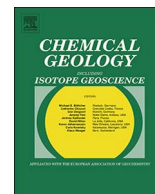




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## Fingerprinting coal-derived gases from the UK

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### ABSTRACT

The large-scale extraction of unconventional hydrocarbons in the United States has led to fears of methane contamination of shallow groundwaters. Differentiating between the deep gas released during extraction (shale gas, coal bed methane and underground coal gasification) and natural shallow-sourced methane is imperative for the monitoring and managing of environmental risks related to the extraction process. Here, for the first time, we present measurements of the major gas, and stable and noble gas isotope composition of coal bed methane (CBM) from central Scotland and coal mine methane (CMM) from central England, UK. The molecular ( $C_1 / (C_2 + C_3) = 21$  to 121) and stable isotope compositions ( $\delta^{13}C_{CH_4} = -39.5$  to  $-51.1\%$ ;  $\delta D_{CH_4} = -163$  to  $-238\%$ ) indicate a thermogenic origin for the methane. They are distinct from the majority of shallow-sourced gases in UK. Both sample suites exhibit high He concentrations (338 to 2980 ppmv) that are considerably above atmospheric and groundwater levels. Simple modelling shows that these high  $^4He$  concentrations cannot be solely derived from in situ production since coal deposition, and hence the majority is derived from the surrounding crust. The Scottish CBM contains a resolvable mantle He, Ne and Ar contribution that may originate from melts in the deep crust, demonstrating the UK coals have acted as a store for deep volatiles for 10s of millions of years. The high  $^4He$  in the coal-derived gases has the potential to be used as a novel diagnostic fingerprint to track fugitive release of deep methane from future unconventional gas extraction operations in the UK.

### 1. Introduction

The development of horizontal drilling and hydraulic fracturing techniques has permitted the extraction of oil and gas from an array of unconventional reservoirs (e.g. Tour et al., 2010). The economic impact of unconventional shale gas exploitation in the US has been significant, and it has prompted investigation of the potential for unconventional hydrocarbons around the world. Many existing (North America, Australia) and emerging (e.g. China, Argentina, Russia, Brazil) unconventional gas reservoirs are close to potable water resources (Conti et al., 2013; Day, 2009; Mauter et al., 2014; Measham and Fleming, 2014; Vörösmarty et al., 2010), and concern has been raised over the impact of unconventional hydrocarbon exploitation, often by hydraulic fracturing, on groundwater resources (e.g. Vengosh et al., 2014). While several studies have identified deep methane in groundwater near unconventional production wells (Jackson et al., 2013a; Osborn et al., 2011), in the majority of cases this is the result of leakage from the casing of new or pre-existing wells and is not due to fractures to surface caused by the hydraulic fracturing process (Darrach et al., 2014; Molofsky et al., 2011; Molofsky et al., 2013; Warner et al., 2012).

A more rigorous assessment of the environmental effects of unconventional hydrocarbon extraction requires baseline measurement of methane levels in groundwaters prior to exploration and extraction, along with the robust methods for resolving the sources of methane already present, and distinguishing them from the exploited gas (Jackson et al., 2013b; Masters et al., 2014; Moritz et al., 2015; Vidic et al., 2013). The molecular (e.g.  $C_1 / (C_2 + C_3)$ ) and stable isotopic (e.g.  $\delta^{13}C_{CH_4}$ ,  $\delta D_{CH_4}$  or  $\Delta^{13}C = \delta^{13}C_{CH_4} - \delta^{13}C_{C_2H_6}$ ) composition of hydrocarbon gases can be used to differentiate between thermogenic and biogenic sources (Jackson et al., 2013a; Kornacki and McCafrey, 2011; Osborn et al., 2011; Whiticar, 1999). However, methane oxidation can change the isotopic signature of biogenic methane to make it similar to that of thermogenic methane (e.g. Molofsky et al., 2013; Moritz et al., 2015; Sherwood Lollar and Ballentine, 2009) as bacterial activity (aerobic or anaerobic) enriches the residual  $CH_4$  in  $^{13}C$ . Further, simple mixing between biogenic and thermogenic methane can also mask the initially diagnostic isotopic composition (e.g. Whiticar, 1999).

