Natural Gas Hydrates Update 1998-2000

by

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Significant events have transpired on the natural gas hydrate research and development front since "Future Supply Potential of Natural Gas Hydrates" appeared in *Natural Gas 1998 Issues and Trends* and in the Potential Gas Committee's 1998 biennial report.[1]

- The United States established an expanded, centrally coordinated natural gas hydrates research program.
- The first integrated scheme for commercial production of oceanic natural gas hydrates was granted a U.S. patent.
- The Third International Conference on Gas Hydrates was a resounding success.
- Of the several countries that now have gas hydrates research programs, Japan in particular has been resolutely forging ahead, especially on the drilling front.
- The past two years have witnessed increased research emphasis on the long-term environmental implications of worldwide natural gas hydrate occurrence.

U.S. Government Actions

Research Authorization Process Completed

The Methane Hydrate Research and Development Act of 2000, initiated as Senate Resolution 330 on January 1, 1999, and as House Resolution 1753 on May 11, 1999, became Public Law 106-193 on May 2, 2000.

The Act requires the Secretary of Energy to establish a program of methane hydrate research in consultation with the Secretaries of Commerce, Defense, and Interior and the Director of the National Science Foundation. It empowers the Secretary to award competitive merit-based grants or contracts to institutions of higher education and industrial enterprises, or to establish cooperative agreements with these entities, for the purposes of:

- conducting basic and applied research to identify, explore, assess, and develop methane hydrate as a source of energy;
- assisting in the development of technologies required for efficient and environmentally sound development of methane hydrate resources;
- undertaking research programs to provide safe means of transport and storage of methane produced from methane hydrates;
- conducting basic and applied research to assess and mitigate the environmental impacts of hydrate degassing (including both natural degassing and degassing associated with commercial development);
- developing technologies to reduce the risks of drilling through methane hydrates; and
- conducting exploratory drilling in support of these activities.

[1] Similarly, portions of this document also appear at the end of the Natural Gas Hydrates section of *Potential Supply of Natural Gas in the United States, Report of the Potential Gas Committee, December 31, 2000*, Potential Gas Agency, Colorado School of Mines, