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.

1Biogenic methane in shale gas and coal bed methane: a review of current 2knowledge and gaps

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13

14Abstract

15Biogenic CH₄ generation has been observed in many shallow, low temperature shale gas

16basins and coal seams. The depletion of conventional resources and the increasing demand of

17natural gas for human consumption have spurred the development of so-called

18unconventional gas resources such as shale gas (SG) and coal-bed methane (CBM). Such

19unconventional systems represent the opportunity for the stimulation of biogenic CH₄

20generation. Biogenic CH₄ in shale and coal is produced by anaerobic biodegradation of

21organic matter (OM): methanogenic *Archaea* represent only the final step of biogenic CH₄

22generation. Several communities of microorganisms are involved in the initial breakdown of

23complex geopolymers and the production of intermediate compounds used by methanogens.

24There are several key knowledge gaps on biogenic CH₄ production in unconventional gas

25systems, such as the exact fraction of bioavailable OM, the microbial communities involved

26and how they can be stimulated to enhance microbial methanogenesis. Progress on

27biodegradation studies, isotopic signatures, as well as DNA analyses and proteomics could

28help unravel interactions within the syntrophic community involved in the methanogenic
29biodegradation of OM. Questions also remain regarding the environmental impact of
30unconventional gas production, such as water quality and the mobility of toxic metals and
31radionuclides. The answers to these questions might have implications for both recovery
32practices and a sustainable development of unconventional resources. This review
33summarises the current knowledge regarding biogenic CH₄ in SG and CBM: from the nature
34of the rocks to the producing microbial community and the indicators of biogenic CH₄,
35illustrating how these two environments show remarkably similar opportunities for the
36stimulation of biogenic CH₄ generation.

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38**Keywords**

39Shale gas; Coal-bed methane; Microbial methane; Organic matter; Biodegradation.

401. Introduction

41

42In recent decades, unconventional gas production from fractured shales and coal seams has
43experienced a rapid development in many parts of the world (Pearson et al., 2012). The
44success of SG and CBM is linked to the increasing demand of natural gas and the progressive
45depletion of conventional gas resources (McIntosh et al., 2008). Historically, the first
46extraction of SG began in Fredonia, Pennsylvania in the USA in 1821, in shallow, low-
47pressure fractures (Peebles, 1980; Trembath et al., 2012). Similarly, CBM was first extracted
48in the USA in the late 1930s, but economic production started in 1980s, when the United
49States Congress enacted a tax credit for “Non-conventional energy” production (US EPA
501994). Both SG and CBM industries have experienced rapid growth during the past 20 years,
51thanks to significant advances in extraction technologies (Jenkins and Boyer II, 2008). The
52combination of horizontal drilling and hydraulic fracturing has allowed access to large
53volumes of SG that were previously uneconomical to extract (Yang et al., 2014). SG wells
54typically produce significantly more gas per well, but cost substantially more to drill than
55CBM wells (Ritter et al., 2015). In spite of the large use of hydraulic fracturing, very little is
56known about the microbiological implications of this process. Hydraulic fracturing is a well-
57established technology to increase the permeability of a formation and, together with other
58stimulation strategies, could be applied *in situ* to achieve or maintain optimised conditions for
59microbial activity. Stimulation strategies could be used to enhance the productive lifespans of
60depleted microbial SG and CBM wells, extending and/or regenerating biogenic CH₄
61production. *Ex situ* treatments could involve the use of wastewater and coal/shale waste
62materials to produce CH₄ and reduce the environmental impact of SG and CBM production.
63This review is not intended to be an exhaustive review of biogenic CH₄ generation, it rather
64describes the current knowledge of biogenic CH₄ generation in shales and coals, illustrating

65the analogies and differences of the two environments, and focusing on biodegradation
66process of complex OM. We also demonstrate how the vast literature available from
67bioremediation studies can significantly improve our understanding of microbial processes in
68unconventional gas systems. Lastly, we present the current knowledge about enhanced
69biogenic CH₄ generation in SG and CBM basins, pointing out how current engineering
70technologies may be adapted to stimulate biogenic CH₄ production and favour positive
71microbial processes.

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732. Biogenic CH₄ in unconventional gas basins

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752.1. *Generation and accumulation of CH₄*

76The advances of biogeochemical studies on organic-rich sedimentary rocks and gas isotopic
 77analysis, have allowed a better understanding of the origin of CH₄ in the subsurface. These
 78studies highlighted the microbial or mixed origin of CH₄ in both coal beds (Faiz and Hendry,
 792006; Scott et al., 1994; Zhou et al., 2005; Kinnon et al., 2010; Hamilton et al., 2014 and
 802015; Baublys et al., 2015) and shales (A. M. Martini et al., 1996; McIntosh et al., 2008;
 81Schlegel et al., 2013, 2011a) in many parts of the world (Fig. 1). Early estimations of
 82microbial gas suggest that approximately 20% of total natural gas production in the world is
 83biogenic (Rice and Claypool, 1981), and an additional 10% of the gas resources may also be
 84of microbial origin (Grunau, 1983). In general, CH₄ in shale and coal beds, is generated from
 85OM, sourced from the remains of organisms deposited as fine particles in sedimentary rocks,
 86along with the mineral grains that constitute such rocks. Microbial methanogenesis in
 87unconventional gas systems is a multi-step, syntrophic process that involves a consortium of
 88bacteria and methanogenic Archaea. Bacteria break down complex OM into intermediate
 89compounds (e.g. long chain fatty acids, alkanes, and low molecular weight aromatics; Orem
 90et al., 2010), which are then biodegraded into substrates that are converted by methanogens
 91(e.g. acetate, CO₂ and H₂, methanol, formate; Strapoc et al., 2011) into CH₄. Typically, all
 92other potential electron acceptors (e.g. ferric iron and sulfate) must be exhausted before
 93microbial methanogenesis will proceed (Claypool and Kaplan, 1974; Kuivila et al., 1988;
 94Mah et al., 1977; Martens and Berner, 1974; Reeburgh and Heggie, 1977).