Trace quantities of the noble gases (He, Ne, Ar, Kr and Xe) are present in natural hydrocarbons and provide a complimentary

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fingerprinting tool that are not affected by chemical or biological processes. When combined with stable isotopes they have proved to be effective tracers of gas origin, migration and gas-fluid interactions in the crust in conventional and enhanced oil recovery hydrocarbon fields, natural CO<sub>2</sub> reservoirs and coal bed fields (Ballentine and O'Nions, 1994; Ballentine and Sherwood Lollar, 2002; Gilfillan et al., 2008; Gilfillan et al., 2009; Györe et al., 2015, 2017; Holland and Gilfillan, 2013; Pinti and Marty, 1995; Zhou et al., 2005). Noble gases have been used to provide a model to describe coal derived methane and groundwater interactions quantifying the water associated with gas production and the presence of the gas desorbed from the coal (Zhou et al., 2005). Recent studies have shown that noble gas isotopes can clearly distinguish between CH<sub>4</sub> which had migrated from overlying formations through faulty well casings, or migrated diffusively through the subsurface as a result of an underground well integrity failure (Darrah et al., 2015; Darrah et al., 2014; Wen et al., 2016).

The United Kingdom has promising shale gas and coal bed methane resources, hosted mainly in Carboniferous strata (Andrews, 2013; Creedy et al., 2001; Harvey and Gray, 2013; Jardine et al., 2009; Masters et al., 2014). Although there is a history of hydraulic fracturing of conventional hydrocarbon and water wells in the onshore UK (Cobbing and Dochartaigh, 2007; Mair et al., 2012), only the Preese Hall well (National Grid Reference: SD 37532 36,627) which directly targets a shale formation, has been subjected to high volume hydraulic fracturing techniques to date. Despite abundant evidence that undertaken correctly, hydraulic fracturing can be employed safely (Mair et al., 2012; Masters et al., 2014; Younger, 2016), the extraction of unconventional gas remains controversial and it is essential to build trust with the public if the reserves are to be exploited. This can be partially achieved by identifying robust techniques for monitoring unplanned migration of any extraction related gases to the surrounding groundwaters. Here, we document the major gas, and the stable and noble gas isotope composition of (i) coal bed methane (CBM) from the Midland Valley of Scotland, and (ii) coal mine methane (CMM) from former coal mines in the east central England (Fig. 1). We use these measurements to place constraints on the gas origin, and to identify the presence of natural fingerprints which can be used in robust future monitoring regimes.

## 2. Geological setting

### 2.1. Airth CBM field, Central Scotland

The methane from Airth is extracted from coal seams that are part of the North-East Stirlingshire Coalfield in the Midland Valley of central Scotland (Fig. 1). The Midland Valley is a NE-SW trending terrane bounded to the north by the Highland Boundary Fault and to the south by the Southern Upland Fault, and is filled principally with Carboniferous and Devonian sediments. The targeted coal seams are in the Limestone Coal Formation of the Clackmannan Group, defined at the base by the Top Hosie Limestone and at the top by the base of the Index Limestone. The coals are 326.4 to 326 Ma in age (Upper Mississippian) (Waters et al., 2011) (Fig. 2).

Gas exploration was initiated in 1993 with the drilling of the Airth-1 well. Initially coal-bed methane production was 1.7 million m<sup>3</sup>/day and targeted the 14 potentially productive seams that were > 0.3 m thick. Wells Airth-2 to -4 were drilled in 1996 and Airth-5 to -7 between 2004 and 2007. Dart Energy acquired the site in 2011 and a further 3 new wells and 2 side-tracks off existing wells were drilled (Masters et al., 2014 and references therein). Well depths vary between 892 m (Airth-8) and 1059 m (Airth-1) below sea level (UK Onshore Geophysical Library [www.ukog.org.uk](http://www.ukog.org.uk)) (Table 1). The field has been pumped for gas flow rate testing during resource appraisal, but so far has not been put into commercial production. The locations of the sampled wells are provided in Table 1.

