Highlights

- Shale gas and coal-bed methane show remarkably similar opportunities for the in situ stimulation of microbial methane generation.
- The vast literature available from bioremediation studies can significantly improve our understanding of microbial processes in unconventional gas systems.
- Engineering technologies such as hydraulic fracturing may be adapted to stimulate biogenic gas production and favour positive microbial processes.
- Managing microbial communities in unconventional gas systems have implications for both recovery practices and a sustainable development of unconventional resources.

Biogenic methane in shale gas and coal bed methane: a review of current knowledge and gaps

Fabrizio Colosimo[a,*], Russell Thomas[b], Jonathan R Lloyd[c], Kevin G Taylor[c], Christopher Boothman[c], Anthony D Smith[d], Richard Lord[a] and Robert M Kalin[a]

[a]Department of Civil and Environmental Engineering, University of Strathclyde, 75 Montrose Street, Glasgow G1 1XJ, United Kingdom. [b]WSP Parsons Brinckerhoff Ltd. (WSP PB), Kings Orchard, Queens Street, Bristol BS2 OHQ, United Kingdom. [c]Williamson Research Centre for Molecular Environmental Science, School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom. [d]Peel Gas and Oil, Peel Dome, The Trafford Centre Manchester M17 8PL. [*]To whom correspondence should be addressed at: *email:* fabrizio.colosimo@strath.ac.uk. Tel: +44(0)7446898984.

Abstract

Biogenic CH_4 generation has been observed in many shallow, low temperature shale gas basins and coal seams. The depletion of conventional resources and the increasing demand of natural gas for human consumption have spurred the development of so-called unconventional gas resources such as shale gas (SG) and coal-bed methane (CBM). Such unconventional systems represent the opportunity for the stimulation of biogenic CH_4 generation. Biogenic CH_4 in shale and coal is produced by anaerobic biodegradation of organic matter (OM): methanogenic *Archaea* represent only the final step of biogenic CH_4 generation. Several communities of microorganisms are involved in the initial breakdown of complex geopolymers and the production of intermediate compounds used by methanogens. There are several key knowledge gaps on biogenic CH_4 production in unconventional gas systems, such as the exact fraction of bioavailable OM, the microbial communities involved and how they can be stimulated to enhance microbial methanogenesis. Progress on biodegradation studies, isotopic signatures, as well as DNA analyses and proteomics could

help unravel interactions within the syntrophic community involved in the methanogenic biodegradation of OM. Questions also remain regarding the environmental impact of unconventional gas production, such as water quality and the mobility of toxic metals and radionuclides. The answers to these questions might have implications for both recovery practices and a sustainable development of unconventional resources. This review summarises the current knowledge regarding biogenic CH_4 in SG and CBM: from the nature of the rocks to the producing microbial community and the indicators of biogenic CH_4, illustrating how these two environments show remarkably similar opportunities for the stimulation of biogenic CH_4 generation.

Keywords

Shale gas; Coal-bed methane; Microbial methane; Organic matter; Biodegradation.

1. Introduction

In recent decades, unconventional gas production from fractured shales and coal seams has experienced a rapid development in many parts of the world (Pearson et al., 2012). The success of SG and CBM is linked to the increasing demand of natural gas and the progressive depletion of conventional gas resources (McIntosh et al., 2008). Historically, the first extraction of SG began in Fredonia, Pennsylvania in the USA in 1821, in shallow, low-pressure fractures (Peebles, 1980; Trembath et al., 2012). Similarly, CBM was first extracted in the USA in the late 1930s, but economic production started in 1980s, when the United States Congress enacted a tax credit for "Non-conventional energy" production (US EPA 1994). Both SG and CBM industries have experienced rapid growth during the past 20 years, thanks to significant advances in extraction technologies (Jenkins and Boyer II, 2008). The combination of horizontal drilling and hydraulic fracturing has allowed access to large volumes of SG that were previously uneconomical to extract (Yang et al., 2014). SG wells typically produce significantly more gas per well, but cost substantially more to drill than CBM wells (Ritter et al., 2015). In spite of the large use of hydraulic fracturing, very little is known about the microbiological implications of this process. Hydraulic fracturing is a well-established technology to increase the permeability of a formation and, together with other stimulation strategies, could be applied *in situ* to achieve or maintain optimised conditions for microbial activity. Stimulation strategies could be used to enhance the productive lifespans of depleted microbial SG and CBM wells, extending and/or regenerating biogenic CH_4 production. *Ex situ* treatments could involve the use of wastewater and coal/shale waste materials to produce CH_4 and reduce the environmental impact of SG and CBM production. This review is not intended to be an exhaustive review of biogenic CH_4 generation, it rather describes the current knowledge of biogenic CH_4 generation in shales and coals, illustrating

the analogies and differences of the two environments, and focusing on biodegradation process of complex OM. We also demonstrate how the vast literature available from bioremediation studies can significantly improve our understanding of microbial processes in unconventional gas systems. Lastly, we present the current knowledge about enhanced biogenic CH_4 generation in SG and CBM basins, pointing out how current engineering technologies may be adapted to stimulate biogenic CH_4 production and favour positive microbial processes.

2. Biogenic CH_4 in unconventional gas basins

2.1. Generation and accumulation of CH_4

The advances of biogeochemical studies on organic-rich sedimentary rocks and gas isotopic analysis, have allowed a better understanding of the origin of CH_4 in the subsurface. These studies highlighted the microbial or mixed origin of CH_4 in both coal beds (Faiz and Hendry, 2006; Scott et al., 1994; Zhou et al., 2005; Kinnon et al., 2010; Hamilton et al., 2014 and 2015; Baublys et al., 2015) and shales (A. M. Martini et al., 1996; McIntosh et al., 2008; Schlegel et al., 2013, 2011a) in many parts of the world (Fig. 1). Early estimations of microbial gas suggest that approximately 20% of total natural gas production in the world is biogenic (Rice and Claypool, 1981), and an additional 10% of the gas resources may also be of microbial origin (Grunau, 1983). In general, CH_4 in shale and coal beds, is generated from OM, sourced from the remains of organisms deposited as fine particles in sedimentary rocks, along with the mineral grains that constitute such rocks. Microbial methanogenesis in unconventional gas systems is a multi-step, syntrophic process that involves a consortium of bacteria and methanogenic Archaea. Bacteria break down complex OM into intermediate compounds (e.g. long chain fatty acids, alkanes, and low molecular weight aromatics; Orem et al., 2010), which are then biodegraded into substrates that are converted by methanogens (e.g. acetate, CO_2 and H_2, methanol, formate; Strapoc et al., 2011) into CH_4. Typically, all other potential electron acceptors (e.g. ferric iron and sulfate) must be exhausted before microbial methanogenesis will proceed (Claypool and Kaplan, 1974; Kuivila et al., 1988; Mah et al., 1977; Martens and Berner, 1974; Reeburgh and Heggie, 1977).

OM is first converted to CH_4 by bacterial processes (*primary biogenic* CH_4), and later by high temperatures and pressures as the sedimentation proceeds (*thermogenic* CH_4) (Jones et al., 2008). Further episodes of microbial methanogenesis are often observed after meteoric recharge of water or other geological events (*secondary biogenic* CH_4) (Milkov, 2011). After generation, the gas rises upward through the pore system, until it encounters a trap such as an impermeable rock, forming a conventional reservoir. However, some of the gas generated during thermogenic and biogenic process, remains trapped in the fine grained source rock (e.g. shales and coals), forming unconventional basins (Pearson et al., 2012).

Fig. 1. World map showing locations where biogenic CH_4 from CBM (black circles) and SG (red circles) has been observed. For CBM basin names and references, see Strąpoć et al., (2011) and Ritter et al., (2015). For SG: (1) Antrim shale (Martini et al., 1996, 1998, 2003). (2) New Albany shale (Martini et al., 2008; McIntosh et al., 2010; Schlegel et al., 2011a, 2011b; Strąpoć et al., 2010). (3) Cretaceous Mancos shale (L. R. Krumholz et al., 1997). (4) Eastern Paris Basin (Meslé et al., 2015). (5) Alum shale (Krüger et al., 2014). (6) Po basin (Mattavelli et al., 1992).

2.2. Gas storage

The gas generated through thermogenic or biogenic process is stored in three modes (Curtis et al., 2002): (*i*) *free gas* in intergranular porosity and natural fractures, (*ii*) *adsorbed gas* onto kerogen and inorganic minerals and (*iii*) *dissolved gas* in water, kerogen and bitumen. Characterisation of porosity and pore size distribution is particularly important when considering biogenic CH_4 production, since a major constraint to microbial colonisation of organic-rich rocks would be the limited space available, as well as the contact surface area of microorganisms with OM. There are several challenges in establishing a relationship between the presence and activity of microorganisms and physical properties of the host rocks, such as the pore size, pore size distribution and permeability. Fig. 2 shows the three modes of gas storage and the main transport mechanisms from the source rock to production well. Pores in solid material can be divided in: (*i*) macropores (>50 nm), (*ii*) mesopores (2-50 nm), and (*iii*) micropores (or nanopores) (<2 nm) (Rouquerolt et al., 1994). This classification is particularly important for unconventional basins since a significant portion of gas is sorbed onto the surfaces of mesopores and micropores (Ross and Bustin, 2009). It has been hypothesised that the primary role of macro- and mesopores is to act as a transport conduits (Moore, 2012). Micropores play a significant role in CH_4 adsorption, typically contributing the most to the total surface area, as demonstrated for both coal (Beliveau, 1993; Mastalerz et al., 2008) and shale (Chalmers and Bustin, 2007; Ross and Bustin, 2009). Gas storage has long been studied for CBM, identifying a number of factors that influence gas sorption process, including maceral type (Lamberson and Bustin, 1993), ash content (Laxminarayana and Crosdale, 1999), rank (Levine, 1996; Bustin and Clarkson, 1998), moisture (Levy et al., 1997) and temperature (Bustin and Clarkson, 1998). In unconventional gas systems, most of the CH_4 is adsorbed (Milewska-duda et al., 2000), therefore pore surface area rather than pore

volume is the most crucial factor for gas storage (Moore, 2012). The pore surface area is directly correlated to the pore size distribution. As pore size decreases, the ratio of free gas to sorbed gas storage capacity decreases (Bustin et al., 2008). In general, for pores less than 0.01 μm, the sorbed gas component exceeds the free gas storage (Beliveau, 1993). Micropores in shale formations contribute the most to the total surface area, as observed by porosimetry in the Haynesville, Marcellus and Doig shales (Chalmers et al., 2012). Macropores and mesopores in these formations are associated with either kerogen and clay aggregates or kerogen and carbonate aggregates (Chalmers et al., 2012). The association between mesopores and micropores with kerogen has been identified in both CBM and SG studies (Chalmers and Bustin, 2008, 2006; Clarkson and Bustin, 1996; Larsen et al., 1995; Marsh et al., 1985; Unsworth et al., 1989). Interconnection between pores of different size and fractures is an important control on the matrix permeability, which influence CH_4 transport (Chalmers et al., 2012). In tight source rock, CH_4 transport occurs by different mechanisms depending on the flow and porous formation conditions (Civan et al., 2011; Roy et al., 2003). Flow in the fractures is controlled by advection and is modelled using Darcy's law. Within the micropores, transport mechanisms include diffusion (molecular flow) and advection (Darcy flow) (Schlömer and Krooss, 1997). Simple Darcy's law based analyses and interpretation are insufficient to characterise permeability and diffusivity of gas in shale (Civan et al., 2011). In fact, at the nanometer scale, the Darcy's law is no longer applicable: flow in the nanopore matrix is controlled by diffusion, molecule-molecule and molecule-pore wall interactions (Bustin et al., 2008; Javadpour, 2009; Schettler et al., 1989). In organic-rich rocks, microporosity is often correlated with total organic carbon (TOC) (Chalmers and Bustin, 2007; Passey et al., 2010), the organic fraction of shale and coal is an important control on CH_4 storage, as demonstrated by positive correlations between TOC and sorbed gas (Gasparik et al. 2013; Ross and Bustin, 2009, 2007; Chalmers and Bustin, 2008). During thermal

maturation, the decomposition of OM leads to the production of hydrocarbons and allows the formation of intraparticle organic pores, as observed for coal (Bustin and Clarkson, 1998; Laxminarayana and Crosdale, 1999; Levy et al., 1997) and shale (Chalmers et al., 2012; Chalmers and Bustin, 2007; Jarvie et al., 2007). In general, at higher thermal maturity, the diagenesis transforms OM, creating more microporosity and decreasing the heterogeneity of the pore surface (Levy et al., 1997). This process was often observed in high rank coal, where usually there is a high sorbed gas capacity (Bustin and Clarkson, 1998). The correlation between nanopore abundance in grains of OM and Vitrinite Reflectance (VRo) is consistent with observation made by Hover et al., (1996). They found no visible intercrystalline or intraparticle matrix porosity for low thermal-maturity rocks of the Antrim and New Albany shales. Such conclusions were also supported in a study of Cretaceous shales (Chalmers and Bustin, 2007) where the highest CH_4 sorption was observed in samples with highest concentrations of inertodetrinite and vitrinite. For thermally immature Jurassic shales, no relationship between TOC and micropore volume or surface area was found (Ross and Bustin, 2009), indicating that surface area alone is not the only factor controlling CH_4 capacity. A component of solute CH_4 within the internal structure of the matrix bituminite was proposed as a dominant mechanism of gas storage in Jurassic shales (Ross and Bustin, 2009). In CBM, gas content increases with depth and coal rank (Scott, 2002). The relationship between macropores and carbon content is inversely proportional: macropores decrease and micropores increase with rank, with an unexpected increasing number of macropores at low volatile bituminous rank (Levine, 1996). In general, OM is a primary control on gas adsorption: the higher the TOC content, the greater the gas-sorption rates in organic-rich sedimentary rocks (Zhang et al., 2012). Higher gas content values are typically associated with higher rank coals in many reservoirs: for example, gas content in the Piceance Basin show an overall increase in gas content with increasing rank (Scott, 2002). These results were

confirmed for low and high rank coal and for organic-rich shales of different origin (Chalmers and Bustin, 2007). With increasing coalification, thermal cracking of n-alkanes, waxes, and other hydrocarbons not only generates thermogenic methane but increases methane adsorptive capacity by unplugging pores, resulting in higher sorption capacity and gas content values since methane accessibility to the micropore network is improved (Scott, 2002). Controversially, in the San Juan Basin, lower rank coals have higher gas contents than higher rank coals (Scott, 2002). In this hydrogeological settings, weathering process introduced bacteria into the coal beds that produced secondary biogenic gases by metabolizing wet gases, n-alkanes, and other hydrocarbons generated during coalification (Scott, 2002). The generation of secondary biogenic gases increases gas contents beyond that expected from coal rank and if generated in sufficient quantities can actually resaturate the coal to the sorption isotherm (Scott et al., 1994). Overall, despite the similarities between shale and coal, the direct comparison of sorption characteristics of the two rocks is complicated by factors such as type and amount of OM, the mineral composition, pore volume and pore size distribution (Ross and Bustin, 2009). The controls on resource volume and productivity in SG reservoirs are similar to those in CBM, although SG reservoirs typically have lower permeability (with values in the nano- to microdarcy range), are thicker (30 to 300 ft), have lower sorbed-gas content (<10 m^3/tonne), and contain a larger volume of free gas in the pore space (Jenkins and Boyer II, 2008). Of note is that although most of the pores in SG and CBM basins seem to be too small to host microbial life, evidences of microbial activity come from enrichment and isotope experiments (Martini et al., 1996 and 1998; Krumholz et al., 2002; Formolo et al., 2008; Kinnon et al., 2010; Hamilton et al., 2014 and 2015; Baublys et al., 2015).

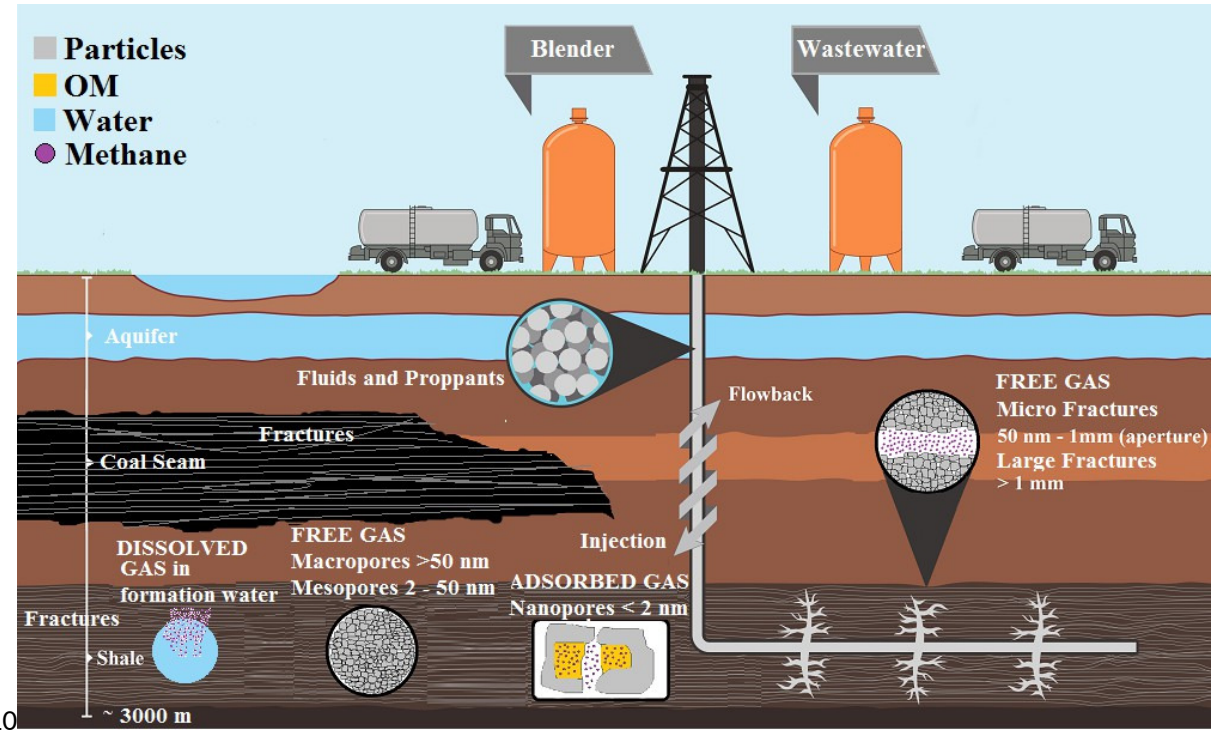

Fig. 2. Storage and transport of gas in a SG/CBM basin from CH_4 trapped in nanopores, mesopores, macropores, microfractures and large fractures to the production well.

