methane and in-place thermogenic wet gas.

4.2. Metabolic pathways involved in formation of microbial methane

The isotopic compositions of CH_4 and CO_2 resulting from methanogenesis are related to the carbon and hydrogen isotope compositions of the organic substrate and formation water, with actual values determined in large part by the metabolic pathways involved in formation of microbial methane (Whiticar, 1999; Whiticar et al., 1986). The CO_2-reduction pathway is distinguished from acetate/methyl type fermentation by somewhat lower $\delta^{13}C$–CH_4 and higher δD–CH_4 on a Whiticar style plot of methane δD versus $\delta^{13}C$, but can also have overlapping values depending on how open or closed the microbial system is and the extent of substrate depletion (Whiticar, 1999). In such circumstance, crossplots of $\delta^{13}C$–CH_4 versus $\delta^{13}C$–CO_2 and δD–CH_4 versus $\delta^{13}C$–H_2O illustrate the carbon and hydrogen isotope differences ($\Delta^{13}C_{CO2-CH4}$ and $\Delta D_{CH4-H2O}$) between these phases, and may provide a better indication of the origin of the gases and the dominant methanogenic pathway. In the majority of cases, microbial CBM and shale gases have carbon and hydrogen isotope fractionations close to those expected for CO_2 reduction.

At the basin-scale, the distribution of carbon and hydrogen isotope fractionation factors quantified as αCO_2–CH_4 and αH_2O–CH_4 where $\alpha A–B = (1000 + \delta A) / (1000 + \delta B)$ have been used to estimate the relative fraction of methane resulting from CO_2 reduction and acetate/methyl-type fermentation in the Powder River Basin (Flores et al., 2008). This study suggested that acetate/methyl-type fermentation mainly occurred at the basin margins, with CO_2 reduction dominating in deeper levels of the basin. Bates et al. (2011) interpreted an expanded carbon and hydrogen isotope isotopic dataset for gases and production waters from the Powder River Basin somewhat differently, and concluded that the carbon isotope values of CH_4 and CO_2 and the differences between them reflect the extent of methanogenesis rather than the methanogenic pathway. This indicates that detailed field and basin scale geochemical studies of coal bed and shale gas and related production waters are essential to determine not only the origins of the gas but also the dominant methanogenic pathway in the case of microbial gas.

4.3. Source and thermal maturity effects

For thermogenic CBM (methane and wet gases) and shale gas, source, maturity and chemical kinetics have the primary controls on the gas composition and the proportion of gaseous and liquid hydrocarbons (Jarvie, 2012; Jarvie et al., 2007; Rice, 1993; Tissot and Welte, 1984). Coal (Type III organic matter) is the obvious source for CBM while Type II marine organic matter is the dominant source for large shale gas reserves (Jarvie, 2012; Jarvie et al., 2007). As such, these fundamentally opposed organic sources impart their own diagnostic molecular and isotopic compositions on the generated hydrocarbon gases (Jarvie et al., 2007; Prinzhofer and Huc, 1995; Rice, 1993; Rooney et al., 1995; Tang et al., 2000; Tissot and Welte, 1984). For both CBM and shale gas, where the source and reservoir are the same, increase in maturation over the oil window sees the wet gases associated with residual oil and on further maturation the residual bitumen crack to dry gas and pyrobitumen. On the other hand, microbial gas generation is limited to a much narrower, low temperature range up to approximately 80°C (Milkov, 2011 and references therein), which is below the thermogenic oil window temperature-wise.

With maturity, the $\delta^{13}C$ and δD values of thermogenic gases systematically increase from C_1 to C_5 and define a relatively straight line when plotted against reciprocal carbon number (Boreham et al., 2001b, 2008; Burruss and Laughrey, 2010; Chung et al., 1988; Prinzhofer and Huc, 1995; Schoell, 2011), although terrestrially sourced gases do not always conform with the Chung model and can show little variation in the $\delta^{13}C$ values of the higher wet gases (cf. James, 1990). A possible explanation for this is the heterogeneous nature of coal that is likely to involve a wide variety of gas precursors with their own unique isotopic compositions contributing to the gaseous hydrocarbons generated over the oil window. At the overmature stage, the variety of primary gas precursors becomes more restricted and a more uniform isotopic trend may be expected. Nevertheless, the Chung natural gas model breaks down at the higher level of maturity in deep basin shale gas where full isotopic reversals commonly occur, i.e., $\delta^{13}C–CH_4 > \delta^{13}C–C_2 > \delta^{13}C–C_3$, most likely due to secondary cracking of liquids to wet gas in a closed system (cf. Tilley et al., 2011; Xia et al., 2013) or, alternatively, abiogenic processes (Burruss and Laughrey, 2010; Zumberge et al., 2012). A return to a normal gas isotopic trend, i.e., $\delta^{13}C–CH_4 < \delta^{13}C–C_2 < \delta^{13}C–C_3$ accompanies wet gas cracking (Tilley and Muehlenbachs, 2013). Indeed, such isotopic rollovers and reversals are seen as an indicator of shale gas 'sweet spots' (Zumberge et al., 2012). However, where the system is more open isotopic reversals are not seen in shale gases (Tilley et al., 2011) and most likely similarly with CBM where high maturity coals retain fracture permeability.

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