

# Exploring the Potential for Biogenic Methane Formation Using Hydrogeochemical Thermodynamics\*

Hans-Martin Schulz<sup>1</sup>, Wolfgang van Berk<sup>2</sup>, and Esther T. Arning<sup>1</sup>

Search and Discovery Article #41524 (2015)\*\*

Posted January 19, 2015

\*Adapted from article published in AAPG European Region Newsletter, April, 2013. Appreciation is expressed to AAPG European Region Council, Vlastimila Dvořáková, President, their Editorial Board, Karen Wagner, Chief Editor, William Sassi, Coordinator R&D Projects, and Jeremy Richardson, Office Director, AAPG European Region.

\*\*AAPG European Regional Newsletter©2013 Serial rights given by author. For all other rights contact author directly.

<sup>1</sup>Helmholtz Centre Potsdam - GFZ German Research Centre for Geosciences ([schulzhm@gfz-potsdam.de](mailto:schulzhm@gfz-potsdam.de))

<sup>2</sup>Technical University of Clausthal

## Introduction

In Europe biogenic gas is being produced from several major gas fields in, for example, the Molasse Basin of Austria and the Po Basin of Italy, and the recently discovered Eastern Mediterranean Tamar gas field off Israel is argued to be also partly filled with biogenic methane.

The latter discovery offers encouragement for further exploration success in similar settings, which, however, have been underestimated up to now.

## Biogenic Methane Prediction: Learning from Marine Geology

To investigate biogenic methane potential, a different petroleum system analysis is required than for thermogenic gas fields. Considerations about early diagenetic processes are essential, and many numerical approaches have been published to explain the fate and behaviour of biogenic methane in young marine sediments. With the exception of some early models (e.g., Clayton, 2008), there has been a lack of numerical tools in the petroleum industry to predict the biogenic methane potential. This is due to the complexity of formation processes involved, geomechanical uncertainties of the overburden, and only few data about seal integrity at often shallow depths.

Interestingly, there is a wealth of complex high-resolution data sets from the IODP programme (the former ODP and DSDP), which provide not only important basic data for the retracing of biogenic methane formation in marine sediments, but also help in the design of new numerical tools for predicting biogenic methane potential in ancient rocks.

## **Biogenic Methane Formation: Multiple Sources, Multiple Processes**

Early diagenetic methane formation is a common process in organic-matter-rich sediments both in marine and terrestrial settings. Under suitable conditions, biogenic methane released en-masse from TOC-rich sediments may be trapped in sedimentary basins and form commercial accumulations.

As sediments accumulate in marine settings the methanogenic zone is rapidly reached after sulfate is exhausted. In simple terms, methanogenic microbes use the refractory organic matter for conversion, and, in addition to carbon dioxide, methane is generated. The later diagenetic fate and behavior of methane depends on the hydrogeochemical and lithological conditions in a sedimentary basin. Methane can be dissolved in the pore water, it may exsolve at saturation and may occur in a solid state as hydrate. Diffusion of methane and/or contact to dissolved sulfate can lead to anaerobic methane oxidation (AOM). This process prevents large methane exhalations into the overlying water column. Consequently, the preservation of such early formed methane at shallow depth is mainly controlled by the sedimentation rate and water depth, which may lead to the trapping of methane in the form of hydrate. Thus, methane can be trapped over geological time scales until rising temperatures linked with continuing burial again leads to the dissolution of hydrate and the filling of adjacent porosity, provided that impermeable and thick shale units acting as seals prevent further migration and leakage. Scenarios similar to this were operative when the large biogenic methane gas fields in the Upper Austrian Molasse basin were charged (Schulz and van Berk, 2009).

As further calibration, laboratory experiments have shown that methanogenic bacteria are most productive best at temperatures around 40°C (Zeikus and Winfrey, 1976). Additionally, oil degradation in subsurface reservoirs, operative up to 80°C, is a further process which leads to biogenic methane formation. [Figure 1](#) summarizes the different processes dependent on burial depth and thermal maturation.

Besides these conventional scenarios, biogenic methane is also successfully produced from unconventional plays, such as gas shales. The production success of the Upper Devonian Antrim Shale in the Michigan Basin highlights that also geologically young biogenic methane formation is possible from relatively old organic matter (Formolo et al., 2008; Johnson and Max, 2012; Max and Johnson, 2012).

## **Early Biogenic Methane Formation: A New Quantitative Approach**

There is intense microbial life in surficial marine sediments, but the number of microbes decreases rapidly with depth (Lipp et al., 2008). This is due to rapidly developing oxygen- and oxidant-depleted conditions (such as less available dissolved nitrate and sulfate), and the lower availability of labile organic matter during methanogenesis. The availability of organic matter coupled to its irreversible redox-conversion in aqueous systems drives a sequence of interrelated and complex hydro and biogeochemical reactions, which are reflected by early diagenetic mineral precipitation/dissolution, gas formation and subsequent pore water compositional changes.

Sulfate reduction delivers bicarbonate and sulfide to the system until sulfate is exhausted. Deeper methanogenesis via the CO<sub>2</sub> reduction pathway is often the dominant biogenic methane formation process in marine sediments. The products of early diagenetic reactions initiate coupled equilibrium reactions that induce a new state of chemical equilibrium. Such early diagenetic processes in marine sediments are complex and can be retraced and reproduced by hydrogeochemical mass transport models.

Conceptually, concurrent and interdependent reactions in an early diagenetic system can be best described by a modeling approach that is based on chemical equilibrium thermodynamics together with reaction kinetics, which considers all coupled reactions and the fundamental principles of mass and charge balance (Arning et al., 2011). The modeling tool is the PHREEQC computer code which is a freeware from the USGS.

The model concepts include a multi-process, multi-component, and multiphase approach, and are based on chemical thermodynamics. The modeling concepts incorporate interdependent diagenetic reactions evolving into a diffusive mass transport system and are coupled to thermodynamic equilibrium calculations of species distribution. The reaction kinetics of organic carbon conversion is integrated into the set of equilibrium reactions by defining type and amount of converted organic matter at a given time step. The model set-up describes a growing sediment column. One-dimensional molecular diffusion of aqueous and gaseous species, compaction flow, as well as burial of solids, and aqueous species are considered ([Figure 2](#)).

### **From Science to Application: Examples from Case Studies**

The above-mentioned concept was applied to the biogenic methane gas field Atzbach-Schwanenstadt in the Austrian Molasse Basin (Schulz et al., 2009; Schulz and van Berk, 2009).

Free gas phases developed during early diagenetic methanogenesis in the ca. 700- m-thick Upper Puchkirchen Formation (Aquitania), and may have been trapped as gas hydrate (water depth 1000 m, bottom water temperature of about 4 °C). Due to basin subsidence and high sedimentation rates in a deep-sea fan environment, hydrate decay below the base of the gas hydrate stability zone (200–400 mbsf) occurred already still in the Aquitania, and thus, during or shortly after deposition of the Upper Puchkirchen Formation. The results from this test site enabled the development of a first tool to retrace the biogenic methane potential by analysis of diagenetic cement as a quantitative indicator in a “closed” system ([Figures 3](#) and [4](#)). Additionally, water salinity and hydrochemistry of the gas field may be applied in similar architectural elements of deepwater channels as tracers for fossil gas hydrate formation, because low chloride concentrations were the result from sediment compaction and dilution by pure H<sub>2</sub>O in closed systems due to gas hydrate dissociation.

To verify such findings, hydrogeochemical properties of recent marine test sites with biogenic methane formation have to be retraced in order to calibrate signals like alkalinity, pH, distribution of dissolved, mineral, and gaseous species including methane hydrate formation. Three different settings (well site 1246 of ODP Leg 204, Hydrate Ridge; Amazon fan; Peruvian shelf) have been investigated (Arning et al., 2011, 2012, 2013), and reveal the importance of sedimentation rate and AOM for the fate and behaviour of early formed methane. Furthermore, the results of the three settings show that the formation of diagenetic carbonates is an important storage mechanism for carbon in sediments ([Figure 5](#)).