3. Microbial ecology of SG and CBM

The first evidence of active, microbial populations in deep sediments was reported about 30 years ago, when microbial activity was observed in sediment depths of about 150 m in the framework of the Deep Sea Drilling Program (DSDP) (Oremland and Polcin, 1982; Tarafa et al., 1987; Whelan et al., 1986). In the past decades, the existence of prokaryotes in deep continental sedimentary rocks was proven (Pedersen, 2000) at up to 2800m. It has been suggested that the biomass into the deep biosphere constitutes one-tenth (Parkes et al., 2000), or even one-third (Whitman et al., 1998) of the total global, living biomass. The capabilities of the subsurface microbial communities to convert shale and coal OM to CH_4 was proved in laboratory (Fallgren et al., 2013; Jones et al., 2010, 2008; Warwick et al., 2008) and field studies (see Luca Technologies Inc. and Ciris Energy websites). The pathways of biodegradation of OM are microbially and biochemically complex (Jones et al., 2010), are site-specific, and could involve several communities of hydrocarbon degraders, fermenters and methanogenic Archaea. DNA-based assessment of the microbial community structure in unconventional gas basins have shown that bacterial diversity is higher than archaeal diversity (Barnhart et al., 2013; Penner et al., 2010; Green et al., 2008). The chemical complexity of OM requires the syntrophic cooperation of these microorganisms. Syntrophic metabolism accounts for much of the carbon flux in methanogenic environments (Schink and Stams, 2006). Our understanding of the *intermediary ecosystem metabolisms* (Drake et al., 2009) is limited. Bacteria related to Proteobacteria (mostly Beta, Delta and Gammaproteobacteria), Actinobacteria, Bacteroidetes and Firmicutes seem to be widespread in CBM (Green et al., 2008; Jones et al., 2008 and2010; Li et al., 2008; Strapoć et al., 2008; Robbins et al., 2016; Warwick et al., 2008) and SG (Meslé et al., 2015, and 2013; Struchtemeyer and Elshahed, 2012). These taxonomic groups are known for their versatile

metabolic activity and hydrocarbon degrading capabilities. The archaeal diversity in shale and coal is usually dominated by methanogens from the orders Methanosarcinales, Methanomicrobiales and Methanobacteriales (An et al., 2013; Meslé et al., 2013; Fichter et al., 2012; Kirk et al., 2012).

3.2. Actinobacteria

Actinobacteria are common in soil and sediments environments, and might play a central role in the decomposition of OM. Within the Actinobacteria, the Actinomycetales and the Rubrobacterales (Prince et al., 2010) possess known hydrocarbon-degrading capabilities. Strains of *Gordonia*, *Mycobacterium*, and *Rhodococcus* are able to remove sulfur from dibenzothiophene, yielding hydroxybiphenyl (Mohebali and Ball, 2008). Actinobacteria are typically aerobic hydrocarbon-degraders, but their role in anaerobic OM degradation remains unknown (Meslé et al., 2013). Metagenomic studies have also identified high proportions of genes for enzymes involved in aerobic hydrocarbon metabolism in CBM produced water samples (An et al., 2013), suggesting that the sequential degradation of complex OM causes the partial dominance of a group of microorganism in a given interval. Other studies, for example, reported that in anoxic environment the operation of different redox conditions is not mutually exclusive (Lovley et al., 1991) or cannot be explained satisfactorily by a simple microbial competition (Conrad et al., 1987).

3.3. Bacteroidetes

Bacteroidetes are commonly found in sediments, and their metabolism is chemoheteroorganotrophs. Many of such organisms can degrade macromolecules such as protein, chitin, pectin, agar, starch, or cellulose. Many others are thought to be involved in oil biodegradation (Stra et al., 2008). Species within *Cytophaga* are mesophilic anaerobes able to

ferment polysaccharides into acetate, propionate, succinate, H_2 and CO_2 (Haack and Breznak, 1993). The genus *Petrimonas* is mesophilic anaerobic fermenter, use carbohydrates and volatile fatty acids (VFAs) releasing acetate, H_2 and CO_2 (Grabowski et al., 2005). Within the *Prolixibacter* there are acid fermenters that produce propionate, succinate and acetate (Holmes et al., 2007). Bacteroidetes also feature in coal (Li et al., 2008; Shimizu et al., 2007; Strapoć et al., 2008) and shale (Wuchter et al., 2013) microbial assemblages, although belonging to undescribed orders and families.

3.4. Firmicutes

Within the phylum Firmicutes, Clostridia of the family Clostridiaceae include pH-neutral solvent producers, mixed acid and alcohol producers, and homoacetogenic fermenters (Wiegel et al., 2006). Species like *Clostridium* have been isolated from coal sources. For example *Clostridium* BC1 (Francis and Dodge, 1988), isolated from coal-cleaning residues, presented the ability to reduce heavy metals and fix nitrogen; *Clostridium scatologenes* is an acetogenic bacteria found in a coal mine (Küsel et al., 2000). In general, *Clostridiaceae* are widespread spore-forming, anaerobic bacteria that catalyse a wide range of metabolic reactions. *Clostridia* are known to depolymerize starch, chitin, xylan, and cellulose and are known to occur in sediments (Wiegel et al., 2006). Similarly, the *Thermoanaerobacterales* include thermophilic, anaerobic, fermentative bacteria that utilize a variety of carbon substrates and may have an important role in hydrocarbon-bearing formations (Wiegel et al., 2006). The role of *Firmicutes* in coal activation has been observed before (Jones et al., 2008; Shimizu et al., 2007; Strapoć et al., 2008; Wawrik et al., 2012). *Sporomusa*, for example, can demethylate aromatic compounds; *Acidoaminococcus sp*. can ferment simple amino acids as a sole energy source. These microorganisms may potentially participate in the recycling of microbial biomass in unconventional gas systems. Although members of the *Firmicutes* often

represent a minor component of the community structure in CBM basins (Ritter et al., 2015), they play an important role in laboratory experiments (Barnhart et al., 2013; Green et al., 2008; Jones et al., 2010; Li et al., 2008; Meslé et al., 2013; Penner et al., 2010). In microcosm experiments the addition of methanol stimulated Firmicutes growth compared with experiments with no carbonaceous nutrients (Wuchter et al., 2013), suggesting a role of this family in the syntrophic metabolism.

3.1. Proteobacteria

The phylum Proteobacteria constitutes at present the largest and phenotypically most diverse phylogenetic lineage (Kersters et al., 2006). Syntrophic Beta, Delta and Gammaproteobacteria are commonly found in CBM (Guo et al., 2012a; Meslé et al., 2013; Penner et al., 2010; Robbins et al., 2016), but also in SG flowback water (Mohan et al., 2013). Betaproteobacteria consist of several groups of aerobic or facultative bacteria that are highly versatile in their degradation capacities and often containing chemolithotrophic genera. Deltaproteobacteria include a branch of strictly anaerobic genera, which contains most of the known sulfate^{-}-reducing bacteria (SRB) (*Desulfovibrio*, *Desulfobacter*, *Desulfococcus*, *Desulfonema*, etc) and sulfur-reducing bacteria (e.g. *Desulfuromonas* spp.). Deltaproteobacteria includes SRB which are able to degrade naphthalene or other aromatic hydrocarbons (Musat and Widdel, 2008). Propane and butane degraders within the SRB were also detected in marine hydrocarbon cold seeps (Jaekel et al., 2013). *Geobacter* species are known to syntrophically degrade aromatics (Lovley and Lonergan, 1990; Rooney-varga et al., 1999) and long-chain fatty acids (Coates et al., 1995) coupled to reduction of Fe(III) as a terminal electron acceptor. *Geobacter metallireducens*, for example, is genetically similar to *Syntrophus*, which can degrade a wide range of organics with a methanogenic partner

(McInerney et al., 2007). In the Bowen basin pumped coal mine waters from the subsurface were dominated by bacteria belonging to the family Rhodocyclaceae (Raudsepp et al., 2016). Gammaproteobacteria is a very large heterogeneous class; some denitrifying toluene-degrading strains belong to the Gammaproteobacteria and are able to degrade hydrocarbons with nitrate as electron acceptor (Alain et al., 2012). Although the majority of Gammaproteobacteria are chemoorganotrophs, this group also includes several chemolithotrophs that derive their energy via hydrogen-, sulfur- or iron- oxidation (Gao et al., 2009; Kersters et al., 2006).