95OM is first converted to CH₄ by bacterial processes (*primary biogenic* CH₄), and later by high
 96temperatures and pressures as the sedimentation proceeds (*thermogenic* CH₄) (Jones et al.,
 972008). Further episodes of microbial methanogenesis are often observed after meteoric
 98recharge of water or other geological events (*secondary biogenic* CH₄) (Milkov, 2011). After
 99generation, the gas rises upward through the pore system, until it encounters a trap such as an
 100impermeable rock, forming a conventional reservoir. However, some of the gas generated
 101during thermogenic and biogenic process, remains trapped in the fine grained source rock
 102(e.g. shales and coals), forming unconventional basins (Pearson et al., 2012).

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105**Fig. 1.** World map showing locations where biogenic CH₄ from CBM (black circles) and SG (red circles) has
 106been observed. For CBM basin names and references, see Strapoć et al., (2011) and Ritter et al., (2015). For SG:
 107(1) Antrim shale (Martini et al., 1996, 1998, 2003). (2) New Albany shale (Martini et al., 2008; McIntosh et al.,
 1082010; Schlegel et al., 2011a, 2011b; Strapoć et al., 2010). (3) Cretaceous Mancos shale (L. R. Krumholz et al.,
 1091997). (4) Eastern Paris Basin (Meslé et al., 2015). (5) Alum shale (Krüger et al., 2014). (6) Po basin (Mattavelli
 110et al., 1992).

1122.2. Gas storage

113The gas generated through thermogenic or biogenic process is stored in three modes (Curtis
114et al., 2002): (i) *free gas* in intergranular porosity and natural fractures, (ii) *adsorbed gas* onto
115kerogen and inorganic minerals and (iii) *dissolved gas* in water, kerogen and bitumen.
116Characterisation of porosity and pore size distribution is particularly important when
117considering biogenic CH₄ production, since a major constraint to microbial colonisation of
118organic-rich rocks would be the limited space available, as well as the contact surface area of
119microorganisms with OM. There are several challenges in establishing a relationship between
120the presence and activity of microorganisms and physical properties of the host rocks, such as
121the pore size, pore size distribution and permeability. Fig. 2 shows the three modes of gas
122storage and the main transport mechanisms from the source rock to production well. Pores in
123solid material can be divided in: (i) macropores (>50 nm), (ii) mesopores (2-50 nm), and (iii)
124micropores (or nanopores) (<2 nm) (Rouquerolt et al., 1994). This classification is
125particularly important for unconventional basins since a significant portion of gas is sorbed
126onto the surfaces of mesopores and micropores (Ross and Bustin, 2009). It has been
127hypothesised that the primary role of macro- and mesopores is to act as a transport conduits
128(Moore, 2012). Micropores play a significant role in CH₄ adsorption, typically contributing
129the most to the total surface area, as demonstrated for both coal (Beliveau, 1993; Mastalerz et
130al., 2008) and shale (Chalmers and Bustin, 2007; Ross and Bustin, 2009). Gas storage has
131long been studied for CBM, identifying a number of factors that influence gas sorption
132process, including maceral type (Lamberson and Bustin, 1993), ash content (Laxminarayana
133and Crosdale, 1999), rank (Levine, 1996; Bustin and Clarkson, 1998), moisture (Levy et al.,
1341997) and temperature (Bustin and Clarkson, 1998). In unconventional gas systems, most of
135the CH₄ is adsorbed (Milewska-duda et al., 2000), therefore pore surface area rather than pore

136volume is the most crucial factor for gas storage (Moore, 2012). The pore surface area is
 137directly correlated to the pore size distribution. As pore size decreases, the ratio of free gas to
 138sorbed gas storage capacity decreases (Bustin et al., 2008). In general, for pores less than 0.01
 139 μm , the sorbed gas component exceeds the free gas storage (Beliveau, 1993). Micropores in
 140shale formations contribute the most to the total surface area, as observed by porosimetry in
 141the Haynesville, Marcellus and Doig shales (Chalmers et al., 2012). Macropores and
 142mesopores in these formations are associated with either kerogen and clay aggregates or
 143kerogen and carbonate aggregates (Chalmers et al., 2012). The association between
 144mesopores and micropores with kerogen has been identified in both CBM and SG studies
 145(Chalmers and Bustin, 2008, 2006; Clarkson and Bustin, 1996; Larsen et al., 1995; Marsh et
 146al., 1985; Unsworth et al., 1989). Interconnection between pores of different size and
 147fractures is an important control on the matrix permeability, which influence CH_4 transport
 148(Chalmers et al., 2012). In tight source rock, CH_4 transport occurs by different mechanisms
 149depending on the flow and porous formation conditions (Civan et al., 2011; Roy et al., 2003).
 150Flow in the fractures is controlled by advection and is modelled using Darcy's law. Within the
 151micropores, transport mechanisms include diffusion (molecular flow) and advection (Darcy
 152flow) (Schlömer and Krooss, 1997). Simple Darcy's law based analyses and interpretation are
 153insufficient to characterise permeability and diffusivity of gas in shale (Civan et al., 2011). In
 154fact, at the nanometer scale, the Darcy's law is no longer applicable: flow in the nanopore
 155matrix is controlled by diffusion, molecule-molecule and molecule-pore wall interactions
 156(Bustin et al., 2008; Javadpour, 2009; Schettler et al., 1989). In organic-rich rocks,
 157microporosity is often correlated with total organic carbon (TOC) (Chalmers and Bustin,
 1582007; Passey et al., 2010), the organic fraction of shale and coal is an important control on
 159 CH_4 storage, as demonstrated by positive correlations between TOC and sorbed gas (Gasparik
 160et al. 2013; Ross and Bustin, 2009, 2007; Chalmers and Bustin, 2008). During thermal

