196118

C isotope fractionation in coal and marine source rocks and implications for exploration – examples from Bowen and Beetaloo basins

Mohinudeen Faiz*
Origin Energy Ltd
GPO Box 148
Brisbane, Qld 4001
Mohinudeen.faiz@originenergy.com.au

Alison Zoitsas
Origin Energy Ltd
GPO Box 148
Brisbane, Qld 4001
Alison.Zoitsas@originenergy.com.au

Carl Altmann
Origin Energy Ltd
GPO Box 148
Brisbane, Qld 4001
Carl.Altmann@originenergy.com.au

Elizabeth Baruch-Jurado
Origin Energy Ltd
GPO Box 148
Brisbane, Qld 4001
Elizabeth.Baruch-Jurado@originenergy.com.au

David Close
Origin Energy Ltd
GPO Box 148
Brisbane, Qld 4001
David.close@originenergy.com.au

**presenting author asterisked*

SUMMARY

Stable isotope composition of gas is widely used in hydrocarbon exploration to determine the composition and thermal maturity of source rocks. Many published isotope classification systems are primarily based on observations made in conventional reservoirs and the kinetic isotope effects shown during hydrocarbon generation within its source rocks. However, such relationships may not be routinely applicable to unconventional reservoirs due to the strong molecular and isotope fractionation that occurs during extensive gas expulsion.

The analyses of Australian coal and marine shale samples indicate that during gas desorption both molecular and isotopic compositions of gas change at variable rates. Early desorbed gas is relatively dry (enriched in CH_4) whereas later desorbed gas becomes increasingly wet (enriched in C_2H_6 and higher hydrocarbons) with time. The hydrocarbon molecules also fractionate according to their C isotopic composition where the later desorbed gases are enriched in the heavier ^{13}C isotope (relative to ^{12}C). In a set of high volatile to medium bituminous coals from the Bowen Basin studied the difference in $\delta^{13}C$-CH_4 ratio between early and late desorbed gas ranges between 2‰ and 21‰ depending on thermal maturity and the overall hydrocarbon composition. For C_2H_6 and higher hydrocarbons the fractionation between early and late desorbed gas is lower, with C_2H_6 <7‰ and C_3H_8 <2‰. Similar isotope fractionation occurs during gas desorption from marine source rocks. A gas mature middle Velkerri sample from the Beetaloo Basin shows $\delta^{13}C$-CH_4 fractionation of up to 28‰ between early desorbed and later released residual gas. The $\delta^{13}C$-C_2H_6 fractionates by up to 3‰ whereas $\delta^{13}C$-C_3H_6 shows insignficant fractionation.

The fractionation behaviour of molecules during expulsion of gas is primarily related to their adsorption-desorption properties on organic matter and diffusivity through the overall rock matrix. In general, heavier hydrocarbon molecules are strongly adsorbed on organic matter and desorb slower compared with lighter molecules. The differential isotope fractionation behaviour between the hydrocarbon molecules can lead to inconsistent compound specific isotope trends where an inverse trend can be seen for later desorbed gas. This phenomenon can also contribute to the so-called "isotope reversal" behaviour in some gas mature North American shale reservoirs which, at present, is ambiguously described in literature.

Key words: Coal seam gas, shale gas, desorption, isotopes, fractionation

INTRODUCTION

The correlation of stable isotope composition of fluids in a reservoir with a specific source material, depositional environments and the thermal maturity has been extensively applied in conventional hydrocarbon exploration. More recently, the study of stable isotope signature of gases in "unconventional" hydrocarbon reservoirs including coal seam gas (CSG) and shale gas systems has proven to be beneficial in answering general exploration and specific production related questions. Unlike conventional reservoirs, unconventional reservoirs represent both the source and reservoir rocks and, therefore interpreting the isotope signatures of fluids requires a different approach to that traditionally used for conventional reservoirs.

The C and H isotope compositions of CH_4 are most commonly and routinely used to identify the origin and source of gas in reservoirs. However, the use of compound specific isotopes (CSI) for C_{2+} (C_2H_6 and higher hydrocarbons) components can provide more detailed information on thermal maturity, expulsion and migration behaviour of hydrocarbons within the source rock and reservoirs.

