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**Methanogenesis: A Part of the Carbon Cycle with Implication for Unconventional Biogenic Gas Resources**

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Through geological times the carbon cycle has impacted deeply fields like atmospheric composition of gases and climate, pH and erosion, redox potential and development of life. The carbon cycle has ever since been intimately linked to the development of life. It can be split schematically into primary production (photosynthesis and autotrophic methanogenesis in Figure 1) and heterotrophic mineralization (respiration and heterotrophic methanogenesis in Figure 1). The primary production is the transformation process of inorganic carbon into organic carbon, mainly biomass. The heterotrophic mineralization is its use by other living organisms in order to recover the stored chemical energy and organic carbon. At the early ages of Earth, before evolving of photosynthesis, a chemoautotrophic assimilation of CO<sub>2</sub> by hydrogen consuming methanogens following eq. 1 is likely to have occurred (Kral et al. 1998). This reaction generated methane lowering in the mean time carbon dioxide and hydrogen concentration in the atmosphere.



Photosynthesis appeared later on and became the predominant biological process producing organic carbon in the carbon cycle. This process generates molecular oxygen according to equation 2 with the apparition of the cyanobacteria. The emission of oxygen to the atmosphere modified dramatically its composition and the redox potential. This rising redox potential allowed the establishment of aerobic heterotrophs having metabolic pathways with higher energetic outputs and consequently better quantitative biomass production. A synthetic view of terrestrial carbon cycle is proposed in Figure 1.



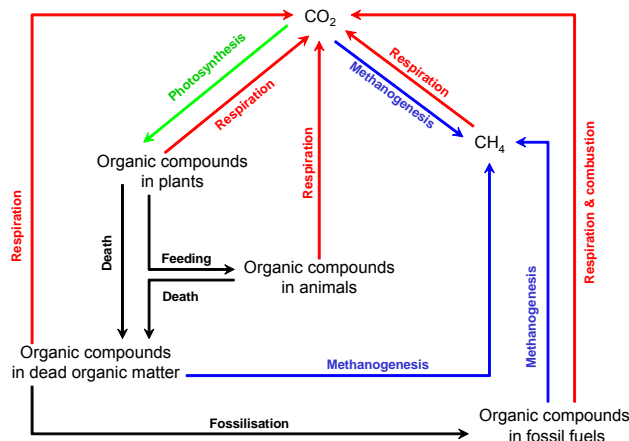


Figure 1: Proposed synthetic carbon cycle. Organic matter derived from photosynthesis (plants, algae and cyanobacteria) provides nutrition for heterotrophs (e.g. animals and associated bacteria), which convert it back to CO<sub>2</sub> by respiration. Organic compounds from dead plants, animals and micro-organisms in the soil and water, are ultimately broken down to CO<sub>2</sub> by microbial processes of biodegradation but they also can fossilise to fossil fuels. Methane can be produced from CO<sub>2</sub> by hydrogenotrophes or from organic compounds (fossilised or not).

Bacteria and archaea contribute in the final steps of the mineralization. According to the environmental redox potential (Figure 2), different pathways and different micro-organisms shall be successively involved for the mineralization of the organic matter. Using the model proposed by Berner (1977) it is possible to compute the SO<sub>4</sub><sup>-</sup> profile against depth versus sedimentation rate. When the level of 1 mmole is reached, estimation of generated biogenic gas can be directly calculated according to the stoichiometric equation 6.

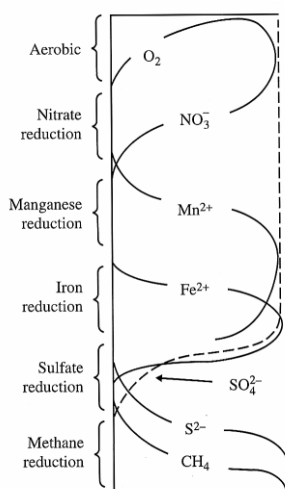
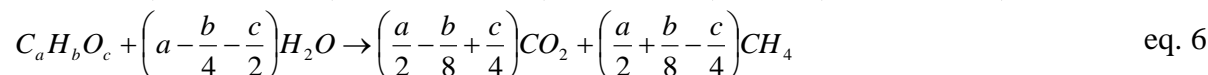
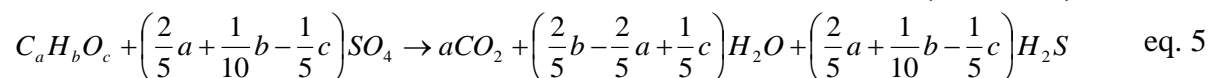
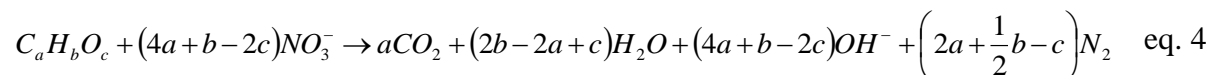
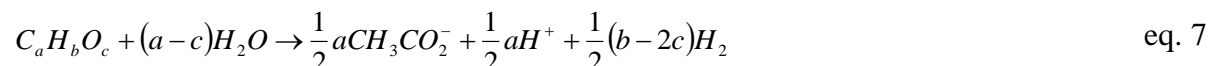


Figure 2: Vertical biogeochemical zones in sediments (after Megonical et al., 2004).