161maturation, the decomposition of OM leads to the production of hydrocarbons and allows the
162formation of intraparticle organic pores, as observed for coal (Bustin and Clarkson, 1998;
163Laxminarayana and Crosdale, 1999; Levy et al., 1997) and shale (Chalmers et al., 2012;
164Chalmers and Bustin, 2007; Jarvie et al., 2007). In general, at higher thermal maturity, the
165diagenesis transforms OM, creating more microporosity and decreasing the heterogeneity of
166the pore surface (Levy et al., 1997). This process was often observed in high rank coal, where
167usually there is a high sorbed gas capacity (Bustin and Clarkson, 1998). The correlation
168between nanopore abundance in grains of OM and Vitrinite Reflectance (V_{Ro}) is consistent
169with observation made by Hover et al., (1996). They found no visible intercrystalline or
170intraparticle matrix porosity for low thermal-maturity rocks of the Antrim and New Albany
171shales. Such conclusions were also supported in a study of Cretaceous shales (Chalmers and
172Bustin, 2007) where the highest CH₄ sorption was observed in samples with highest
173concentrations of inertodetrinite and vitrinite. For thermally immature Jurassic shales, no
174relationship between TOC and micropore volume or surface area was found (Ross and
175Bustin, 2009), indicating that surface area alone is not the only factor controlling CH₄
176capacity. A component of solute CH₄ within the internal structure of the matrix bituminite was
177proposed as a dominant mechanism of gas storage in Jurassic shales (Ross and Bustin, 2009).
178In CBM, gas content increases with depth and coal rank (Scott, 2002). The relationship
179between macropores and carbon content is inversely proportional: macropores decrease and
180micropores increase with rank, with an unexpected increasing number of macropores at low
181volatile bituminous rank (Levine, 1996). In general, OM is a primary control on gas
182adsorption: the higher the TOC content, the greater the gas-sorption rates in organic-rich
183sedimentary rocks (Zhang et al., 2012). Higher gas content values are typically associated
184with higher rank coals in many reservoirs: for example, gas content in the Piceance Basin
185show an overall increase in gas content with increasing rank (Scott, 2002). These results were

186confirmed for low and high rank coal and for organic-rich shales of different origin
187(Chalmers and Bustin, 2007). With increasing coalification, thermal cracking of n-alkanes,
188waxes, and other hydrocarbons not only generates thermogenic methane but increases
189methane adsorptive capacity by unplugging pores, resulting in higher sorption capacity and
190gas content values since methane accessibility to the micropore network is improved (Scott,
1912002). Controversially, in the San Juan Basin, lower rank coals have higher gas contents than
192higher rank coals (Scott, 2002). In this hydrogeological settings, weathering process
193introduced bacteria into the coal beds that produced secondary biogenic gases by
194metabolizing wet gases, n-alkanes, and other hydrocarbons generated during coalification
195(Scott, 2002). The generation of secondary biogenic gases increases gas contents beyond that
196expected from coal rank and if generated in sufficient quantities can actually resaturate the
197coal to the sorption isotherm (Scott et al., 1994). Overall, despite the similarities between
198shale and coal, the direct comparison of sorption characteristics of the two rocks is
199complicated by factors such as type and amount of OM, the mineral composition, pore
200volume and pore size distribution (Ross and Bustin, 2009). The controls on resource volume
201and productivity in SG reservoirs are similar to those in CBM, although SG reservoirs
202typically have lower permeability (with values in the nano- to microdarcy range), are thicker
203(30 to 300 ft), have lower sorbed-gas content ($<10 \text{ m}^3/\text{tonne}$), and contain a larger volume of
204free gas in the pore space (Jenkins and Boyer II, 2008). Of note is that although most of the
205pores in SG and CBM basins seem to be too small to host microbial life, evidences of
206microbial activity come from enrichment and isotope experiments (Martini et al., 1996 and
2071998; Krumholz et al., 2002; Formolo et al., 2008; Kinnon et al., 2010; Hamilton et al., 2014
208and 2015; Baublys et al., 2015).

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210

211**Fig. 2.** Storage and transport of gas in a SG/CBM basin from CH₄ trapped in nanopores, mesopores, macropores,
212microfractures and large fractures to the production well.

2133. Microbial ecology of SG and CBM

214

215The first evidence of active, microbial populations in deep sediments was reported about 30
216years ago, when microbial activity was observed in sediment depths of about 150 m in the
217framework of the Deep Sea Drilling Program (DSDP) (Oremland and Polcin, 1982; Tarafa et
218al., 1987; Whelan et al., 1986). In the past decades, the existence of prokaryotes in deep
219continental sedimentary rocks was proven (Pedersen, 2000) at up to 2800m. It has been
220suggested that the biomass into the deep biosphere constitutes one-tenth (Parkes et al., 2000),
221or even one-third (Whitman et al., 1998) of the total global, living biomass. The capabilities
222of the subsurface microbial communities to convert shale and coal OM to CH₄ was proved in
223laboratory (Fallgren et al., 2013; Jones et al., 2010, 2008; Warwick et al., 2008) and field
224studies (see Luca Technologies Inc. and Ciris Energy websites). The pathways of
225biodegradation of OM are microbially and biochemically complex (Jones et al., 2010), are
226site-specific, and could involve several communities of hydrocarbon degraders, fermenters
227and methanogenic Archaea. DNA-based assessment of the microbial community structure in
228unconventional gas basins have shown that bacterial diversity is higher than archaeal
229diversity (Barnhart et al., 2013; Penner et al., 2010; Green et al., 2008). The chemical
230complexity of OM requires the syntrophic cooperation of these microorganisms. Syntrophic
231metabolism accounts for much of the carbon flux in methanogenic environments (Schink and
232Stams, 2006). Our understanding of the *intermediary ecosystem metabolisms* (Drake et al.,
2332009) is limited. Bacteria related to Proteobacteria (mostly Beta, Delta and
234Gammaproteobacteria), Actinobacteria, Bacteroidetes and Firmicutes seem to be widespread
235in CBM (Green et al., 2008; Jones et al., 2008 and 2010; Li et al., 2008; Strapoc et al., 2008;
236Robbins et al., 2016; Warwick et al., 2008) and SG (Meslé et al., 2015, and 2013;
237Struchtemeyer and Elshahed, 2012). These taxonomic groups are known for their versatile

238metabolic activity and hydrocarbon degrading capabilities. The archaeal diversity in shale
239and coal is usually dominated by methanogens from the orders Methanosarcinales,
240Methanomicrobiales and Methanobacteriales (An et al., 2013; Meslé et al., 2013; Fichter et
241al., 2012; Kirk et al., 2012).