Another geological feature for not only retracing methane formation, but also its prediction, is the application of these concepts to biogenic shale gas formation. The GASH project (Shale Gases in Europe) considered the question of whether sediments, among other things, still today act as kitchen for biogenic methane formation, and which processes would occur during production.

Interestingly, methanogenic microbes are still capable of consuming the organic matter in marine black shales up to a thermal maturity of around 2% vitrinite reflectance. These findings, from incubation experiments, indicate a shallow subsurface potential for biogenic methane. Infiltration of meteoric water may dilute the original total dissolved solids and may stimulate methanogenic microbes to “start their engine.” Especially if oil window maturity prevails, organic compounds from the bitumen may dissolve in the pore water and can be converted to biogenic methane.

### **Conclusions**

New concepts are being elaborated to numerically retrace the biogenic methane potential of marine sediments. These concepts are based on chemical thermodynamics and are also able to predict the biogenic methane phase behaviour as well as general gas composition, and coupled mineralogical changes. The application of the approach, furthermore, can help to predict early diagenetic processes in frontier regions.

### **Acknowledgements**

Samples and data for our research were provided by the Ocean Drilling Program (ODP), by Rohoel Aufsuchungs AG, and Petrobras. Financial support was provided by our industrial partners Devon Energy, Petrobras, and Total (and further GASH sponsors). Furthermore, Brian Horsfield (GFZ Potsdam) supported our work financially.

### **Selected References**

Arning, E.T., Y. Fu, W. van Berk, and H.-M. Schulz, 2011, Organic carbon remineralisation and complex, early diagenetic solid–aqueous solution–gas interactions: Case study ODP Leg 204, Site 1246 (Hydrate Ridge): *Marine Chemistry*, v. 126/1-4, p. 120-131.

Arning, E.T., W. van Berk, and H.-M. Schulz, 2012, Quantitative geochemical modelling along a transect off Peru: Carbon cycling in time and space, and the triggering factors for carbon loss and storage: *Global Biochemical Cycles*, v. 26/4, 18 p.

Arning, E.T., W. van Berk, E. Vaz dos Santos Neto, R. Naumann, R., and H.-M. Schulz, 2013. The quantification of methane formation in Amazon Fan sediments (ODP Leg 155, Site 938) by hydrogeochemical modeling solid – aqueous solution – gas interactions: *Journal of South American Earth Sciences*, v. 42, p. 205-215.

Clayton, C., 1992, Source volumetrics of biogenic gas generation, *in* R. Vially, ed., *Bacterial Gas*, Editions Technip, Paris, p.191-204.

Formolo, M.J., S.T. Petsch, A.M. Martini, and K. Nüsslein, 2008, A new model linking atmospheric methane sources to Pleistocene glaciation via methanogenesis in sedimentary basins: *Geology*, v. 36/2, p. 139–142.

Johnson, A. H., and M.D. Max, 2012, Could Gas Hydrate in Fine Grained Sediments be a Precursor for Some Shale Gas Deposits?(abstract): AAPG Search and Discovery Article #90142 (website accessed January 12, 2015) (<http://www.searchanddiscovery.com/abstracts/html/2012/90142ace/abstracts/john.htm>).

Lipp, J., Y. Morono, F. Inagaki, and K.-U. Hinrichs, 2008, Significant contribution of Archaea to extant biomass in marine subsurface sediments. *Nature*, v. 454, p. 991-994.

Max, M., and A.H. Johnson, 2012, Could gas hydrate in fine-grained sediments be a precursor for some shale gas deposits?: *Petroleum Geoscience*, v. 18, p. 231-238.

Schulz, H.-M., W. van Berk, A. Bechtel, U. Struck, and E. Faber, 2009, Bacterial methane in the Atzbach-Schwanenstadt gas field (Upper Austrian Molasse Basin), Part I: Geology. *Marine and Petroleum Geology*, v. 26/7, p. 1163-1179.

Schulz, H.-M., and W. van Berk, 2009, Bacterial methane in the Atzbach-Schwanenstadt gas field (upper Austrian Molasse Basin), Part II: Retracing gas generation and filling history by mass balancing of organic carbon conversion applying hydrogeochemical modelling: *Marine and Petroleum Geology*, v. 26/7, p. 1180-1189.