The Bowen Basin contains a large resource of Permian coal deposited in fluvio-deltaic environments (Figure 1). The coals are high volatile to low volatile bituminous in rank with the highest rank coals located in northeastern parts of the basin. The coals also host a large gas resource with the majority of current CSG production being derived from Late Permian high volatile bituminous coals. Gas in these coals comprise both thermogenically and biogenically generated hydrocabons. Thermogenic gas was generated during the Jurassic to Early Cretaceous periods as a result of deep burial of the coals (>2 km). Most of the biogenic gas in the coals is "secondary" biogenic gas that was generated since the Late Cretaceous when the basin was uplifted to shallower depths (<800m). Biogenic gas predominantly contains CH_4 whereas thermogenic gas (generated up to low volatile bituminous rank) contains significant amounts (>1%) of C_{2+} hydrocarbons. In general, eastern Australian coals at depths >500mMSL contain mostly thermogenic gas with high concentrations of C_{2+} hydrocarbons (Faiz et al, 2012; Figure 2). At shallower depths thermogenic gas is mixed with secondary biogenic gas formed by the decomposition of pre-existing thermogenic gas and degradation of the matrix component of the coal (Smith, 1999; Faiz and Hendry, 2006). In many highly permeable CSG reservoirs of the Bowen Basin secondary biogenic gas is a significant component with $\delta^{13}C\text{-}CH_4$ typically < -50‰.

The Mesoproterozoic Beetaloo Sub-Basin (Beetaloo Basin) located in the Northern Territory hosts several organic rich shales within the Velkerri and Kyalla formations. The shales were deposited in marine environments and the organic matter derived from primitive bacteria and filamentous organisms such as blue green algae (Cyanobacteria). The organic rich shales of the middle Velkerri section of the Velkerri Formation are estimated to have a large unconvetional gas resource potential (Close et al., 2016). Unconventional gas exploration in the basin, however, is in its infancy which limits the availability of isotope data from produced gas. In 2016 Origin drilled, fractured stimulated and tested the first horizontal well in the basin. The gas produced during the test primarily consisted of CH_4 with $\delta^{13}C$ values ranging between -39‰ and -41‰.

Unconventional reservoirs have the capacity to store gas in both organic and inorganic fraction of the rock. Gas hosted in organic matter is mostly held as adsorbed molecules on internal surfaces where the pores are generally < 2nm in diameter. In the mineral matrix gas is largely held as compressed pore filling fluid ("free gas") within larger pores (>2nm) in intra- and intergranular porosity (Loucks et al., 2009; Zhang et al. 2016). The organic matter content and pore-size distribution therefore determine the proportions of molecules stored in adsorbed and free gas phases in an unconventional reservoir. This paper investigates the behaviour of various hydrocarbon molecules during desorption and expulsion from coal and carbonaceous shales.

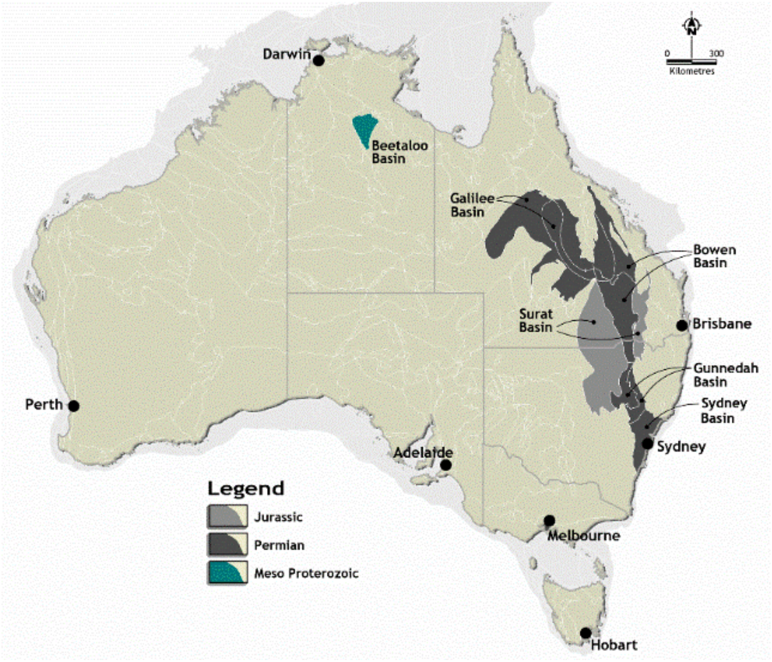


Figure 1: Map showing the location of the Beetaloo Basin and the major coal seam gas bearing basins in eastern Australia

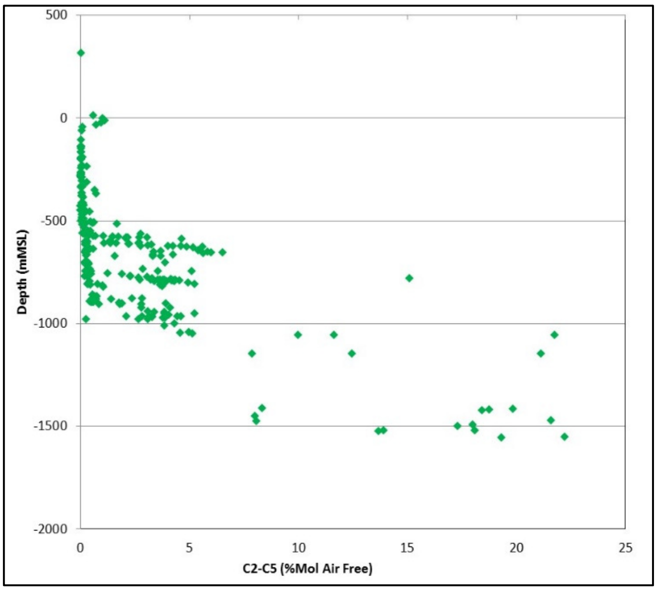


Figure 2: Depth (relative to mean sea level) *vs* C_{2+} hydrocarbon content of coal seam gas in the Bowen Basin (modified from Faiz et al., 2012).

SAMPLES AND ANALYSES

Coal samples from the Bowen Basin

Data from nine coal core samples obtained from deep CSG exploration wells drilled in the Bowen Basin were used for this study (Table 1). The gas content of the core samples was measured using the "direct desorption method" according to the procedures described in the Australian Standards (Australian Standard AS3980:1999 and AS3980:2016). During the desorption measurements, three sub-samples were collected at time intervals in order to determine the molecular and compound specific isotopic compositions of the gas. The sampling time intervals include:

- Sample 1 – first 24 hours of start of desorption
- Sample 2 – after 7 days of desorption
- Sample 3 – end of desorption (prior to crushing the core to determine the residual gas content)

Shale sample from the Beetaloo Basin

Gas content of a carbonaceous shale from the Velkerri Formation in the well K-1 was determined by means of recovered pressurised side wall cores samples. Ten closely spaced sidewall core samples from the depth interval 2263-2290 m were acquired using Halliburton's CoreVault Fluid and Rock sampling system (Halliburton, 2014). Gas content of the composite sample was determined using a customised desorption analyses canister at Weatherford Laboratories in Brisbane. During the process three sets of gas content and compositional data were acquired:

- Gas contained in CoreVault – mostly representing "free gas" and minor amounts of early desorbed gas
- Desorbed gas in the caniser
- Residual gas from crushed sample subsequent to canister desorption

In addition to the volume of gas released from the shale, the molecular and isotopic compositions of the samples were also determined.

Molecular and isotopic composition of gas

The samples were collected in "IsoTubes®" and were analysed using standard gas chromatography (GC) techniques using an Agilent Natural Gas Analyser with thermal conductivity (TCD) and Flame Ionisation detectors (FID). The C isotopic composition of gas was measured using a gas chromatography/combustion/isotope-ratio mass spectrometry (GC-C-IRMS) system. The C isotope value of hydrocarbon components is indicated by the δ (delta) notation relative to a Vienna Pee Dee Belemnite standard (VPDB; ‰). The CSG samples from the Bowen Basin were analysed by the CSIRO (Commonwealth Scientific Industrial Research Organisation) and the shale gas samples from the Beetaloo Basin were analysed by Isotech laboratories.

Sample ID	Basin	Sample type	Depth (m)		Vitrinite reflectance%	Tmax (°C)	Sample sequence/type	Time since desorption commenced (days)	Gas sample type	Proportion of total desorbed gas %	Hydrocarbon composition %						$C_1/(C_1\text{-}C_{5+})$	δ13C‰ (VPDB)				
			Top	Base							CH_4	C_2H_6	C_3H_8	iC_4H_{10}	nC_4H_{10}	C_{5+}		CH_4	C_2H_6	C_3H_8	iC_4H_{10}	nC_4H_{10}
Coal1	Bowen	Coal	1829.66	1830.39	0.8		A	1	Direct desorption	86	82.72	11.20	2.04	0.20	0.30	0.05	0.86	-34.0	-31.5	-29.6	-30.2	-29.5
							B	9	Direct desorption	97	53.82	32.17	8.26	1.04	1.06	0.29	0.56	-23.2	-29.5	-27.9	-30.0	-28.8
							C	27	Direct desorption	99	40.45	37.78	12.50	1.84	1.68	0.16	0.43	-21.5	-28.2	-28.4	-29.7	-28.5
Coal2	Bowen	Coal	1740.88	1741.68	1.12		A	14	Direct desorption	90	87.96	6.57	1.18	0.17		0.09	0.92	-38.3	-33.1	-29.3	-29.1	-28.1
							B	72	Direct desorption	97	47.48	24.84	6.58	0.74		0.20	0.59	-22.0	-29.8	-28.9	-29.4	-28.0
							C	90	Direct desorption	99	26.36	33.48	9.78	1.00	0.10	0.12	0.37	-17.0	-26.7			
Coal 3	Bowen	Coal	1789.6	1790.35	1.15		A	4	Direct desorption	90	85.18	9.36	2.00	0.10	0.30		0.88	-31.2	-31.7	-27.4	-27.9	-26.5
							B	70	Direct desorption	97	60.59	24.18	7.54	0.65	0.94	0.14	0.64	-22.0	-29.0	-27.7	-29.4	-28.0
							C	90	Direct desorption	99	44.44	33.15	12.97	1.24	1.69	0.21	0.47	-20.0	-26.6			
Coal4	Bowen	Coal	948.39	949.16	0.68		A	0.5	Direct desorption	66	97.99	0.21	0.003				1.00	-42.1	-12.8			
							D	7	Direct desorption	94	*97.70*	*1.06*					0.99					
							E	63	Direct desorption	100	*98.20*	*0.61*					0.99	-38.6	-8.1			
Coal5	Bowen	Coal	915.84	916.64	0.69		A	0.5	Direct desorption	60	96.00	0.22	0.00				1.00	-39.2	-13.1			
							D	9	Direct desorption	96	*97.50*	*0.52*					0.99					
							E	68	Direct desorption	100	95.78	0.66	0.01				0.99	-37.2	-8.6			
Coal6	Bowen	Coal	1099.26	1100.08	0.73		A	0.4	Direct desorption	55	92.82	2.38	0.36	0.05	0.02	0.01	0.97	-40.4	-29.4			
							E	67	Direct desorption	100	87.54	8.44	1.81	0.41	0.08	0.02	0.89	-37.5	-26.8			
Coal7	Bowen	Coal	919.73	920.52	0.7		A	0.5	Direct desorption	68	93.68	2.94	0.46	0.08	0.05	0.01	0.96	-39.6	-28.7			
							E	61	Direct desorption	100	83.90	9.41	0.58	0.27	0.04	0.06	0.89	-36.9	-26.7			
Coal8	Bowen	Coal	842	842.79	0.68		A	0.4	Direct desorption	34	96.48	0.16	0.02	0.00			1.00	-41.4	-20.5			
							E	59	Direct desorption	100	96.08	0.55	0.10	0.09	0.03		0.99	-37.1	-16.5			
Coal9	Bowen	Coal	894.1	894.89	0.68		A	0.3	Direct desorption	50	96.52	0.14					1.00	-44.9	-20.2			
							E	60	Direct desorption	100	98.00	0.55					0.99	-37.9	-16.4			
K1-7	Beetaloo	Shale (TOC ~ 4%)	2263	2290		542	Free+early desorbed	0.0	Free+early desorbed	3	98.44	1.42	0.02	0.00	0.00		0.99	-38.0	-40.0	-41.0		
							Avg early desorbed	1.0	Avg early desorbed	4	98.36	1.47	0.02	0.00	0.00		0.99	-41.0	-43.0			
							7_1_15GC	53	Direct desorption	37	93.40	3.31	0.16	0.01	0.04		0.96	-34.2	-43.7	-38.8		-35.2
							7_1_17GC	74	Direct desorption	40	92.76	3.53	0.05	0.00	0.00		0.96	-32.7	-43.4	-42.4		
							7_1_18GC	82	Direct desorption	40	91.87	3.81	0.05	0.00	0.00		0.96	-30.1	-42.5	-42.0		
							7_1_19GC	100	Direct desorption	41	91.07	3.99	0.05	0.00	0.00		0.96	-31.5	-43.1	-42.2		
							Crushed coal		residual gas	100	19.59	28.13	2.22	0.02	0.06		0.39	-15.0	-39.4	-41.3		
							Crushed coal		residual gas	100	16.16	33.53	2.49	0.03	0.06		0.31	-11.6	-39.8	-41.5		-39.4

Table 1: Details of the samples studied including molecular and carbon isotope compositions. VPDB – relative to the Vienna Pee Dee Belemnite standard

RESULTS AND DISCUSSION

The Bowen Basin samples studied are from the Late Permian Baralaba Formation (or equivalent) and primarily contain vitrinite and inertinite with subsidiary amounts of liptinite. The mean vitrinite reflectance (VR) for the samples ranges between 0.68 to 1.15% indicating high volatile to medium volatile coal ranks. The Beetaloo Basin samples are from the Mesoproterozoic middle Velkerri with an average of ~4% organic content (by weight). Organic matter was primarily derived from cyanobacteria and is fully mature for dry gas generation. The average pyrolysis derived Tmax for the samples is 542°C which is equivalent to a VR of approximately 2.5%.

The hydrocarbon composition of CSG shows considerable variability according to thermal maturity of the coals. In general, thermally mature coals (i.e. VR 0.8 – 1.15%) contain more C_{2+} components compared with less mature coals (VR 0.68 – 0.73%). The dryness index (DI), defined as the ratio between CH_4 and the total hydrocarbons (i.e. [C_1/ (C_1 to C_5]) for gas in the marginally mature coals is higher (average ~0.98) compared with mature coals (average ~0.64). This observation suggests that during thermal maturation, where the VR evolved from 0.7% to 1.15%, increasing amounts of C_{2+} hydrocarbons were generated and preserved within the coal. Regional data have demonstrated that such high concentration of C_{2+} hydrocarbons only occur in coals at depths >800m where the coal seams have been preserved from extensive degassing and biodegradation (Faiz et al., 2012).

The mode of gas storage and migration are important factors that determine the rate of gas expulsion from carbonaceous rocks. Under the influence of hydrostatic pressure gas is mostly stored as adsorbed molecules on the internal surface area of organic matter. When pressure decreases, gas desorbs from the organic matter and the rate of gas released shows an exponential decay with time. In coals containing wet gas the early released gas is relatively enriched in CH_4 and the proportion of C_{2+} increases during later stages of desorption; the enrichment of C_{2+} is more pronounced in thermally mature coals where the overall gas is wetter compared with less mature coals (Figure 3).

The overall composition of the gas in the middle Velkerri core sample is very dry (due to its high thermal maturity). Similar to that seen for the coal samples early released "free" and desorbed gas from the shale is primarily CH_4 with a DI of 0.99. As desorption progresses the later desorbed gas becomes more enriched in C_{2+} hydrocarbons. The residual gas released from the shale after crushing the sample was extremely wet with a DI in the range of 0.31-0.39.

The C isotope ratio (^{12}C /^{13}C or $\delta^{13}C$) of hydrocarbons stored in convetional and CSG reservoirs vary according to their molecular number with CH_4 being isotopically light (i.e. most depleted in ^{13}C relative to VPDB) and the longer chain hydrocarbons becoming progressively isotopically heavier; $\delta^{13}C$ for $CH_4<C_2H_6<C_3H_8<C_4H_{10}$. This trend is typically caused by the kinetic isotope fractionation occurring during hydrocarbon generation. Similarly, the isotopic composition of hydrocarbons also changes during desorption where the early released gas is isotopically light compared with later desorbed gases. For example, in the most thermally mature coal sample studied from the Bowen Basin (i.e. VR = 1.15%) $\delta^{13}C$ of CH_4 released during early stages is -38‰ whereas that for the CH_4 released at the end of the desorption experiment is -17‰ (Figure 3); this represent a C isotope fractionation of approximately 11‰. Coal samples containing wetter gas show the largest isotopic fractionation with the difference in $\delta^{13}C$ between early and late desorbed CH_4 ranging from ~11 to 21‰. The isotope fractionation effect for higher hydrocarbons, however, is considerably lower with the difference in $\delta^{13}C$ between early and late desorbed gas ranging from 2 to 6‰ for C_2H_6 and ≤ 1‰ for C_3H_8 (Figure 4 and 5). Butanes also appear to show minor fractionation, however, the trends seen in the dataset studied are not consistent possibly due to the very small molecular volumes present in samples.

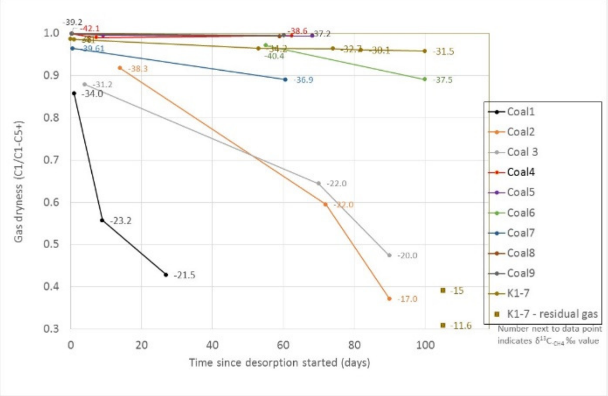
C isotopes also fractionate during release of gas from the middle Velkerri core where $\delta^{13}C$-CH_4 changes from ~-40‰ in early desorbed to ~-30‰ in late desorbed gas. CH_4 in the residual gas in the shale not released during regular desorption testing is extremely enriched in ^{13}C with $\delta^{13}C$ vaues up to -11‰. Higher hydrocarbons in the shale do not show a strong fractionation effect during desorption although C_2H_6 in the residual gas is relatively enriched in ^{13}C ($\delta^{13}C$ ~-39 to -40‰).

The molecular and isotope fractionation effects during gas release can be related to multiple factors including:

- mass of the hydrocarbon molecule,
- adsorption properties of hydrocarbon molecules,
- partial pressure of gas,
- diffusivity of gas,
- proportions of adsorbed an free gas,
- the pore size distribution in the host rock.

As the majority of gas in organic matter is stored as adsorbed molecules on its internal surfaces, the release of various hydrocarbon molecules is related to their relative adsorption and desorption capacities. In general, the adsorption capacity of hydrocarbons on organic matter increases according to carbon number with CH_4 being less adsorptive compared with C_{2+} hydrocarbons (Ruppel et al., 1972). This phenomenon is reflected in the compositional changes seen during desorption from carbonaceous rocks where stronger adsorbed heavier hydrocarbons are released later than CH_4. Subsequent to desorption, diffusivity properties of the molecules through the matrix further determine the rate of overall gas release from the rock. The rate of diffusion through the matrix is expected to be faster for smaller hydrocarbon molecules compared with the larger and heavier molecules. Hence the combination of differential adsorption capacities and diffusivity results in molecular fractionation during release of gas from unconventional reservoirs. Similarly, isotopically lighter hydrocarbon molecules appear to desorb and diffuse leading to strong isotope fractionation during gas release. The differences in adsorption capacity and diffusivity of hydrocarbon molecules with varying isotopic compositions have not been directly measured through controlled laboratory experiments. Therefore, it is not possible to categorically determine which of these factors has a stronger influence on the observed isotope fractionation effects.