242

2433.2. *Actinobacteria*

244Actinobacteria are common in soil and sediments environments, and might play a central role
245in the decomposition of OM. Within the Actinobacteria, the Actinomycetales and the
246Rubrobacterales (Prince et al., 2010) possess known hydrocarbon-degrading capabilities.
247Strains of *Gordonia*, *Mycobacterium*, and *Rhodococcus* are able to remove sulfur from
248dibenzothiophene, yielding hydroxybiphenyl (Mohebbi and Ball, 2008). Actinobacteria are
249typically aerobic hydrocarbon-degraders, but their role in anaerobic OM degradation remains
250unknown (Meslé et al., 2013). Metagenomic studies have also identified high proportions of
251genes for enzymes involved in aerobic hydrocarbon metabolism in CBM produced water
252samples (An et al., 2013), suggesting that the sequential degradation of complex OM causes
253the partial dominance of a group of microorganism in a given interval. Other studies, for
254example, reported that in anoxic environment the operation of different redox conditions is
255not mutually exclusive (Lovley et al., 1991) or cannot be explained satisfactorily by a simple
256microbial competition (Conrad et al., 1987).

257

2583.3. *Bacteroidetes*

259Bacteroidetes are commonly found in sediments, and their metabolism is
260chemoheteroorganotrophs. Many of such organisms can degrade macromolecules such as
261protein, chitin, pectin, agar, starch, or cellulose. Many others are thought to be involved in oil
262biodegradation (Stra et al., 2008). Species within *Cytophaga* are mesophilic anaerobes able to

263ferment polysaccharides into acetate, propionate, succinate, H₂ and CO₂ (Haack and Breznak,
2641993). The genus *Petrimonas* is mesophilic anaerobic fermenter, use carbohydrates and
265volatile fatty acids (VFAs) releasing acetate, H₂ and CO₂ (Grabowski et al., 2005). Within the
266*Prolixibacter* there are acid fermenters that produce propionate, succinate and acetate
267(Holmes et al., 2007). Bacteroidetes also feature in coal (Li et al., 2008; Shimizu et al., 2007;
268Strapoć et al., 2008) and shale (Wuchter et al., 2013) microbial assemblages, although
269belonging to undescribed orders and families.

270

2713.4. *Firmicutes*

272Within the phylum Firmicutes, Clostridia of the family Clostridiaceae include pH-neutral
273solvent producers, mixed acid and alcohol producers, and homoacetogenic fermenters
274(Wiegel et al., 2006). Species like *Clostridium* have been isolated from coal sources. For
275example *Clostridium* BC1 (Francis and Dodge, 1988), isolated from coal-cleaning residues,
276presented the ability to reduce heavy metals and fix nitrogen; *Clostridium scatologenes* is an
277acetogenic bacteria found in a coal mine (Küsel et al., 2000). In general, *Clostridiaceae* are
278widespread spore-forming, anaerobic bacteria that catalyse a wide range of metabolic
279reactions. *Clostridia* are known to depolymerize starch, chitin, xylan, and cellulose and are
280known to occur in sediments (Wiegel et al., 2006). Similarly, the *Thermoanaerobacterales*
281include thermophilic, anaerobic, fermentative bacteria that utilize a variety of carbon
282substrates and may have an important role in hydrocarbon-bearing formations (Wiegel et al.,
2832006). The role of *Firmicutes* in coal activation has been observed before (Jones et al., 2008;
284Shimizu et al., 2007; Strapoć et al., 2008; Wawrik et al., 2012). *Sporomusa*, for example, can
285demethylate aromatic compounds; *Acidoaminococcus* sp. can ferment simple amino acids as
286a sole energy source. These microorganisms may potentially participate in the recycling of
287microbial biomass in unconventional gas systems. Although members of the *Firmicutes* often

288represent a minor component of the community structure in CBM basins (Ritter et al., 2015),
289they play an important role in laboratory experiments (Barnhart et al., 2013; Green et al.,
2902008; Jones et al., 2010; Li et al., 2008; Meslé et al., 2013; Penner et al., 2010). In microcosm
291experiments the addition of methanol stimulated Firmicutes growth compared with
292experiments with no carbonaceous nutrients (Wuchter et al., 2013), suggesting a role of this
293family in the syntrophic metabolism.

294

2953.1. *Proteobacteria*

296The phylum Proteobacteria constitutes at present the largest and phenotypically most diverse
297phylogenetic lineage (Kerstens et al., 2006). Syntrophic Beta, Delta and
298Gammaproteobacteria are commonly found in CBM (Guo et al., 2012a; Meslé et al., 2013;
299Penner et al., 2010; Robbins et al., 2016), but also in SG flowback water (Mohan et al.,
3002013). Betaproteobacteria consist of several groups of aerobic or facultative bacteria that are
301highly versatile in their degradation capacities and often containing chemolithotrophic
302genera. Deltaproteobacteria include a branch of strictly anaerobic genera, which contains
303most of the known sulfate⁻-reducing bacteria (SRB) (*Desulfovibrio*, *Desulfobacter*,
304*Desulfococcus*, *Desulfonema*, etc) and sulfur-reducing bacteria (e.g. *Desulfuromonas* spp.).
305Deltaproteobacteria includes SRB which are able to degrade naphthalene or other aromatic
306hydrocarbons (Musat and Widdel, 2008). Propane and butane degraders within the SRB were
307also detected in marine hydrocarbon cold seeps (Jaekel et al., 2013). *Geobacter* species are
308known to syntrophically degrade aromatics (Lovley and Lonergan, 1990; Rooney-varga et al.,
3091999) and long-chain fatty acids (Coates et al., 1995) coupled to reduction of Fe(III) as a
310terminal electron acceptor. *Geobacter metallireducens*, for example, is genetically similar to
311*Syntrophus*, which can degrade a wide range of organics with a methanogenic partner

312(McInerney et al., 2007). In the Bowen basin pumped coal mine waters from the subsurface
313were dominated by bacteria belonging to the family Rhodocyclaceae (Raudsepp et al., 2016).
314Gammaproteobacteria is a very large heterogeneous class; some denitrifying toluene-
315degrading strains belong to the Gammaproteobacteria and are able to degrade hydrocarbons
316with nitrate as electron acceptor (Alain et al., 2012). Although the majority of
317Gammaproteobacteria are chemoorganotrophs, this group also includes several
318chemolithotrophs that derive their energy via hydrogen-, sulfur- or iron- oxidation (Gao et al.,
3192009; Kersters et al., 2006).