Zeikus, J.G., and M.R. Winfrey, 1976, Temperature limitation of methanogenesis in aquatic sediments: *Applied and Environmental Microbiology*, v. 31/1, p. 99-107.

# Biogenic methane formation

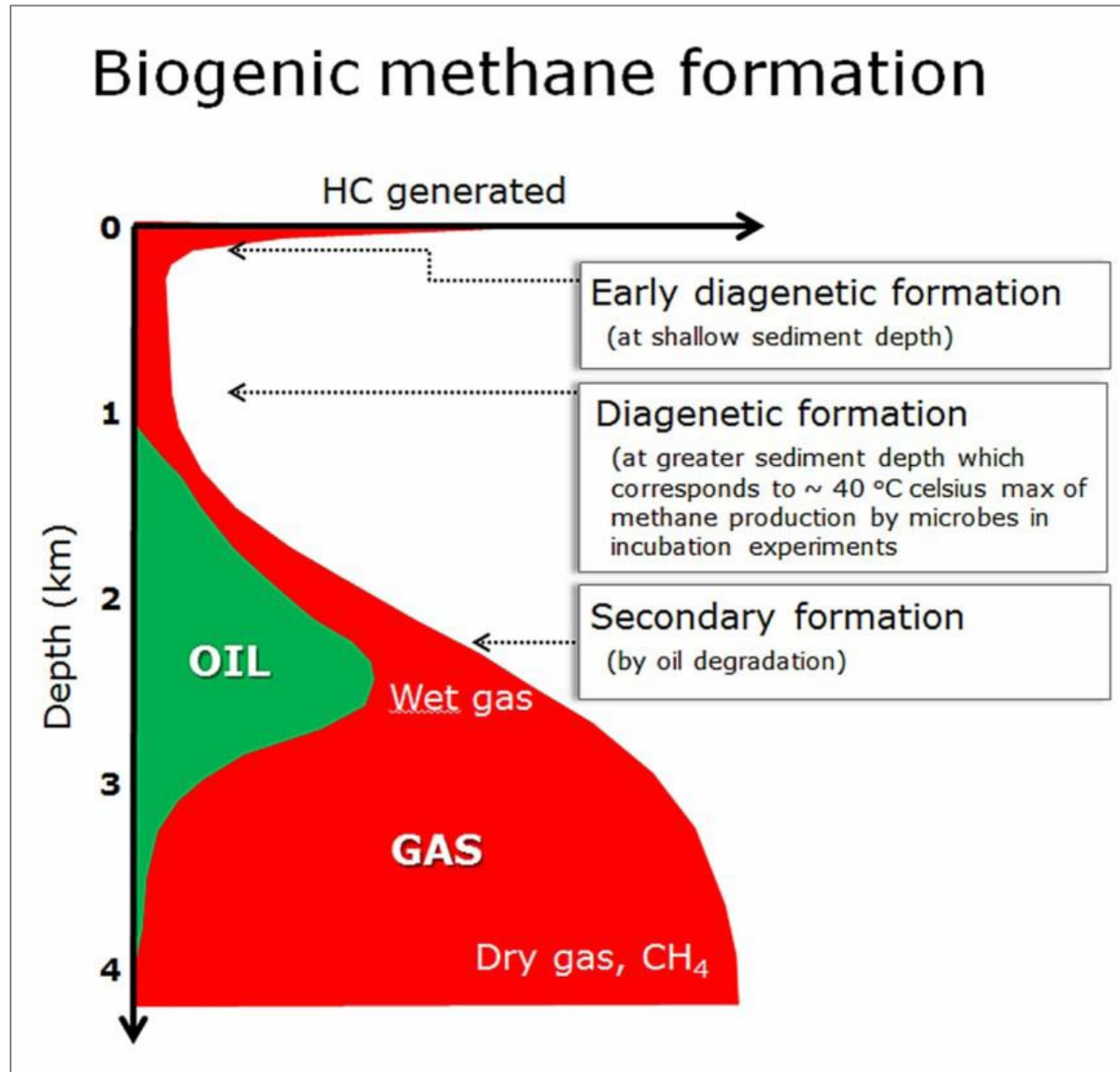


Figure 1. Biogenic methane forms at different depth, different thermal maturities of the organic matter (dissolved in aqueous solution or as bitumen), and as result of different processes.