The mineralization reaction of organic matter composed by carbon, hydrogen and oxygen can be written as follows for respectively aerobic conditions (equation 3), denitrifying conditions (equation 4), sulfate reducing conditions (equation 5), methanogenic conditions (equation 6).



The heterotrophic methanogenesis reaction, also known as Buswell reaction (eq. 6), results in fact from three separate biological reactions by three different types of syntrophic microorganisms. The acetogenic bacteria (equation 7) generate hydrogen that is toxic to them selves. Therefore it is necessary that hydrogenotrophic methanogens (described to fulfil equation 1) are present to remove the hydrogen. Finally acetoclastic bacteria use the acetate to form methane and CO<sub>2</sub> according to equation 8.



Heterotrophic methanogenesis is present in a large variety of ecosystems. Methanogens can be found in different animals like wood termites and herbivorous mammals respectively in relation to their lignolytic and cellulolytic microflora which allows them to digest their diet, but they also can form association with protozoae. Methanogens can also be found in anoxic soils and sediments and particularly in paddy fields which rapidly become anoxic when flooded. They are also found in geothermic habitats like hydrothermal submarine vents (Charlou et al., 2002) and their presence is also very likely in other terrestrial habitats presenting hydrogen fluxes.

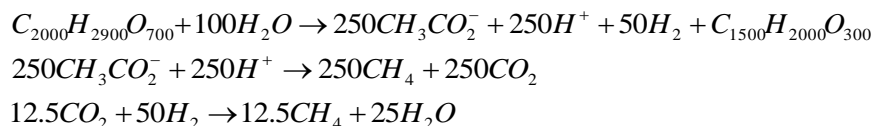
Methanogenesis also contributes to different industrial applications. It is a major process for waste water treatment where the anaerobic digestors can transform up to 50% of the sludges. But it also plays an important role in the management of landfills (Li et al., 2009) as well as the management of contaminated sites where they contribute to remove various xenobiotic compounds including hydrocarbons, phenols etc.

Depending on the origin of the carbon source and the methanogenic process involved in the methanogenesis (autotrophic or heterotrophic) the stable isotope fractionation of the methane carbon may be varying from -30‰ to -80‰. This type of values informs about the process involved in methanogenesis (Conrad et al., 2010).

Methanogenesis appears to be an ubiquitous biological process which occurs every time adequate conditions are fulfilled. It appeared very early in Earth history and might have contributed to high biogenic accumulations in sedimentary systems. In order to predict the amount of those accumulations it is necessary to determine an average molecular formula of the chemical structures of the protokerogen submitted to methanogenesis. This chemical structure will become the substrate for the reaction described by the equation 6.

We propose a conceptual 0D model (BioGas 0D) based on this approach: for that purpose we will apply literature data providing an average composition for Type II kerogens at the beginning of the methanogenesis with typical O/C values of 0.35, corresponding in the van Krevelen diagram to H/C of 1.4 leading to a global molecular formula of  $C_{2000}H_{2900}O_{700}$ . Behar and Vandenbroucke (1986) proposed a representative molecular structure for a Type II kerogen at the beginning of the diagenesis (so just after the methanogenesis) with a global molecular formula of  $C_{1500}H_{2000}O_{300}$  leading to atomic ratio at 1.33 and 0.20 for H/C and O/C respectively.

Based on these 2 global molecular formula, it is possible to determine the stoichiometric coefficients of equations 7, 8 and 1:



The resulting global Buswell equation is the following:



From a stoichiometric point of view, the oxidation of the organic matter should be the main source of hydrogen for the autotrophic methane production provided that oxygenated organic matter is present to initiate the reaction described by the equation 7. In this overall chemical schema, 262.5 atoms of carbon are produced, representing 13 % of the initial carbon. As biological process rates are usually hyperbolic functions it should also describe the carbon loss due to methanogenesis. The initial point being the total organic carbon of the rock for an organic matter with an atomic ratio O/C equal to 0.35, the final one corresponds to a kerogen with an atomic ratio O/C of 0.20.

For example: 1 m<sup>3</sup> of rock with 4% TOC, will contain 100 kg of organic carbon. With a molecular formula of  $C_{2000}H_{2900}O_{700}$  for the protokerogen corresponding to 4 moles (submitted to equation 6). The resulting biogenic gas is consequently 24.4 m<sup>3</sup> CH<sub>4</sub>/m<sup>3</sup> of rock. According to these values it appears that the methanogenesis was responsible a carbon loss of 10% of the protokerogen. Even with this efficiency the TOC that may later undergo thermal cracking will still have a concentration of 3.6%.

## Literature

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