### 2.2. South Yorkshire and Nottinghamshire coal mines, Central England

The South Yorkshire and Nottinghamshire coalfields are located in the north east of the Midlands region of England (Fig. 1). The coalfields are within the East Pennine coalfield, the most productive of all the UK coal measures (Allen, 1995). In contrast to the Airth CBM extraction, the Central England gases are from methane extracted from former coal mines. The majority of the mines in the region exploit the Top Hard (Barnsley) coal seam, with various other seams contributing to mined output depending on local conditions. The majority of the mined seams are Middle – Upper Pennsylvanian (313 to 304 Ma). The coals were deposited in cycles typically grading upwards from mudstone, siltstone, sandstone and coal (Waters, 2009). In general, the coals crop out in a NNW-SSE orientated band west of Doncaster and Nottingham, and dip gently to the east under Permian sandstones where they form the significant resources of the concealed coalfields.

The Prince of Wales Colliery was constructed on the site of an existing mine, on the northern edge of Pontefract in West Yorkshire. Work on the drift tunnels was started in 1975 and production commenced in the Castleford Four Foot seam in 1980 and three other seams have since been exploited. The colliery closed in 2002 after producing 1.5 million tonnes of coal per year. The Newmarket Lane Colliery, near Stanley in West Yorkshire, opened in 1837 and closed in 1983, making it one of the oldest mines in the UK. The vent well of Newmarket Lane-1 is 273 m in depth and was finished in 2008. Bevercotes Colliery in Nottinghamshire opened in 1963 and closed in 1993. Bevercotes-1 was completed in 2002 and targets the deepest seam at 700 m below sea level. The Warsop Main Colliery opened in 1893 and closed in 1989. The Warsop-1 well was completed in 2002 and is the shallowest among those sampled at 222 m. The Crown Farm (also known as Mansfield) Colliery and the Sherwood Colliery (targeted by the Old Mill Lane-1 well) located close to Mansfield. The Crown Farm Colliery opened in 1904 and closed in 1989. The well reaches 310 m below sea level and was completed in 2006. Sherwood Colliery closed in 1992 with the associated well being drilled in 2002 to a depth of 300 m. The wells have been operated by Alkane Energy UK Ltd. since drilling. Depth data in Table 1 are from the UK Onshore Geophysical Library ([www.ukog.org.uk](http://www.ukog.org.uk)) and completion dates are from the BGS Borehole Record, (<http://www.bgs.ac.uk/data/boreholescans/home.html>). The locations of the sampled wells are provided in Table 1.

## 3. Sampling and analytical techniques

Six wells from the Airth CBM field and six CMM wells in England were sampled for this study, with duplicates taken in all cases (Table 1). The Airth gases were collected in August 2013, following production of formation water from Airth-1 for production testing from the Airth-10 well. Airth-1 was re-sampled in August 2014 after the field had been shut-in for a year. CMM samples from England were collected in July 2014. All samples were collected in Cu-tubes using the method described in Györe et al. (2015). Samples from Scotland were analysed in two batches in January–February 2015 and in May–July 2015. In addition, tubes from the Airth-1 2014 well was analysed four times between 2 and 303 days after sampling. The England gases were analysed in March 2016.

Major gas analysis was carried out at the University of Edinburgh. Gas from the Cu tube was expanded into an evacuated all-metal line and aliquots of gas were taken by a syringe via a silicone septum. Gas was injected manually into a Perkin-Elmer AutoSystem XL gas chromatograph (GC) via a 30 m long and 0.53 mm internal diameter Sigma-Aldrich Carboxen 1010 PLOT column using helium carrier gas. A thermal conductivity detector was used for nitrogen and oxygen detection, whereas all other species were detected on a flame ionisation detector. The GC was programmed for a ramp of 40 °C for 7 min to allow resolution between O<sub>2</sub> and N<sub>2</sub>, then 30 °C/min ramp up to 250 °C for heavier components. The system was calibrated with gas mixtures

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