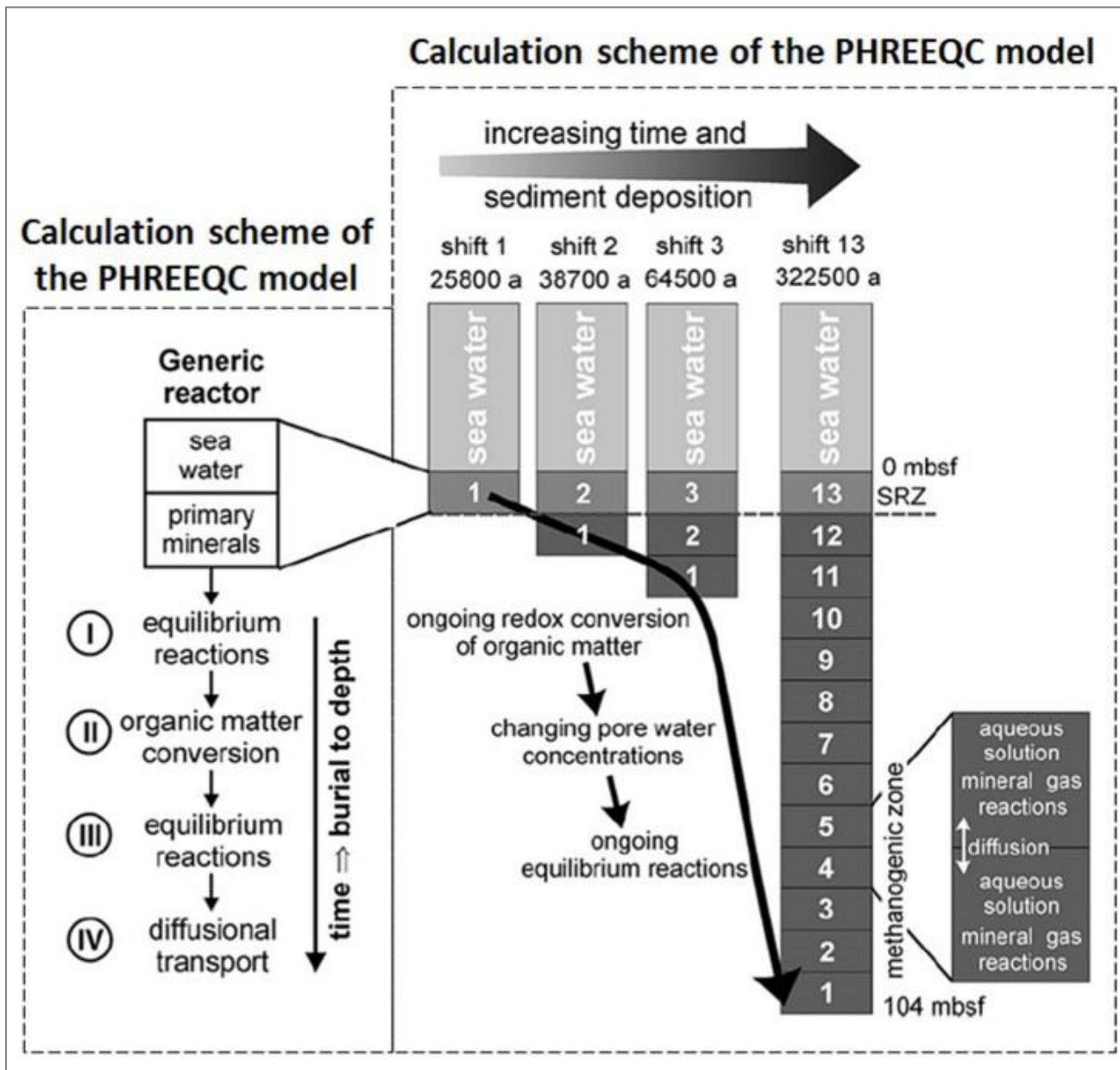


Figure 2. (Left) Calculation scheme of the PHREEQC model. (Right) Concept of the PHREEQC model. (Modified after Arning et al., 2011.)