3.5. Archaea

The archaeal diversity in SG and CBM is mostly restricted to methanogens from three orders: Methanosarcinales, Methanomicrobiales and Methanobacteriales (Green et al., 2008; Penner et al., 2010; Strapoć et al., 2011b). Within Methanosarcinales there are metabolically diverse methanogens capable of utilizing H_2-CO_2, acetate, and methyl compounds as substrates for methanogenesis (Whitman et al., 2006). In the San Juan Basin, sequence libraries analysis highlighted the presence of two families: Methanosaeta (obligate acetate utilizers) and Methanosarcina (metabolically versatile) (Wawrik et al., 2012). Methanosarcinales accounted for the majority of the methanogens in coal samples from an abandoned mine in Germany (Beckmann et al., 2011) and also predominate in a consortium enriched from a CBM well from the Powder River Basin (Green et al., 2008). Cultivated strains of these taxa can utilize methyl compounds, including methanol and methylamines, where *Methanolobus* is not known to utilize acetate or H_2-CO_2. All species within the order Methanomicrobiales are known to utilize H_2-CO_2 to generate CH_4, while none are capable of utilizing acetate (Garcia et al., 2006). The presence of *Methanosarcina* in numerous worldwide CBM may suggest acetoclastic methanogenesis but also intermittent oxygen intrusion in the formation (Ritter et

al., 2015), since *Methanosarcina* can survive to short oxygen exposure when in mixed cultures. In the Antrim Shale, the main methanogenic pathway is hydrogenotrophic, as discovered by Martini et al., (1996) and later confirmed by Waldron et al., (2007). In the same study, Martini et al., (1996) found that gases from a deeper producing well of the Antrim Shale, are thermogenic, suggesting that microbial gas could be limited to shallow formations.

4. Methanogenic pathways

The range of substrates that methanogens can utilise is limited (Table 1). Biogenic CH_4 is primarily produced via CO_2-reduction (Eq. 1) and acetate fermentation (Eq. 2). In the first pathway H_2 is used as the electron donor and CO_2 as the electron acceptor (Weimer and Zeikus, 1978); in the second acetate and hydrogen are used to produce CH_4 and carbon dioxide (Conrad et al., 1989).

(1) $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

(2) $CH_3COOH \rightarrow CH_4 + CO_2$

The first and second pathways are called respectively hydrogenotrophic and acetoclastic methanogenesis. Methanogens can also use other substrates, such as methanol (Eq. 3) (Deppenmeier et al., 1999) and formate (Eq. 4) (Whiticar, 1999).

(3) $4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$

(4) $4HCOOH \rightarrow 3CO_2 + CH_4 + 2H_2O$

The possible relevance for CH_4 production of other substrates such as methylamines, dimethyl sulfide, ethanol, and isopropanol is not well documented; however, methylotrophic methanogens have been detected in coal, sandstone, produced water samples (Guo et al., 2012b) and shales (Waldron et al., 2007). These substrates might be the important compounds for the enhancement of biogenic CH_4 generation in sedimentary rocks. In particular, methylamines and dimethyl sulfide are considered non-competitive substrates: when sufficient concentration of methylamines and dimethyl sulfide are present, methanogenesis and sulfate reduction are not mutually exclusive (Mitterer, 2010). For the conversion of more complicated organic substrates to CH_4, other microorganisms such as acetogenic and fermentative bacteria are also present.

Table 1. Substrates of major taxonomic groups of methanogens

Order	Family	Substrates
Methanobacteriales	Methanobacteriaceae	H_2-CO_2, formate, methanol
	Methanothermaceae	H_2-CO_2
Methanococcales	Methanococcaceae	H_2-CO_2, formate
	Methanocaldococcaceae	H_2-CO_2
Methanomicrobiales	Methanomicrobiaceae	H_2-CO_2, formate
	Methanospirillaceae	H_2-CO_2, formate
	Methanocorpuscolaceae	H_2-CO_2, formate
Methanosarcinales	Methanosarcinaceae	H_2-CO_2, methylamine,
	Methanosaetaceae	acetate
Methanopyrales	Methanopyraceae	H_2-CO_2

4.1. Isogeochemical indicators of biogenic CH_4 *in SG and CBM*

Several studies on methanogenic environments in sedimentary basins world-wide have developed a set of geochemical and isotopic indicators for biogenic CH_4 in organic-rich rocks (Whiticar, 1999; Straapoć et al., 2007; McIntosh et al., 2008; Osborn et al., 2010; Golding et al., 2013). Dual plot of carbon ($^{13}C/^{12}C$) and hydrogen (D/H) isotope ratios of CH_4 are applied

for distinguishing microbial from thermogenic CH_4 in the environment (Fig. 3) (Strapoć et al., 2011; Whiticar, 1990), as well as for apportioning pathways of biogenic CH_4 production (Burke et al., 1988). The ratios, expressed in δ notation, are in units per mille (‰), relative to the isotopic composition of the internationally agreed standards VPDB (Vienna Pee Dee Belemnite) and VSMOW (Vienna Standard Mean Ocean Water) respectively for carbon and hydrogen isotopes. Biogenic CH_4 has a wide range of $\delta^{13}C$ (from -110 to -50‰) and δD (from -400 to -150‰) (Whiticar and Faber, 1986). The $\delta^{13}C$ value of CH_4 is commonly coupled with other isotopic indicator in order to distinguish between microbial and thermogenic CH_4, since $\delta^{13}C$ values of biogenic CH_4 are sometimes similar to those of thermogenic CH_4 (Coleman et al., 1988; Jenden et al., 1988; Schoell, 1980; Whiticar and Faber, 1986). The hydrogen isotope signature of CH_4 distinguishes between gas origins and can identify secondary processes such as migration or mixing (Martini et al., 1998). The hydrogen isotope signature of H_2O and CH_4 also provides a powerful analytical tool to distinguish methanogenic pathways independently of the carbon isotope signature (Schoell, 1980; Whiticar and Faber, 1986). Despite the significance of dual carbon and hydrogen isotope signatures, different origins of CH_4 often yield overlapping characteristic isotope signals (Pohlman et al., 2009; Whiticar, 1999, 1990). The empirical-based interpretations of multidimensional isotope signatures should be used with caution and coupled with other available microbiological and geochemical data (Strapoć et al., 2011). For example, carbon isotopic differences between CH_4 and CO_2 ($\delta^{13}C_{CO2-CH4}$) can be helpful to understand gas origin (Strąpoć et al., 2011b): thermogenic process are characterized by low $\delta^{13}C_{CO2-CH4}$ determined by high temperatures; conversely, low-temperature microbial enzymatic process determine a ^{13}C enrichment in residual CO_2 (Conrad and Klose, 2005). In mixtures of thermogenic and biogenic gases, $\delta^{13}C_{CO2-CH4}$ can be more suitable than the absolute value of $\delta^{13}C$ for discriminating gas origin (Smith and Pallasser, 1996; Strapoć et al., 2007). Three diagnostic geochemical variables were identified by Martini et al., (2008): (*i*)

alkalinity and $\delta^{13}C$ of dissolved inorganic carbon (DIC) in the coproduced water, (*ii*) $\delta^{2}H$ of CH_4 and coproduced water and (*iii*) $\delta^{13}C$ of CO_2. Other common indicators, such as the $\delta^{13}C$ of CH_4 and the ratio of C1/[C2 + C3], have proven to be unreliable in unconventional basins where a host of secondary effects occurs and the biogenic CH_4 generated commonly has high $\delta^{13}C$ values (approximately -48‰) which overlap with early thermogenic CH_4 values (Martini et al., 2003; Whiticar, 1999). Isotopic and geochemical indicators of biogenic CH_4 production have been proved to be more effective when accompanied by molecular/microbial methods (Raudsepp et al., 2015). For example, isotopic studies indicated that in the Wilcox Group CMB, CO_2 reduction was the dominant pathways of CH_4 production (McIntosh et al., 2010; Warwick et al., 2008), but microbiological data pointed out that methylotrophic methanogens (Doerfert et al., 2009) or acetoclastic methanogens (Jones et al., 2010) were likely to be the main pathways of CH_4 generation. In the Powder River Basin, isotopic data of CH_4 indicated that hydrogenotrophic methanogenesis was the dominant pathway (Flores et al., 2008; Rice et al., 2008), while microbial enrichments from the same area of the basin have shown a predominance of acetoclastic methanogens (Green et al., 2008). The different conclusions of these studies indicate that the microbial communities enriched in laboratory may not be representative of the dominant microbial populations *in situ*. The relationship between carbon isotope signature of CH_4 and CO_2 ($\delta^{13}C_{CO2\text{-}CH4}$) could be a better indicator of the extent of methanogenesis than the methanogenic pathway (Brown, 2011; Hamilton et al., 2015, 2014; Strapoc et al., 2007). The typical $\delta^{13}C_{CO2\text{-}CH4}$ range for microbial CO_2-reduction to methane is of 60–80% (Smith and Pallasser, 1996). This carbon isotopic difference arises from preferential microbial utilization of $^{12}CO_2$. As a result, residual CO_2 becomes ^{13}C-enriched (average $\delta^{13}C_{CO2}$ of about 4.3%) and thus contrasts sharply against CO_2 in thermogenic gases with $\delta^{13}C$ values of around 20% (Smith and Pallasser, 1996).