Different desorption rates according to isotopic composition can cause inconsistent compound specific isotope trends for hydrocarbons released through time. For example, the compound specific isotope trends for later desorbed gas from coals appear to be reversed due to the stronger isotope fractionation effect in CH_4 relative to C_{2+} components (Figure 6). In some cases this phenomenon may also occur over geological time due to extensive gas expulsion from a thermally mature source rock. An example of this may occur in highly mature source rocks (or over-mature)with the remaining gas showing a reversed compound specific isotope trend as a result of severe de-pressuring and degassing during basin uplift.



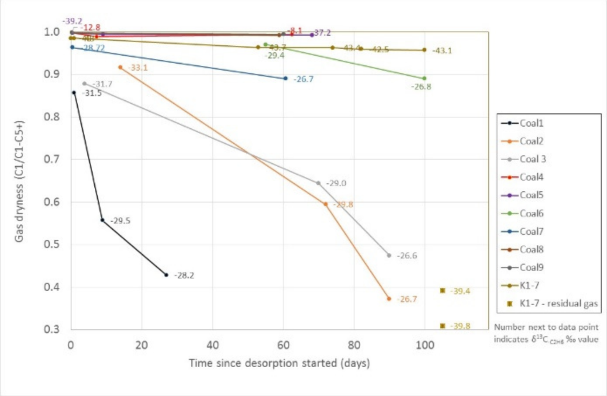


Figure 3: Variation in hydrocarbon composition and isotopic composition for methane.

Figure 4: Variation in hydrocarbon composition and isotopic composition for ethane.

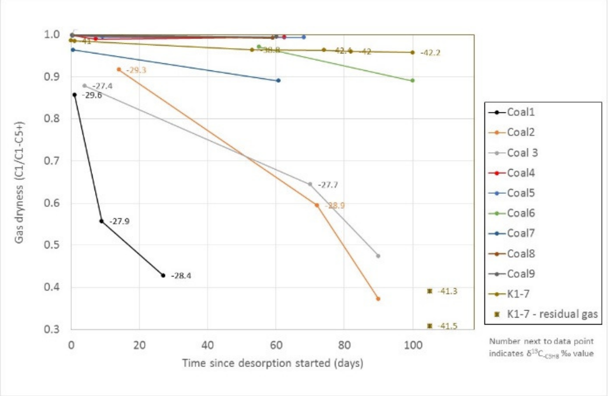


Figure 5: Variation in hydrocarbon composition and isotopic composition for propane.

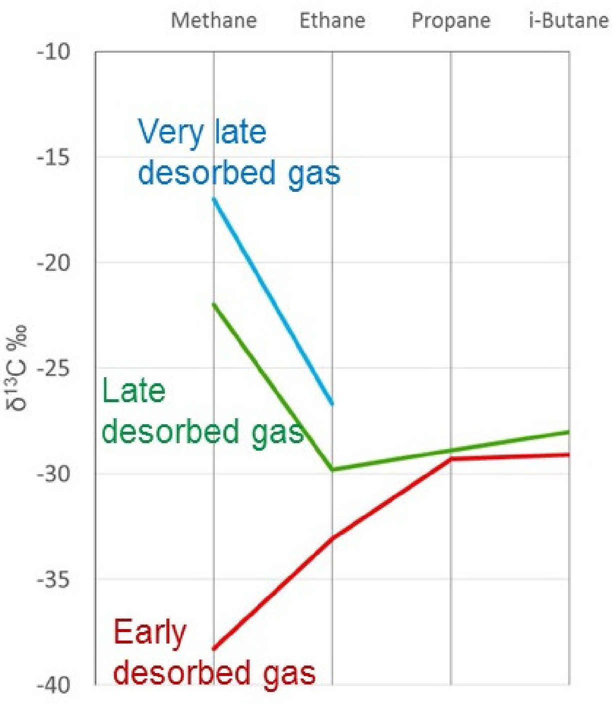


Figure 6: Compound specific isotopes trends for early and late desorbed gas from Coal2