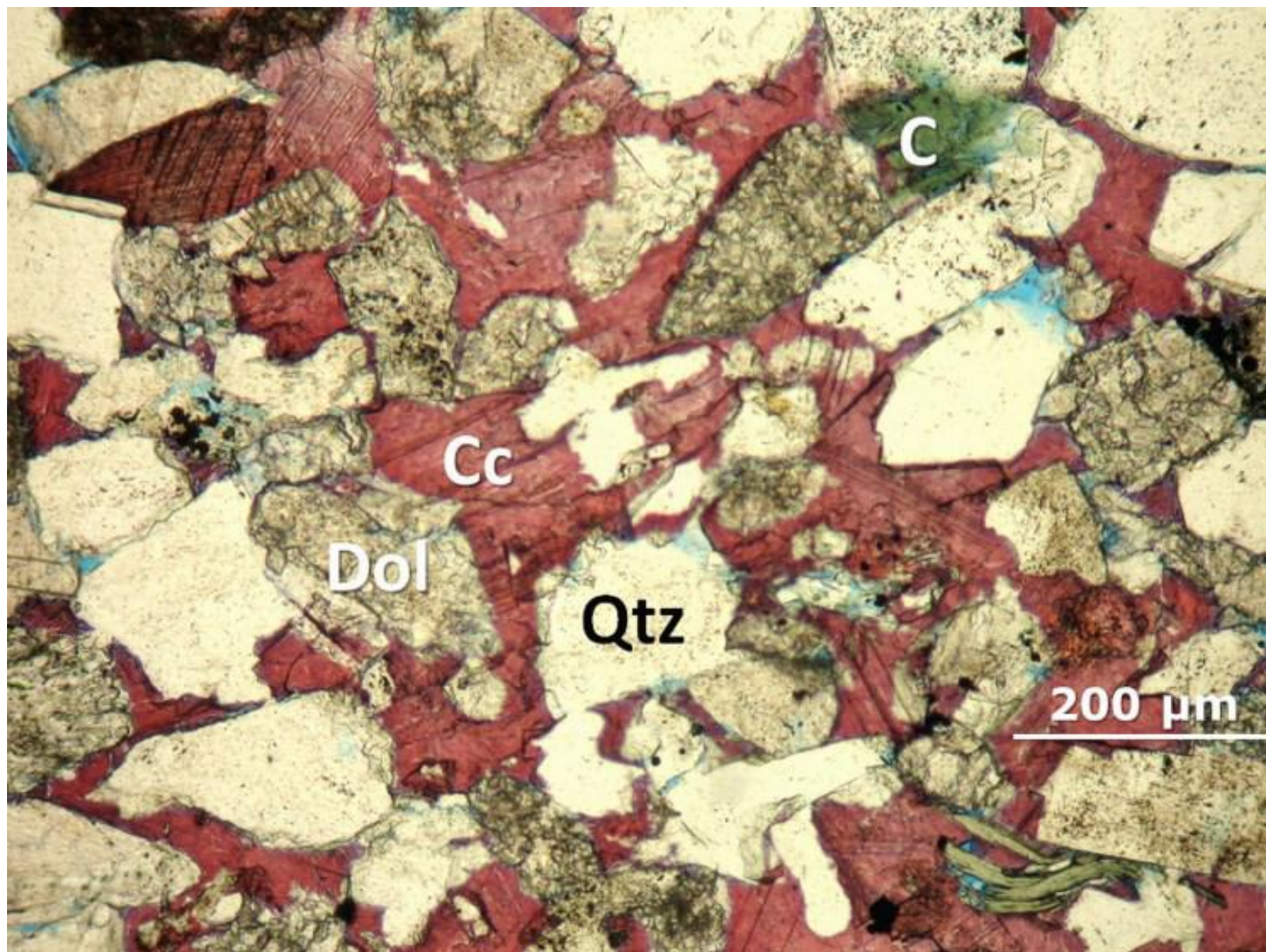


Figure 3. Thin section of a reservoir interval of the Puchkirchen Formation in the Austrian Molasse basin. Abbreviations: Cc: calcite, Dol: dolomite, Qtz: quartz, C: chlorite. Porosity (blue).