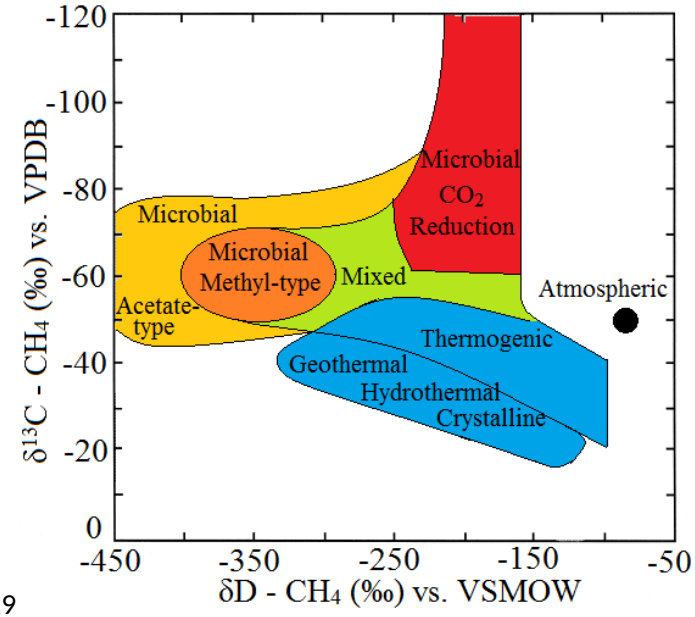

Fig. 3. Dual plot of $\delta^{13}C$ and δD of CH_4 for the classification of microbial and thermogenic CH_4. Adapted from Whiticar (1986).

5. Microbial processes in unconventional gas basins

The pattern of anaerobic mineralisation of OM involves the activation of complex macromolecular compounds, such as aliphatics, aromatics and heteroatoms by primary fermenting bacteria. Then secondary fermenters degrade less complex compounds to a variety of fatty acids, CO_2 and H_2. Acetogenic bacteria degrade (higher) fatty acids to acetate, formate, CO_2 and H_2, that can be used by methanogens. Acetate can also be degraded into H_2 and CO_2 via syntrophic acetate oxidation, as observed in the Yabase oil field in Japan (Mayumi et al., 2011). These processes take place simultaneously, but because of the different growth rates and activities of the microorganisms involved, the processes are partially uncoupled, resulting in the accumulation of organic acids (Stams et al., 2012). Methanogenesis is in fact a dynamic process and strongly influence the metabolism of fermentative and acetogenic bacteria by means of interspecies H_2 transfer (Schink and Stams, 2006; Stams and Plugge, 2009). Hydrogen syntrophy is hypothesised to be also responsible

for anaerobic oxidation of CH_4 (Reeburgh and Heggie, 1977). In organic-rich and anaerobic sediments, SRB play a role in the anaerobic oxidation of CH_4 (Eq. 5) (Zehnder and Brock, 1979) through a process called *reverse methanogenesis.*

(5) $$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

Anaerobic oxidation of CH_4 coupled to sulfate reduction is assumed to be a syntrophic process, where H_2 syntrophy is the basis of the methanogen/SRB consortium (Valentine and Reeburgh, 2000). H_2 concentration is indicative of the dominant terminal electron-accepting process (Lovley and Phillips, 1987; Lovley and Goodwin, 1988; Hoehler et al., 1998). The maintenance of low H_2 allows the syntrophic oxidation of organic material through interspecies H_2 transfer (Schink, 1997; Wolin, 1982). Under sufficiently low H_2, methanogens reverse their metabolism and mediate the reversal of methanogenesis, using water as the terminal electron acceptor. The H_2 is removed and maintained at low concentrations by SRB in syntrophic association with methanogens (Hoehler and Alperin, 1996). SRB are more efficient at using H_2 as an electron donor; thus, they can create conditions that thermodynamically favour the oxidation of CH_4.

Being rich in organic carbon, shale and coal could be considered a suitable substrate for microbial activity, although kerogen is a complex and biologically recalcitrant material, composed of a mix of aliphatics (Orem et al., 2010), aromatic hydrocarbons (Orem et al., 2010, 2007; Ulrich and Bower, 2008) and heteroatoms (Orem et al., 2007). Microorganisms interact with OM in different ways, including biological depyritization, solubilisation by biologically produced alkaline materials and by biological chelators (Polman et al., 1994). The biodegrading capabilities of anaerobic bacteria were discovered in relatively recent time, as compared with aerobic-degraders (Widdel and Grundmann, 2010). The electron acceptors

most frequently studied and used by anaerobic microorganism during biodegradation are nitrate and sulfate, although anaerobic degradation of hydrocarbons has been observed with Fe(III), Mn(IV) reduction (Lovley, 1991), and under methanogenic conditions via syntrophic interspecies electron transfer (Mbadinga et al., 2011).

However, the OM buried in sediments is a complex mixture of geopolymers and the types of organic compounds that can be oxidized to CO_2 and CH_4 are related to the different terminal electron acceptors (Fig.4).

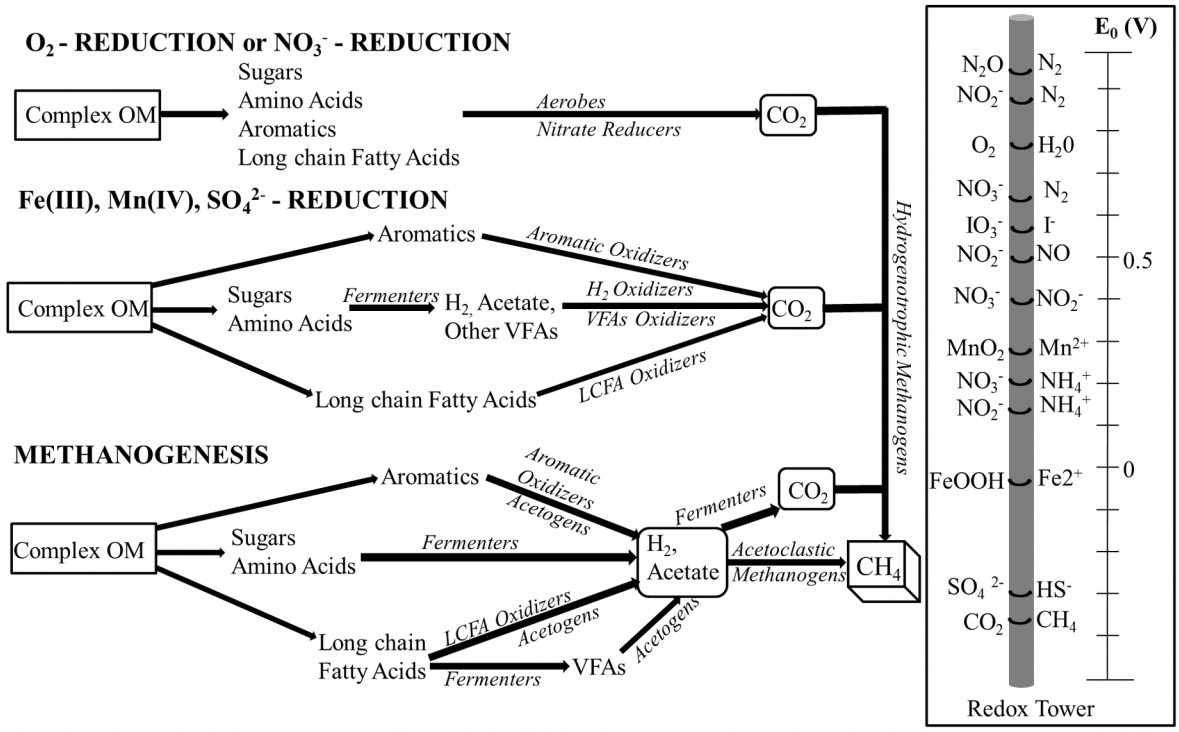

Fig. 4. Schematic of putative microbial processes in subsurface environments. The figure shows the main reactions and groups of microorganisms involved in CH_4 production, highlighting the formation of methanogenic intermediate of biodegradation. Modified from (Lovley and Chapelle, 1995). The insert on the right is the redox tower, showing the reduction potential (E_0) of the microbial processes.

