Microbial methane gas can comprise a significant portion of many commercial natural gas accumulations worldwide. For this reason, understanding its mode and rate of biogenic gas generation is critical in forecasting the occurrence and magnitude of these types of gas reserves. The process of biogenic methane generation is very complex and involves a series of successive chemical reactions carried out by bacterial microorganisms whose metabolic rates are extremely difficult to be predicted from simple kinetic equations. Though temperature plays an important role, its effect on microbial productivity is neither linear nor monotonic. We derived a simple methanogenesis model based on theoretical biogeochemical concepts in order to predict the volumes of gas generated within a temperature interval relevant for the biogeochemical cycle. The model was calibrated against laboratory simulations performed on organic-rich samples that underwent microbial degradation in a controlled environment. Experiments were conducted at 25°C, 30°C and 45°C over a time period of 200 days. The simulations revealed significant systematic variation in CH$_4$ and CO$_2$ yield with time and temperature. The systematics helped constrain our theoretical model and allowed us to tune the empirical relations and to scale the generation rate with temperature. The results suggest that methanogenesis attains peak efficiency at about 30°C. The reaction rate for CH$_4$ generation correlates strongly with the level of free H$_2$ in solution, supporting the theory that CO$_2$ reduction dominates microbial CH$_4$ production. Carbon isotopic composition of CO$_2$ and CH$_4$ was also monitored over time. The observations indicate evolution towards the isotopically heavier carbon (more enriched in $\delta^{13}C$) over time. The trend suggests that certain types of organic substrates might be prone to generate isotopically heavy microbial methane to start with.
Selected Reference

Thermal modeling of microbial methane generation constrained by laboratory experiments

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Microbial Gas Characteristics

After Rice and Claypool (1981)
Microbial Gas Potential and Reserve Estimation

Biogenic gas is generated at rate $R$ from metabolic processes such as aerobic respiration and photosynthesis. The volume of gas $V_g$ trapped at a ratio $K$ can be estimated using

$$V_g \approx K \cdot V \cdot \left( \int R(T) dT \right) \cdot t$$

After Rice and Claypool (1981)
Objectives of Study

- Address the mechanisms of biogenic gas generation.
- Develop a model of gas generation based on biogeochemical kinetic theory.
- Experiment on organic matter.
- Calibrate the model and determine the free parameters.
- Estimate the effect of temperature.
- Monitor changes in isotopic composition.
Methane fermentation is the consequence of a series of metabolic interactions among various groups of microorganisms. A description of microorganisms involved in methane fermentation, based on an analysis of bacteria isolated from sewage sludge digesters and from the rumen of some animals, is summarized in Fig. 4-1. The first group of microorganisms secrete enzymes which hydrolyze polymeric materials to monomers such as glucose and amino acids, which are subsequently converted to higher volatile fatty acids, H2 and acetic acid (Fig. 4-1; stage 1). In the second stage, hydrogen-producing acetogenic bacteria convert the higher volatile fatty acids e.g., propionic and butyric acids, produced, to H2, CO2, and acetic acid. Finally, the third group, methanogenic bacteria convert H2, CO2, and acetate, to CH4 and CO2.
Factors Affecting Methane Generation

- Dissolved oxygen
- Dissolved sulfate
- pH conditions
- Quantity of organic matter
- Type of organic matter
- Sedimentation rate
- Temperature
- Pore space

Presenter’s Notes:

- The process of **anaerobic respiration** occurs in absence of oxygen when certain inorganic compounds, such as nitrate, sulfur, carbon dioxide, ferric or manganese oxide, are used as a terminal electron acceptor instead of oxygen.  *Presenter’s notes continued on next page.*
Fermentation represents the anaerobic catabolic process in which the substrate is transformed in subsequent steps of oxidation/reduction.

In open-marine, organic-rich sedimentary environments, the interactions between sedimentologic and ecologic factors results in three distinct biochemical environments each of which is characterized by a dominant form of respiratory metabolism.

Microbial activity in sediments results in production of several gases: CO₂, H₂, H₂S, CH₄, NH₃, and N₂.

Hydrogen, produced under widespread conditions, is immediately utilized for the reduction of nitrogen, sulfur and oxygen compounds.

Two primary pathways have been identified for the generation of biogenic gas: carbon dioxide reduction and disassociation of acetate (fermentation).

Organic-rich marine sediments pass through these three stages, which adjust automatically to keep pace with the addition of new sediments at the sediment-water interface. Creation of new environments may favor or be unfavorable to the bacteria.

Oxic conditions are easily identified by the presence of intense bioturbation.

Fermentative/methanogenetic processes, the efficiency of which depends highly on the degree of preservation of the organic matter out of the oxic zone above.

Biological methane production occurs in oxygen-free, sulfate-free, organic rich environments and occurs mainly within the top few meters of sediment.

CO₂ reduction: All methanogenic bacteria are able to use this mechanism and are, therefore, autotrophs.
Sample Simulation (T= 30°C)
Presenter’s Notes:
- Vessel and environment.
- Organic-rich pond silt substrate
- Analysis scheme and instruments.
- Methanogenesis experiments conducted at 25°C, 30°C and 45°C
- Weekly to biweekly sampling of gases for %CO₂, %CH₄, and d¹³C
- Six month experiment run time
Bacteria at Work

After Seth-Smith H. (2008)

initial setting
gas bubbles
during production

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Substrate Production - Carbon Dioxide

- Time (day): 0, 50, 100, 150, 200
- Concentration (µmole/cc): 0, 100, 200, 300, 400, 500

- Temperature: 25°C, 45°C
- Conditions: Oxic conditions, Anoxic conditions

Graph showing concentration over time for different temperature conditions.
**Presenter’s Notes:**

- CO2 production starts rapidly at the beginning of the experiment and then continues slowly as the relative equilibrium occurs between its production by the fermenters and consumption by the homoacetogenic methanogens.
- The steep increase at the beginning of each run is related to the activity of highly **efficient aerobes**.
- The point where oxic conditions cease and **anoxic conditions** are established can be easily recognized.
Methane Production
Kinetic Parameters Determination

Data points
Curve fitting

\[ w_t = 4.5 \]
\[ T_p = 42 \]
\[ b_{\text{max}} = 7 \]
\[ b_0 = 3.2 \]
Isotopic Evolution

Presenter’s Notes: The values for $b_0$, $b_{T_{\text{max}}}$, $w_T$ and $T_p$ obtained from the curve fitting operation
Integration into Basin Modeling

\[ R = \frac{dC}{dt} \]

\[ R_a = \frac{dM}{dt} = R \cdot V = \frac{dC}{dt} \cdot V \]

\[ R(h) \approx b_0 + b_{T_{\text{max}}} \cdot \exp \left( -0.5 \left( \frac{T_0 + g_t \cdot h - T_p}{w_T} \right)^2 \right) \]

\[ \frac{dM(t)}{dt} = A \left( \int_{h_{\text{in}}}^{h_{\text{out}}} R(h) \cdot dh \right) \]
Conclusions

- Oil exploration approaches are not directly translatable.
- Different geophysical, geochemical, and geologic data may be important for estimating the generative conditions for microbial gas.
- Microbial gas production peak at ~40°C.
- Development of a model based on geological, geochemical and microbiological data to predict potential gas volumes is highly demanding.
- Experimental work must cover many aspects of this process.