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3213.5. *Archaea*

322The archaeal diversity in SG and CBM is mostly restricted to methanogens from three orders:
323Methanosarcinales, Methanomicrobiales and Methanobacteriales (Green et al., 2008; Penner
324et al., 2010; Strapoc et al., 2011b). Within Methanosarcinales there are metabolically diverse
325methanogens capable of utilizing H₂-CO₂, acetate, and methyl compounds as substrates for
326methanogenesis (Whitman et al., 2006). In the San Juan Basin, sequence libraries analysis
327highlighted the presence of two families: Methanosaeta (obligate acetate utilizers) and
328Methanosarcina (metabolically versatile) (Wawrik et al., 2012). Methanosarcinales accounted
329for the majority of the methanogens in coal samples from an abandoned mine in Germany
330(Beckmann et al., 2011) and also predominate in a consortium enriched from a CBM well
331from the Powder River Basin (Green et al., 2008). Cultivated strains of these taxa can utilize
332methyl compounds, including methanol and methylamines, where *Methanlobus* is not
333known to utilize acetate or H₂-CO₂. All species within the order Methanomicrobiales are
334known to utilize H₂-CO₂ to generate CH₄, while none are capable of utilizing acetate (Garcia
335et al., 2006). The presence of *Methanosarcina* in numerous worldwide CBM may suggest
336acetoclastic methanogenesis but also intermittent oxygen intrusion in the formation (Ritter et

337al., 2015), since *Methanosarcina* can survive to short oxygen exposure when in mixed
338cultures. In the Antrim Shale, the main methanogenic pathway is hydrogenotrophic, as
339discovered by Martini et al., (1996) and later confirmed by Waldron et al., (2007). In the
340same study, Martini et al., (1996) found that gases from a deeper producing well of the
341Antrim Shale, are thermogenic, suggesting that microbial gas could be limited to shallow
342formations.

343

3444. Methanogenic pathways

345

346The range of substrates that methanogens can utilise is limited (Table 1). Biogenic CH₄ is
347primarily produced via CO₂-reduction (Eq. 1) and acetate fermentation (Eq. 2). In the first
348pathway H₂ is used as the electron donor and CO₂ as the electron acceptor (Weimer and
349Zeikus, 1978); in the second acetate and hydrogen are used to produce CH₄ and carbon
350dioxide (Conrad et al., 1989).

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354

355The first and second pathways are called respectively hydrogenotrophic and acetoclastic
356methanogenesis. Methanogens can also use other substrates, such as methanol (Eq. 3)
357(Deppenmeier et al., 1999) and formate (Eq. 4) (Whiticar, 1999).

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The possible relevance for CH₄ 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 CH₄ 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 CH₄, other microorganisms such as acetogenic and fermentative bacteria are also present.

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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
	Methanocorpusculaceae	H ₂ -CO ₂ , formate
Methanosarcinales	Methanosarcinaceae	H ₂ -CO ₂ , methylamine,
	Methanosaetaceae	acetate
Methanopyrales	Methanopyraceae	H ₂ -CO ₂

374

4.1. Isogeochemical indicators of biogenic CH₄ 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 CH₄ 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 (¹³C/¹²C) and hydrogen (D/H) isotope ratios of CH₄ are applied

for distinguishing microbial from thermogenic CH₄ in the environment (Fig. 3) (Strapoć et al., 2011; Whiticar, 1990), as well as for apportioning pathways of biogenic CH₄ 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 CH₄ has a wide range of $\delta^{13}\text{C}$ (from -110 to -50‰) and δD (from -400 to -150‰) (Whiticar and Faber, 1986). The $\delta^{13}\text{C}$ value of CH₄ is commonly coupled with other isotopic indicator in order to distinguish between microbial and thermogenic CH₄, since $\delta^{13}\text{C}$ values of biogenic CH₄ are sometimes similar to those of thermogenic CH₄ (Coleman et al., 1988; Jenden et al., 1988; Schoell, 1980; Whiticar and Faber, 1986). The hydrogen isotope signature of CH₄ distinguishes between gas origins and can identify secondary processes such as migration or mixing (Martini et al., 1998). The hydrogen isotope signature of H₂O and CH₄ 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 CH₄ 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 CH₄ and CO₂ ($\delta^{13}\text{C}_{\text{CO}_2-\text{CH}_4}$) can be helpful to understand gas origin (Strapoć et al., 2011b): thermogenic processes are characterized by low $\delta^{13}\text{C}_{\text{CO}_2-\text{CH}_4}$ determined by high temperatures; conversely, low-temperature microbial enzymatic processes determine a ^{13}C enrichment in residual CO₂ (Conrad and Klose, 2005). In mixtures of thermogenic and biogenic gases, $\delta^{13}\text{C}_{\text{CO}_2-\text{CH}_4}$ can be more suitable than the absolute value of $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) in the coproduced water, (ii) $\delta^2\text{H}$ of CH_4 and coproduced water and (iii) $\delta^{13}\text{C}$ of CO_2 . Other common indicators, such as the $\delta^{13}\text{C}$ of CH_4 and the ratio of $\text{C1}/[\text{C2} + \text{C3}]$, have proven to be unreliable in unconventional basins where a host of secondary effects occurs and the biogenic CH_4 generated commonly has high $\delta^{13}\text{C}$ 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 ($\delta^{13}\text{C}_{\text{CO}_2-\text{CH}_4}$) 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 $\delta^{13}\text{C}_{\text{CO}_2-\text{CH}_4}$ 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 $^{12}\text{CO}_2$. As a result, residual CO_2 becomes ^{13}C -enriched (average $\delta^{13}\text{C}_{\text{CO}_2}$ of about 4.3‰) and thus contrasts sharply against CO_2 in thermogenic gases with $\delta^{13}\text{C}$ values of around 20‰ (Smith and Pallasser, 1996).