Few researchers have aimed to detect the degradation pathways of OM in CBM (Formolo et al., 2008; Jones et al., 2010, 2008Warwick et al., 2008). Yet, the biodegradation pathways and the intricate microbial relationships required to convert complex OM to CH_4 are not well

understood, as acknowledged by Gieg et al., (2010); Jones et al., (2010, 2008); McInerney et al., (2009); Orem et al., (2010); Ritter et al., (2015); Strapoć et al., (2008). A number of studies for bioremediation have investigated the mechanisms by which anaerobic microorganisms activate and degrade complex hydrocarbon compounds. The anaerobic degradation of OM in shale and coal however, is expected to follow different pathways than the most studied biodegradation for bioremediation purposes. The vast body of scientific knowledge on contaminated land bioremediation can help to shed light on the complex degradation pathways of OM in unconventional gas systems. A schematic representation of the anaerobic degradation of OM from shale and coal is illustrated in Figure 3, highlighting putative activation sites of OM, and showing the general pathways of anaerobic biodegradation of aliphatic, aromatic and heteroatom hydrocarbons.

5.1. Aliphatics

The anaerobic activation of alkanes is of particular interest since they are unreactive compounds containing only apolar σ-bonds: the most common activation is the hydrocarbon addition to fumarate, yielding alkylsuccinates (Widdel and Grundmann, 2010). The biodegradation of aliphatic and cyclic hydrocarbons can be a source of metabolites (fatty acids) that can be further oxidised to methanogenic substrates (Warwick et al., 2008); the biochemistry and subsequent degradation of alkylsuccinates is also expected to lead to fatty acid metabolism (Widdel and Rabus, 2001). Although fatty acids are a feedstock for methanogens, the accumulation of such compounds could potentially cause inhibition of methanogenesis, due to lowering of pH, (Jones et al., 2010). Alkenes activation occurs mostly from the hydration of the double bond. The biodegradation of monoterpenes and other isoprenoids in anaerobic ecosystems was observed under denitrifying conditions (Harder, 2000; Hylemon and Harder, 1998).

5.2. Aromatics

The biodegradation of aromatic compounds has been long studied, since the presence of such "contaminants" in many aquifers all around the world. These compounds are often toxic and their aqueous solubility is also an issue. The simple alkyl-substituted aromatic hydrocarbons are more readily degraded under anaerobic conditions than unsubstituted aromatics. For example, the degradation of toluene under methanogenic conditions require the activity of the benzylsuccinate synthase, which catalyses the addition of the methyl carbon of toluene to the double bond of fumarate (Beller and Edwards, 2000). Ethylbenzene can be completely oxidised to CO_2 by an ethylbenzene-oxidising bacterium (Strain EB1) under denitrifying conditions but not under oxic conditions (Ball et al., 1996). The final biodegradation products of ethylbenzene are potential substrates for hydrogenotrophic methanogens. The biodegradation of benzoate by a pure culture of *Syntrophusaciditrophicus* produced 1.5 mol of acetate per mol of benzoate in absence of H_2-utilizing partners or terminal electron acceptors: in co-cultures with *Methanospirillum hungatei* it produced 3 mol of acetate and 0.75 mol of CH_4 per mol of benzoate (Elshahed and McInerney, 2001). *Sporomaculatum hydroxybenzoicum* biodegraded 3-hydroxybenzoate in the absence of hydrogenotrophic microorganisms by using the crotonyl coenzyme A, which results in the final production of butyrate, acetate and HCO_3^- (Müller and Schink, 2000). The results of these studies may be significant to elucidate the degradation pathways of aromatic compounds in OM. Benzoate is a central intermediate in anaerobic degradation of many natural and xenobiotic aromatic compounds (Elshahed and McInerney, 2001). Biodegradation studies with unsubstituted aromatic hydrocarbons were carried out mostly with benzene and naphthalene under sulfate-reducing conditions: for the activation of these compounds, the mechanisms include the addition of CO_2-derived carboxyl group (Annweiler et al., 2002; Widdel and Rabus, 2001).

Recent studies investigated the carboxylation of benzene and naphthalene via the putative enzymes benzene carboxylase (Abu Laban et al., 2009) and naphthalene carboxylase (Bergmann et al., 2011). Polycyclic aromatic hydrocarbons (PAHs) are commonly found in coal formation waters, coal extractable OM and methanogenic coal incubations (Strapoć et al., 2011). Many prokaryotes are capable of mineralising PAHs under anaerobic conditions; the degradation rates are usually fastest under sulfidogenic conditions, followed by methanogenic and finally nitrate-reducing conditions (Chang et al., 2002). A common bacterial strategy, which influences the PAH degradation, is the release of biosurfactants, small detergent-like molecules with a hydrophilic head and a lipophilic tail. Hydrophobic compounds become solubilized in the hydrophobic cores of the micelles, which leads to a transfer of PAHs from solid, liquid, or sorbed PAHs into the water phase (Johnsen et al., 2005). Although in the absence of nitrate or sulfate the anaerobic biodegradation of PAHs is thermodynamically unfavourable, in the presence of active methanogenic bacterial species these complex compounds may be degraded by the syntrophic food chain. The initial steps could involve the degradation of organic compound to H_2 and CO_2: subsequent utilisation of H_2 by methanogens, reducing CO_2 to CH_4, provides enough energy to make the overall reaction thermodynamically favourable (Genthner et al., 1997); thus, methanogenic bacteria serve as terminal electron sink via interspecies hydrogen transfer, and make biodegradation of PAHs thermodynamically feasible (McInerney and Bryant, 1981). The capability for anaerobic hydrocarbon degradation appears to be rather widespread in various lines of phylogenetic descent. The diversity of anaerobic hydrocarbon degraders may indicate that hydrocarbons were already used as growth substrates at an early stage of bacterial evolution and the anaerobic metabolism may be older than the aerobic (Widdel and Rabus, 2001). Altogether the pathways for the biodegradation of organic compounds can be summarized in reactions of fumarate addition, hydroxylation, C1 addition/carboxylation, and methylation

(Strapoć et al., 2011). The anaerobic degradation of organic compounds is less documented as compared with the aerobic biodegradation, and most of these pathways are not completely understood. Many data, however, are available from studies of bioremediation in anoxic soil, and may help to decipher the complicated pathways of biodegradation of geologically-old OM and the microbial consortia involved in the syntrophic chain. The relevance of these studies is not only related to the planning of *in-situ* stimulation strategies, but also to remediate or mitigate accidental contamination due to drilling activities, mining and storage of wastewater.

5.3. Heteroatoms

NSO (nitrogen-, sulfur- and oxygen-containing heterocyclic compounds) were found in coal (Orem et al., 2007; Wawrik et al., 2012) and shale formations (Gross et al., 2015). Heteroatoms were long considered recalcitrant to biodegradation, and in a "susceptibility scale" classified as the last group of compounds, after normal alkanes (usually catabolized first), followed by branched alkanes, monocyclic saturated, monoaromatic hydrocarbons and PAHs (Hunt et al., 1995; Rowland et al., 1986; Volkman et al., 1983; Wenger and Isaksen, 2002). NSO compounds are not as recalcitrant as once believed and could undergo selective degradation process as complex as those for hydrocarbons (Kim et al., 2005) NSO compounds are more soluble in water than PAHs, since the replacement of a carbon atom with a nitrogen, sulfur or oxygen atom result in higher polarity and hence higher water solubility and increased bioavailability and mobility. Also, chemical bonds between carbon and heteroatoms have lower bond dissociation energies than aliphatic or aromatic C-C bonds (Savage, 2000). Thus, heteroatoms are more reactive than PAHs, characterised by C-C bonds; the mechanisms of activation of these compounds are similar to biodegradation pathways

588observed for PAHs, and could include demethoxylation as demonstrated by stable isotope
589probing (Liu and Suflita, 1993).