CONCLUSIONS

Pore-size distribution, gas storage capacity and migration properties of coal and shales reservoirs are dependent on their organic and mineral matter contents. During gas release molecules fractionate according to mass depending on the carbon number and isotopic ratio (^{12}C /^{13}C or $\delta^{13}C$). Accordingly, lighter hydrocarbons including those containing greater proportions of ^{12}C desorb from the organic matter and diffuse faster through the matrix compared with their heavier counterparts. Hence early produced hydrocarbons from coal or that expelled from thermally mature source rocks will be enriched in isotopically lighter molecules. Therefore, compound specific isotope trends for migrated gas stored in a conventional sandstone reservoir may show a different trend to that from the parent source rock. In the case of a fully gas mature or overmature source rock that has been significantly uplifted (e.g. unconventional shale gas reservoirs) the compound specific isotope trend is likely to be reversed compared with that for gas in the overlying sandstone reservoir.

.

ACKNOWLEDGMENTS

Origin Energy for permission to present the data acquired from exploration and production wells. ALS, CSIRO and Weatherford for performing gas desorption, molecular composition and isotope analyses.

REFERENCES

Close, D., Baruch-Jurado, E., Altmann, C., Cote, A., Mohinudeen, F., Richards, B and Stonier, S., 2016, Unconvetional gas potential in Proterozoic source rocks: exploring the Beetaloo Sub-basin: AGES2016, Annual Geoscience Exploration Seminar, Norther Territory Geological Survey, 15-16 March 2016, 95.

Faiz, M., Murphy, A., Lidstrom, U., and Ashby, M., 2012, Geochemical and microbiological evidence for degradation of heavy hydrocarbons in Australian CBM reservoirs: 34th International Geological Congress (IGC), Queensland, Austrlaia, 5-10 August, 2012.

Faiz, M. and Hendry, P., 2006. Significance of microbial activity in Australian coal bed methane reservoirs – a review: Bulletin of Canadian Petroleum Geology 54 (3), 261-272.

Halliburton, 2014, CoreVault® Fluid and Rock Sampling System, it's all about the fluids. [online] Available at: http://www.halliburton.com/public/lp/contents/Data_Sheets/web/H/H011158.pdf [Accessed 21 July 2017]

Leaney, W.S., 1990, Parametric wavefield decomposition and applications: 60th Meeting, SEG, San Francisco, Expanded Abstracts, 1097-1100.

Loucks, R. G., Reed, R.M., Ruppel, S.C., Jarvie, D.M., 2009, Morphology, Genesis and distribution of nanometer-scale pores in siliceous mudstones of the Mississippian Barnett Shale: Journal of sedimentary Research, 79, 848-861.

Ruppel, T.C., Grein, C.T. and Bienstock, D, 1972, Adsorption of methane/ethane mixtures on dry coal at elevated pressure:. Fuel 51, 297-303.

Smith, J.W., 1999, The development of an understanding of origins of the Sydney and Bowen basin gases: Coal Bed Methane – Scientific, Environmental and Economic Evaluation. Kluwer Academic Publishers, 271-278.

Standards Association of Australia, 1999, Guide to the determination of gas content of coal – Direct desorption method, Document number AS3980-1999: Standards Association of Australia, Sydney.

Standards Association of Australia, 2016, Determination of gas content of coal and carbonaceous material – Direct desorption method, Document number AS3980-2016: Standards Australia Ltd, Sydney.

Zhang, Y., Shao, D., Yan, J., Jia, X, Li, Y, Yu, P and Zhang, T, 2016, The pore size distribution and its relationship with shale gas capacity in organic-rich mudstone of Wufeng-Longmaxi Formations, Sichuan Basin, China: Jounral of Natural Gas Geoscience 1, 213-220.