429

430**Fig. 3.** Dual plot of $\delta^{13}\text{C}$ and δD of CH_4 for the classification of
431microbial and thermogenic CH_4 . Adapted from Whiticar (1986).

432

4335. Microbial processes in unconventional gas basins

434

435The pattern of anaerobic mineralisation of OM involves the activation of complex
436macromolecular compounds, such as aliphatics, aromatics and heteroatoms by primary
437fermenting bacteria. Then secondary fermenters degrade less complex compounds to a
438variety of fatty acids, CO_2 and H_2 . Acetogenic bacteria degrade (higher) fatty acids to acetate,
439formate, CO_2 and H_2 , that can be used by methanogens. Acetate can also be degraded into H_2
440and CO_2 via syntrophic acetate oxidation, as observed in the Yabase oil field in Japan
441(Mayumi et al., 2011). These processes take place simultaneously, but because of the different
442growth rates and activities of the microorganisms involved, the processes are partially
443uncoupled, resulting in the accumulation of organic acids (Stams et al., 2012).
444Methanogenesis is in fact a dynamic process and strongly influence the metabolism of
445fermentative and acetogenic bacteria by means of interspecies H_2 transfer (Schink and Stams,
4462006; Stams and Plugge, 2009). Hydrogen syntrophy is hypothesised to be also responsible

447for anaerobic oxidation of CH₄ (Reeburgh and Heggie, 1977). In organic-rich and anaerobic sediments,
448SRB play a role in the anaerobic oxidation of CH₄ (Eq. 5) (Zehnder and Brock, 1979) through
449a process called *reverse methanogenesis*.

450

452

453Anaerobic oxidation of CH₄ coupled to sulfate reduction is assumed to be a syntrophic
454process, where H₂ syntrophy is the basis of the methanogen/SRB consortium (Valentine and
455Reeburgh, 2000). H₂ concentration is indicative of the dominant terminal electron-accepting
456process (Lovley and Phillips, 1987; Lovley and Goodwin, 1988; Hoehler et al., 1998). The
457maintenance of low H₂ allows the syntrophic oxidation of organic material through
458interspecies H₂ transfer (Schink, 1997; Wolin, 1982). Under sufficiently low H₂, methanogens
459reverse their metabolism and mediate the reversal of methanogenesis, using water as the
460terminal electron acceptor. The H₂ is removed and maintained at low concentrations by SRB
461in syntrophic association with methanogens (Hoehler and Alperin, 1996). SRB are more
462efficient at using H₂ as an electron donor; thus, they can create conditions that
463thermodynamically favour the oxidation of CH₄.

464Being rich in organic carbon, shale and coal could be considered a suitable substrate for
465microbial activity, although kerogen is a complex and biologically recalcitrant material,
466composed of a mix of aliphatics (Orem et al., 2010), aromatic hydrocarbons (Orem et al.,
4672010, 2007; Ulrich and Bower, 2008) and heteroatoms (Orem et al., 2007). Microorganisms
468interact with OM in different ways, including biological depyritization, solubilisation by
469biologically produced alkaline materials and by biological chelators (Polman et al., 1994).
470The biodegrading capabilities of anaerobic bacteria were discovered in relatively recent time,
471as 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 CO₂ and CH₄ are related to the different terminal electron acceptors (Fig.4).

479

480

Fig. 4. Schematic of putative microbial processes in subsurface environments. The figure shows the main reactions and groups of microorganisms involved in CH₄ 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 (E₀) of the microbial processes.

485

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 CH₄ 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); Strapóć 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.

500

5015.1. *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).

5155.2. Aromatics

516The biodegradation of aromatic compounds has been long studied, since the presence of such
517“contaminants” in many aquifers all around the world. These compounds are often toxic and
518their aqueous solubility is also an issue. The simple alkyl-substituted aromatic hydrocarbons
519are more readily degraded under anaerobic conditions than unsubstituted aromatics. For
520example, the degradation of toluene under methanogenic conditions require the activity of the
521benzylsuccinate synthase, which catalyses the addition of the methyl carbon of toluene to the
522double bond of fumarate (Beller and Edwards, 2000). Ethylbenzene can be completely
523oxidised to CO₂ by an ethylbenzene-oxidising bacterium (Strain EB1) under denitrifying
524conditions but not under oxic conditions (Ball et al., 1996). The final biodegradation products
525of ethylbenzene are potential substrates for hydrogenotrophic methanogens. The
526biodegradation of benzoate by a pure culture of *Syntrophus aciditrophicus* produced 1.5 mol
527of acetate per mol of benzoate in absence of H₂-utilizing partners or terminal electron
528acceptors: in co-cultures with *Methanospirillum hungatei* it produced 3 mol of acetate and
5290.75 mol of CH₄ per mol of benzoate (Elshahed and McInerney, 2001). *Sporomaculatum*
530*hydroxybenzoicum* biodegraded 3-hydroxybenzoate in the absence of hydrogenotrophic
531microorganisms by using the crotonyl coenzyme A, which results in the final production of
532butyrate, acetate and HCO₃⁻ (Müller and Schink, 2000). The results of these studies may be
533significant to elucidate the degradation pathways of aromatic compounds in OM. Benzoate is
534a central intermediate in anaerobic degradation of many natural and xenobiotic aromatic
535compounds (Elshahed and McInerney, 2001). Biodegradation studies with unsubstituted
536aromatic hydrocarbons were carried out mostly with benzene and naphthalene under sulfate-
537reducing conditions: for the activation of these compounds, the mechanisms include the
538addition of CO₂-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

564(Strapoć et al., 2011). The anaerobic degradation of organic compounds is less documented as
565compared with the aerobic biodegradation, and most of these pathways are not completely
566understood. Many data, however, are available from studies of bioremediation in anoxic soil,
567and may help to decipher the complicated pathways of biodegradation of geologically-old
568OM and the microbial consortia involved in the syntrophic chain. The relevance of these
569studies is not only related to the planning of *in-situ* stimulation strategies, but also to
570remediate or mitigate accidental contamination due to drilling activities, mining and storage
571of wastewater.