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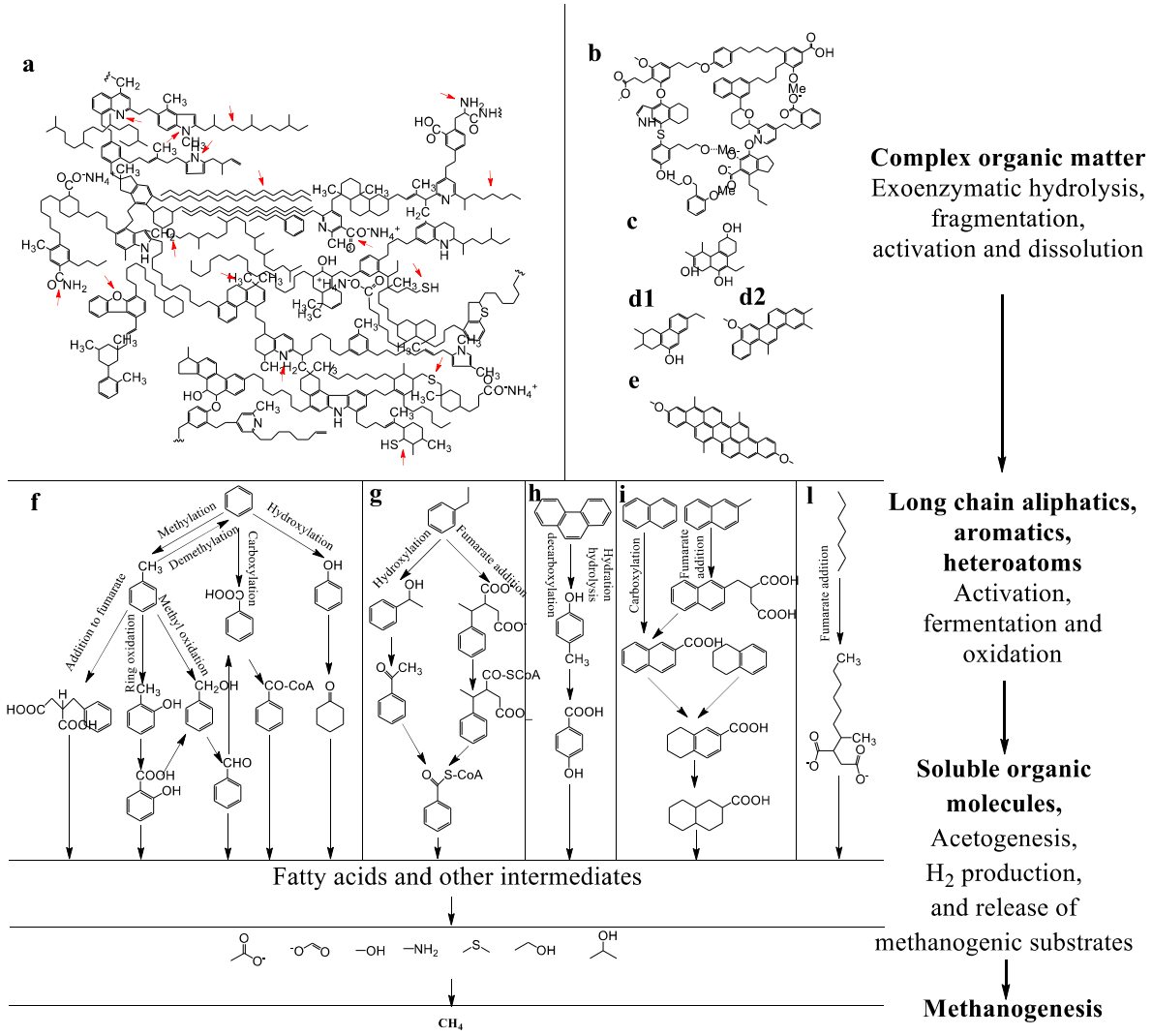

591

592**Fig. 2. General biodegradation pathways of OM from shale and coal.** Schematic representation of the
593microbial anaerobic biodegradation of OM. Red arrows indicate the putative activation sites for the microbial
594transformation of OM (from Strapoć et al., (2011). (a) Structural model of the oil shale kerogen (Green River),
595redraw from Vandenbroucke and Largeau, (2007). (b, c, d1, d2, e) Typical structures of different ranks of coal,
596modified from Fakoussa and Hofrichter, (1999). (f) Schematic biodegradation of benzene, toluene and phenol,
597modified from Grbić-Galić and Vogel, (1987), using McInerney et al., (2009) for benzoate degradation. (g)
598Representation of ethylbenzene biodegradation, redrawn from Kniemeyer and Heider, (2001), (h) anaerobic
599biotransformation of phenanthrene, redrawn from Haritash and Kaushik, (2009). (i) Naphthalene

biodegradation, redrawn from Annweiler et al., (2002). (l) Short schematic degradation of heptane adapted from Strąpoć et al., (2011).

6. Environmental requirements for in situ biogenic CH_4 production

Biogenic CH_4 production is significant in nearly every shallow coal seam at temperatures less than 80°C (Jin et al., 2010; Pfeiffer and Ulrich, 2010), in SG basins the contribution of biogenic CH_4 is also depth related in the majority of basins (Golding et al., 2013; Krumholz et al., 1997; Martini et al., 2008; McIntosh et al., 2008). The relationship between methanogenesis and depth is not controlled only by temperature, but also correlates with possible events of natural groundwater recharge that enhances methanogenesis by either (*i*) transporting microorganisms into organic-rich reservoirs, providing moisture necessary for microbial activity, decreasing salinity, removing waste products, and/or (*ii*) transporting nutrients necessary for microbial growth (Jones et al., 2013; Martini et al., 1996; McIntosh et al., 2002; Strpoć et al., 2010, 2008; Zhang et al., 2013). Reduction in Cl^- concentration is crucial for promoting methanogenesis in basins with high salinities, since methanogens prefer salinity gradient between 0.5 and 4 M Cl^- (Orem et al., 2010; Osborn and McIntosh, 2010; Schlegel et al., 2011b; Patricia J. Waldron et al., 2007; Zinder, 1993). The observation that microbial gas generation occurs at significant rates only in shallow CBM and shale gas basins is also dependant on the bioavailability of readily degradable OM. With increasing depth, the organic compounds become more recalcitrant to biodegradation (Head et al., 2003; Wellsbury et al., 1997; Strapoc et al., 2008; Robbins et al., 2016). Recent studies showed a significant negative correlation between final biogenic methane yield and rank, suggesting that the bioavailability of the coal organic material decreases with increasing thermal maturity (Robbins et al., 2016). The chemistry of coal changes systematically with increasing rank, as oils and gases are generated and then cracked, producing abiotic methane and higher

hydrocarbon gases, thus reducing the fraction of biodegradable moieties (Papendick et al., 2011). The negative correlation between biogenic methane and rank of coal does not provide an exhaustive explanation of biogenic CH_4 production, suggesting that other limiting factors such as the accessibility of microbes to OM could play a more important role. Although the transport/presence of bacteria in organic-rich rocks cannot be completely ruled out, indigenous microbial communities live mainly within fractures (cleats) in shale and coal formations, or at the interface of coal with overlying or underlying rock layers (Fredrickson et al., 1997; Martini et al., 1998; Scott, 1999). This provides limited surface area for the microorganisms to interact with OM. It has been suggested that the pore throat size must be double the diameter of cells to allow bacteria to effectively pass through (Fredrickson et al., 1997). In the Illinois Basin CBM, Strapoć et al., (2008) reported that the dominant methanogen was on average 0.4 μm in diameter, indicating that pores and/or fractures in reservoirs supporting methanogenesis must be much greater in diameter. In sandstone formations with permeability less than 100 mD, the bacterial penetration typically occur slowly (Jenneman et al., 1985), suggesting that in shale-sandstone sequence, microorganisms are slowly, but steadily transported in the deep subsurface. Competition with other groups of microorganisms could be another limiting factor, several studies have investigated the competition between SRB and methanogens. These studies suggested that methanogenesis and sulfate reduction are mutually exclusive due to competition for carbon substrates (Claypool and Kaplan, 1974; Kuivila et al., 1989; Lovley and Phillips, 1987; Mah et al., 1977; Martens and Berner, 1974; Reeburgh and Heggk, 1977). In the absence of sulfate, SRB may play a role in the breakdown of OM into methanogenic substrates (Mah et al., 1977; Raskin et al., 1996; Wawrik et al., 2012). Depending on the redox conditions and availability of substrates, the two processes can take place simultaneously, although the sequential dominance of SRB or methanogens in a given interval is more likely to happen. The

dominance of a particular class of microorganisms is dependent on many factor, such as H_2 concentration, which control also the production and oxidation of CH_4 under anaerobic conditions.

7. Stimulation of biogenic CH_4 production

Research into the stimulation of biogenic CH_4 production in unconventional gas systems is a new focus area for engineers and scientists. There are some similarities with conventional microbial enhanced oil recovery, but many research questions remain unanswered. Recently, there has been considerable work on microbial methanogenesis in CBM (Green et al., 2008; Harris et al., 2008; Jones et al., 2010; Papendick et al., 2011; Penner et al., 2010; Ritter et al., 2015; Singh et al., 2012) and SG (Martini et al., 1998; Jones et al., 2010), reflecting the potential for *in situ* sustainable regeneration of CH_4. While microbial methanogenesis in unconventional formations is complicated by a number of biogeochemical factors, a review of the relevant microbiological and geochemical literature allows the identification of key parameters for *in situ* stimulation strategies that include:

1. presence of viable methanogens and primary/secondary fermenters
2. competition for methanogenic substrates;
3. methanogesis rates;
4. bioavailable/biodegradable OM;
5. temperature;
6. formation salinity;
7. presence of fractures and pore size distribution.