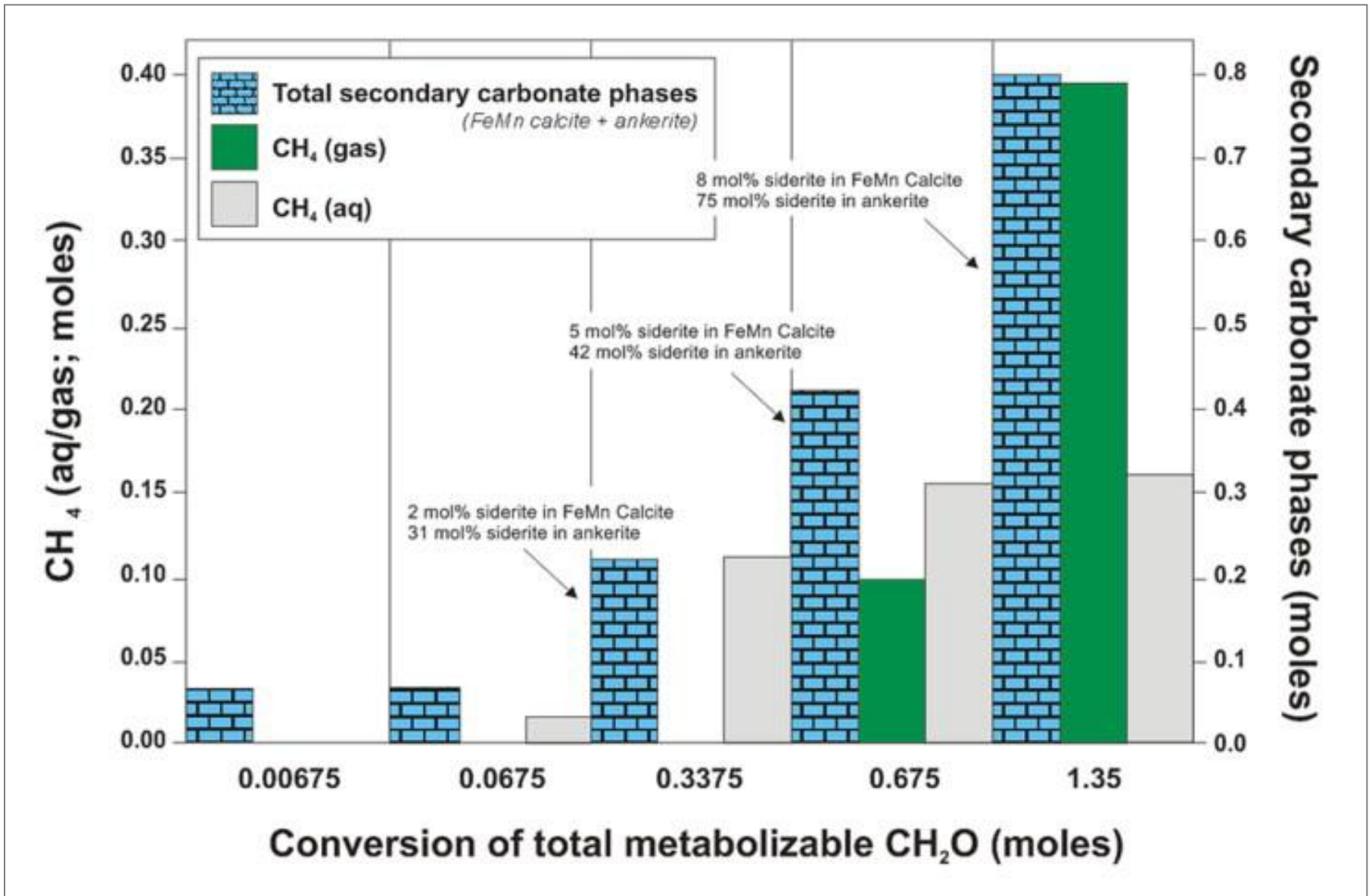


Figure 4. Modelled secondary carbonate phase precipitation and methane generation (aq/gas) in dependence on the conversion of different contents of metabolizable organic matter CH<sub>2</sub>O source. (Modified after Schulz et al., 2009).