572

573**5.3. Heteroatoms**

574NSO (nitrogen-, sulfur- and oxygen-containing heterocyclic compounds) were found in coal
575(Orem et al., 2007; Wawrik et al., 2012) and shale formations (Gross et al., 2015).
576Heteroatoms were long considered recalcitrant to biodegradation, and in a “susceptibility
577scale” classified as the last group of compounds, after normal alkanes (usually catabolized
578first), followed by branched alkanes, monocyclic saturated, monoaromatic hydrocarbons and
579PAHs (Hunt et al., 1995; Rowland et al., 1986; Volkman et al., 1983; Wenger and Isaksen,
5802002). NSO compounds are not as recalcitrant as once believed and could undergo selective
581degradation process as complex as those for hydrocarbons (Kim et al., 2005) NSO
582compounds are more soluble in water than PAHs, since the replacement of a carbon atom
583with a nitrogen, sulfur or oxygen atom result in higher polarity and hence higher water
584solubility and increased bioavailability and mobility. Also, chemical bonds between carbon
585and heteroatoms have lower bond dissociation energies than aliphatic or aromatic C-C bonds
586(Savage, 2000). Thus, heteroatoms are more reactive than PAHs, characterised by C-C bonds;
587the 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).

590

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

600biodegradation, redrawn from Annweiler et al., (2002). (l) Short schematic degradation of heptane adapted from
601Strapoć et al., (2011).

602

6036. Environmental requirements for in situ biogenic CH₄ production

604

605Biogenic CH₄ production is significant in nearly every shallow coal seam at temperatures less
606than 80°C (Jin et al., 2010; Pfeiffer and Ulrich, 2010), in SG basins the contribution of
607biogenic CH₄ is also depth related in the majority of basins (Golding et al., 2013; Krumholz et
608al., 1997; Martini et al., 2008; McIntosh et al., 2008). The relationship between
609methanogenesis and depth is not controlled only by temperature, but also correlates with
610possible events of natural groundwater recharge that enhances methanogenesis by either (i)
611transporting microorganisms into organic-rich reservoirs, providing moisture necessary for
612microbial activity, decreasing salinity, removing waste products, and/or (ii) transporting
613nutrients necessary for microbial growth (Jones et al., 2013; Martini et al., 1996; McIntosh et
614al., 2002; Strapoć et al., 2010, 2008; Zhang et al., 2013). Reduction in Cl⁻ concentration is
615crucial for promoting methanogenesis in basins with high salinities, since methanogens prefer
616salinity gradient between 0.5 and 4 M Cl⁻ (Orem et al., 2010; Osborn and McIntosh, 2010;
617Schlegel et al., 2011b; Patricia J. Waldron et al., 2007; Zinder, 1993). The observation that
618microbial gas generation occurs at significant rates only in shallow CBM and shale gas basins
619is also dependant on the bioavailability of readily degradable OM. With increasing depth, the
620organic compounds become more recalcitrant to biodegradation (Head et al., 2003; Wellsbury
621et al., 1997; Strapoc et al., 2008; Robbins et al., 2016). Recent studies showed a significant
622negative correlation between final biogenic methane yield and rank, suggesting that the
623bioavailability of the coal organic material decreases with increasing thermal maturity
624(Robbins et al., 2016). The chemistry of coal changes systematically with increasing rank, as
625oils 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 CH₄ 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, Strapoc 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 occurs 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

651 dominance of a particular class of microorganisms is dependent on many factor, such as H₂
652 concentration, which control also the production and oxidation of CH₄ under anaerobic
653 conditions.

654

655 7. Stimulation of biogenic CH₄ production

656

657 Research into the stimulation of biogenic CH₄ production in unconventional gas systems is a
658 new focus area for engineers and scientists. There are some similarities with conventional
659 microbial enhanced oil recovery, but many research questions remain unanswered. Recently,
660 there has been considerable work on microbial methanogenesis in CBM (Green et al., 2008;
661 Harris et al., 2008; Jones et al., 2010; Papendick et al., 2011; Penner et al., 2010; Ritter et al.,
662 2015; Singh et al., 2012) and SG (Martini et al., 1998; Jones et al., 2010), reflecting the
663 potential for *in situ* sustainable regeneration of CH₄. While microbial methanogenesis in
664 unconventional formations is complicated by a number of biogeochemical factors, a review
665 of the relevant microbiological and geochemical literature allows the identification of key
666 parameters for *in situ* stimulation strategies that include:

667

- 668 1. presence of viable methanogens and primary/secondary fermenters
- 669 2. competition for methanogenic substrates;
- 670 3. methanogenesis rates;
- 671 4. bioavailable/biodegradable OM;
- 672 5. temperature;
- 673 6. formation salinity;
- 674 7. presence of fractures and pore size distribution.

675

676 Strategies for the *in situ* stimulation of CH₄ production typically include technologies
677 developed for the bioremediation of contaminated sites, such as (i) the addition of inorganic
678 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 CH₄ from existing producing wells or depleted wells.

685

6867.1. *Biostimulation*

687Microbial stimulation involves the addition of nutrients and/or electron donors and acceptors
688to the formation in order to stimulate CH₄ production from indigenous microorganisms.
689Nutrients are typically added in formations where biogenic CH₄ 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 CO₂-H₂ or acetate could stimulate biogenic CH₄ 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 CH₄ 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 CH₄ generation (Jones et al., 2008). Biostimulation seems

704to be the primary approach of current commercial stimulation projects (Luca Technologies:
705Mahaffey et al., (2013); Next Fuel: Fallgren et al., (2013); Ciris: Ciris Energy, 2013).