Strategies for the *in situ* stimulation of CH_4 production typically include technologies developed for the bioremediation of contaminated sites, such as (*i*) the addition of inorganic or organic nutrients in order to stimulate the native microbial populations (*biostimulation*)

679and (*ii*) the addition of a microbial consortium (*bioaugmentation*). Other consolidated
680technologies in the unconventional gas industry could potentially be used to achieve optimal
681conditions in the formation, including hydraulic fracturing that can (*iii*) increase the contact
682surface area of microorganisms to coal/shale and (*iv*) increase the bioavailability of OM.
683These approaches could be used separately or in combination to achieve a continuous
684generation of biogenic CH_4 from existing producing wells or depleted wells.
685
686***7.1. Biostimulation***
687Microbial stimulation involves the addition of nutrients and/or electron donors and acceptors
688to the formation in order to stimulate CH_4 production from indigenous microorganisms.
689Nutrients are typically added in formations where biogenic CH_4 generation is active or where
690methanogenic rates are decreasing over time in the attempt to stimulate the growth of
691methanogenic communities and shift redox conditions to methanogenesis (Barnhart et al.,
6922013; Fallgren et al., 2013; Jones et al., 2010; Ritter et al., 2015). The addition of
693methanogenic substrates such as CO_2-H_2 or acetate could stimulate biogenic CH_4 production,
694but the primary goal of microbial stimulation should be to target primary and secondary
695fermenters (Mahaffey et al., 2013; Schlegel et al., 2013) able to degrade the complex
696geopolymers and release intermediary products that can be converted to CH_4 by methanogens.
697This should take into account that syntrophic and fermentative bacteria, which are likely to be
698the main contributor to OM breakdown, survive near the thermodynamic limits of life
699(Elshahed and McInerney, 2001; McInerney et al., 2008) and, therefore, their growth is slow
700(Lovley, 1991) and dependant on several other factors. The introduction of electron
701donors/acceptors, which could stimulate microbial growth, is likely to divert electrons away
702from methanogenesis, since stimulation of more rapid organic release could result in toxic
703conditions that could limit biogenic CH_4 generation (Jones et al., 2008). Biostimulation seems

to be the primary approach of current commercial stimulation projects (Luca Technologies: Mahaffey et al., (2013); Next Fuel: Fallgren et al., (2013); Ciris: Ciris Energy, 2013).

7.2. Bioaugmentation

Bioaugmentation involves the introduction of microorganisms into the target environment to increase the *in situ* metabolic activity (Silva and Alvarez, 2010). Bioaugmentation may consist of a single microorganism or more typically a consortium of microorganisms (i.e., Bacteria and Archaea). In most cases, the microorganisms to be injected do not originate from the target environment, but are enriched and evaluated for high methanogenesis rates in laboratory experiments. When introducing an enriched consortium in the target formation, CH_4 generation rates could be much lower than in laboratory studies, where incubations are typically carried out with small chips of rock, therefore the accessibility of the microorganisms to OM is greatly increased when compared with *in-situ* conditions. This could bring biases in the results, leading to an overestimation of the CH_4 generation rates. Although the bioaugmentation method was shown to produce more CH_4 than biostimulation (Jones et al., 2010), it may be difficult, in some cases, to obtain permission from regulatory agencies to inject microorganisms into the subsurface, especially in areas where adjacent aquifers are used for drinking water. Very few research groups have pursued the microbial augmentation approach at the field scale (Ritter et al., 2015). MicGas™, for example, used a combination of biostimulation and bioaugmentation, adapting methanogens derived from termites to coal in the presence of appropriate nutrients (see http://www.arctech.com/micgas.html).

7.3. Increase the contact surface area of microorganisms to coal/shale

Since the pore matrix of coal and shale is typically too small for microorganisms, methanogenesis is often limited to fractures (Scott, 1999) and at the fringe between the source rock and more permeable formations, where the pore size is greater, as well as the availability of water (Krumholz et al., 2002; Martini et al., 1998). Increasing the surface area available for microbial colonization could be accomplished through existing techniques, such as hydraulic fracturing. Hydraulic fracturing is carried out to increase the permeability of SG formations and coal seams, and involves the pumping of large volumes of fluids into these formations under high pressure. Water and sand represent 98 to 99.5 % of the fluid used in hydraulic fracturing. Additional additives may include acids to remove drilling mud near the wellbore and biocides to prevent deleterious microbial activity (Davies, 2011). A portion of the so-called “fracking” fluids remains in the formation after the completion of the fracturing process, offering the opportunity to introduce a microbial consortium into the induced fractures, as part of a nutrient-delivery system, or more broadly, to modify the biogeochemical conditions in the formation. Such use of hydraulic fracturing should consider alternative solutions to the addition of biocide, typically used to prevent sulfide production that potentially increase human and environmental health risks, corrosion, and costly degradation of product quality. Possible strategies to prevent sulfide production could be to eliminate sulfur-containing compounds from the drilling mud. For example, dolomite could be substituted for barite when adding weight to bentonite-based drilling mud and, lignosulfonates could be replaced with polyphosphates, leonardite, and tannins (Struchtemeyer et al., 2011). In spite of the importance of hydraulic fracturing, very little is known about the microbiological consequences of this process. Increasing permeability helps facilitate CH_4 production (i.e., enhances transport of gas to the wellbore (Solano-Acosta et al., 2007), and would likely help carry injected nutrients, water, and/or microorganisms to additional coal surfaces. Currently, there are only few studies that evaluate the change in the

753microbial composition of fracking fluids before and after the fracking process (Davis et al.,
7542012; Struchtemeyer and Elshahed, 2012; Struchtemeyer et al., 2012, 2011), but none of
755them aim to enhance the engineering of fracking practices to stimulate microbial processes.
756
757***7.4. Increasing the bioavailability of OM***
758The biotic and abiotic process of breaking down OM into methanogenic intermediates is
759often considered a rate-limiting step in methanogenesis (Scott, 1999; Strapoć et al., 2011a;
760Wawrik et al., 2012). Increasing the bioavailability of complex geopolymers could be
761accomplished through the addition of chemicals to dissolve the coal/shale matrix (Scott,
7621999). Laboratory studies have suggested that the addition of a strong oxidant, such as
763potassium permanganate (Huang et al., 2013) or hydrogen peroxide (Jones et al., 2013) may
764help to convert coal carbon to organic acids, although such chemicals could potentially be
765harmful to methanogens. The addition of surfactants was also tested to reduce surface and
766interfacial tensions between coal molecules (Papendick et al., 2011; Singh and Tripathi,
7672013), however, surfactant micelles can trap substrates and actually reduce their
768bioavailability in some cases (Mihelcic et al., 1993).
769
770**8. Conclusions**
771
772While recent studies have helped to clarify the role of various microbial populations in
773conventional oil reservoir, the broader implications for SG and CBM production are still not
774understood. Laboratory-based and commercial projects studies regarding the stimulation of
775microbial methanogenesis has significantly increased our knowledge about the processes that
776lead to microbial CH_4 generation from complex OM. Laboratory-based research has provided
777insight into locations and environments where microbial CH_4 was observed, the microbial

communities involved and the metabolic pathways that lead to methane production. Commercial projects showed that microbial methane production in unconventional gas basin is significant and can be stimulated *in situ*. Yet, there are very few published shale reservoir microbiology studies, highlighting the need for novel insight into guiding practical strategies for enhanced gas recovery and for mitigating undesirable microbial processes and environmental impact. Any shallow, low temperature SG and CBM basin represent the opportunity for microbial methane stimulation. Shallow gas wells are relatively inexpensive to drill compared to deep basin; as a consequence, biogenic gas systems represent an important component in the mix of natural gas accumulations that will ultimately meet high demands of gas. Shale and coal vary greatly in terms of their physical, geochemical and biological characteristics. Studies on the *in situ* stimulation of microbial methane production should consider the compilation of studies discussed in this review. Current available technologies such as hydraulic fracturing could be adapted and used to stimulate microbial methanogenesis in shallow unconventional systems. Most of the biological activity in SG and CBM occurs in fractures and at the interface between the source rock and more permeable formations, where the pore size is greater, as well as the availability of water. Hydraulic fracturing, typically used to increase the permeability and the fractures network of SG formations, could be adapted to increase the contact surface area of microorganisms with the shale/coal interface and to guarantee a greater accessibility of OM for biodegradative microorganisms. Further research should be focused on issues related to the implementation and sustainability of hydraulic fracturing process. Intensified concerns by the public have prompted some companies to develop more environmentally friendly fracturing fluids. Halliburton, for example, is testing its CleanStim® formulation, composed of ingredients sourced from the food industry. Similarly, Chesapeake Energy eliminated 18% of the chemical additives used in hydraulic fracturing fluids thanks to their GreenFrac® initiative.

FracFocus, a web-based registry with support from the U.S. Department of Energy, provides details on the additives, chemicals and the amount of water typically used in the hydraulic fracturing process.

Research into the microbiology of unconventional gas systems is a new interesting topic for engineers and scientists. Despite the similarities with conventional petroleum microbiology, there are many research questions regarding the bioavailability of OM, what specific microbial communities lead to methane production and their metabolic pathways. Moreover, research on water resources and wastewater management are still an issue. The answers to these research questions have implications for both enhanced recovery of gas and sustainable development of unconventional gas resources.

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