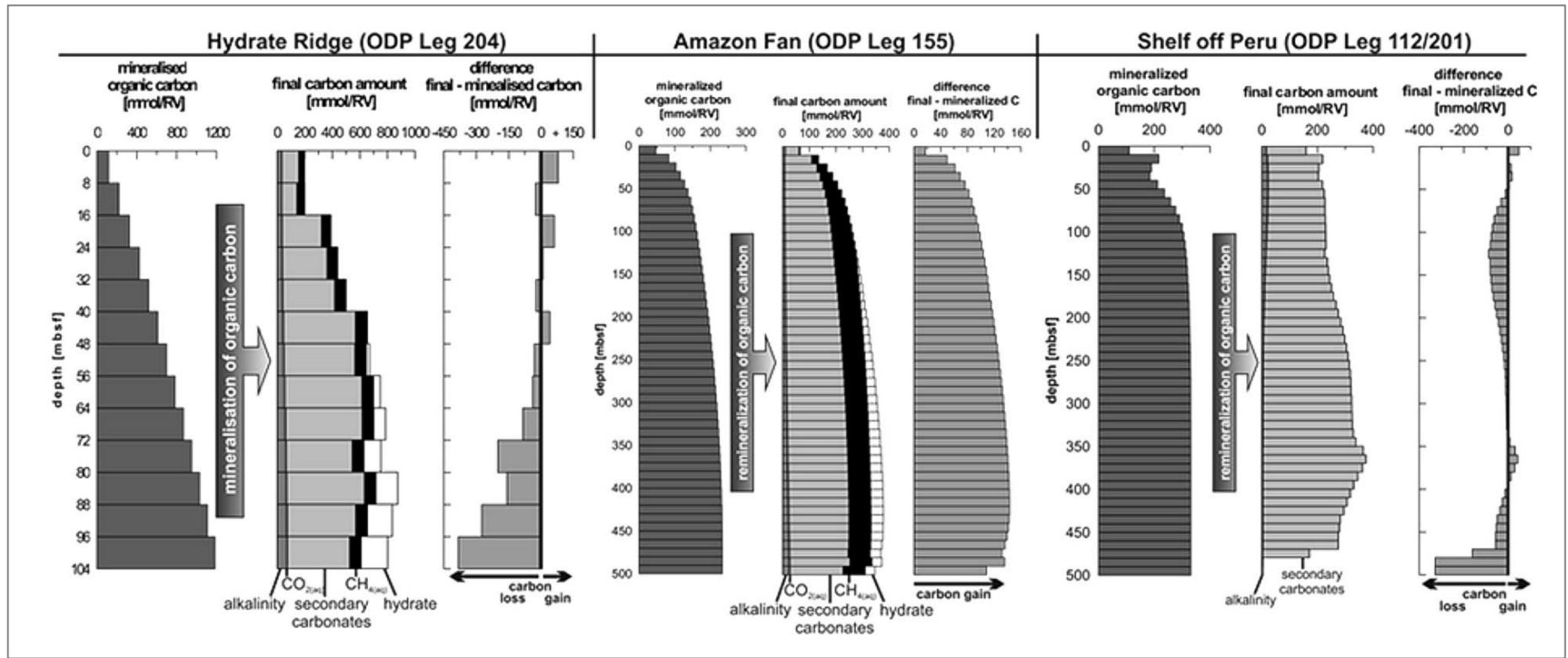


Figure 5. Carbon mass balance calculations of test sites Hydrate Ridge (ODP Leg 204), Amazon Fan (ODP Leg 155), and Shelf off Peru (ODP Leg 112/201).