706

7077.2. **Bioaugmentation**

708Bioaugmentation involves the introduction of microorganisms into the target environment to
709increase the *in situ* metabolic activity (Silva and Alvarez, 2010). Bioaugmentation may
710consist of a single microorganism or more typically a consortium of microorganisms (i.e.,
711Bacteria and Archaea). In most cases, the microorganisms to be injected do not originate from
712the target environment, but are enriched and evaluated for high methanogenesis rates in
713laboratory experiments. When introducing an enriched consortium in the target formation,
714CH₄ generation rates could be much lower than in laboratory studies, where incubations are
715typically carried out with small chips of rock, therefore the accessibility of the
716microorganisms to OM is greatly increased when compared with *in-situ* conditions. This
717could bring biases in the results, leading to an overestimation of the CH₄ generation rates.
718Although the bioaugmentation method was shown to produce more CH₄ than biostimulation
719(Jones et al., 2010), it may be difficult, in some cases, to obtain permission from regulatory
720agencies to inject microorganisms into the subsurface, especially in areas where adjacent
721aquifers are used for drinking water. Very few research groups have pursued the microbial
722augmentation approach at the field scale (Ritter et al., 2015). MicGasTM, for example, used a
723combination of biostimulation and bioaugmentation, adapting methanogens derived from
724termites to coal in the presence of appropriate nutrients (see
725<http://www.arctech.com/micgas.html>).

726

7277.3. **Increase the contact surface area of microorganisms to coal/shale**

728 Since the pore matrix of coal and shale is typically too small for microorganisms,
729 methanogenesis is often limited to fractures (Scott, 1999) and at the fringe between the
730 source rock and more permeable formations, where the pore size is greater, as well as the
731 availability of water (Krumholz et al., 2002; Martini et al., 1998). Increasing the surface area
732 available for microbial colonization could be accomplished through existing techniques, such
733 as hydraulic fracturing. Hydraulic fracturing is carried out to increase the permeability of SG
734 formations and coal seams, and involves the pumping of large volumes of fluids into these
735 formations under high pressure. Water and sand represent 98 to 99.5 % of the fluid used in
736 hydraulic fracturing. Additional additives may include acids to remove drilling mud near the
737 wellbore and biocides to prevent deleterious microbial activity (Davies, 2011). A portion of
738 the so-called “fracking” fluids remains in the formation after the completion of the fracturing
739 process, offering the opportunity to introduce a microbial consortium into the induced
740 fractures, as part of a nutrient-delivery system, or more broadly, to modify the
741 biogeochemical conditions in the formation. Such use of hydraulic fracturing should consider
742 alternative solutions to the addition of biocide, typically used to prevent sulfide production
743 that potentially increase human and environmental health risks, corrosion, and costly
744 degradation of product quality. Possible strategies to prevent sulfide production could be to
745 eliminate sulfur-containing compounds from the drilling mud. For example, dolomite could
746 be substituted for barite when adding weight to bentonite-based drilling mud and,
747 lignosulfonates could be replaced with polyphosphates, leonardite, and tannins
748 (Struchtemeyer et al., 2011). In spite of the importance of hydraulic fracturing, very little is
749 known about the microbiological consequences of this process. Increasing permeability helps
750 facilitate CH₄ production (i.e., enhances transport of gas to the wellbore (Solano-Acosta et al.,
751 2007), and would likely help carry injected nutrients, water, and/or microorganisms to
752 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

7577.4. *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; Strapóć 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

7708. **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 CH₄ generation from complex OM. Laboratory-based research has provided
777insight into locations and environments where microbial CH₄ was observed, the microbial

778communities involved and the metabolic pathways that lead to methane production.
779Commercial projects showed that microbial methane production in unconventional gas basin
780is significant and can be stimulated *in situ*. Yet, there are very few published shale reservoir
781microbiology studies, highlighting the need for novel insight into guiding practical strategies
782for enhanced gas recovery and for mitigating undesirable microbial processes and
783environmental impact. Any shallow, low temperature SG and CBM basin represent the
784opportunity for microbial methane stimulation. Shallow gas wells are relatively inexpensive
785to drill compared to deep basin; as a consequence, biogenic gas systems represent an
786important component in the mix of natural gas accumulations that will ultimately meet high
787demands of gas. Shale and coal vary greatly in terms of their physical, geochemical and
788biological characteristics. Studies on the *in situ* stimulation of microbial methane production
789should consider the compilation of studies discussed in this review. Current available
790technologies such as hydraulic fracturing could be adapted and used to stimulate microbial
791methanogenesis in shallow unconventional systems. Most of the biological activity in SG and
792CBM occurs in fractures and at the interface between the source rock and more permeable
793formations, where the pore size is greater, as well as the availability of water. Hydraulic
794fracturing, typically used to increase the permeability and the fractures network of SG
795formations, could be adapted to increase the contact surface area of microorganisms with the
796shale/coal interface and to guarantee a greater accessibility of OM for biodegradative
797microorganisms. Further research should be focused on issues related to the implementation
798and sustainability of hydraulic fracturing process. Intensified concerns by the public have
799prompted some companies to develop more environmentally friendly fracturing fluids.
800Halliburton, for example, is testing its CleanStim[®] formulation, composed of ingredients
801sourced from the food industry. Similarly, Chesapeake Energy eliminated 18% of the
802chemical additives used in hydraulic fracturing fluids thanks to their GreenFrac[®] initiative.

803FracFocus, a web-based registry with support from the U.S. Department of Energy, provides
804details on the additives, chemicals and the amount of water typically used in the hydraulic
805fracturing process.

806Research into the microbiology of unconventional gas systems is a new interesting topic for
807engineers and scientists. Despite the similarities with conventional petroleum microbiology,
808there are many research questions regarding the bioavailability of OM, what specific
809microbial communities lead to methane production and their metabolic pathways. Moreover,
810research on water resources and wastewater management are still an issue. The answers to
811these research questions have implications for both enhanced recovery of gas and sustainable
812development of unconventional gas resources.

813

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815

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820

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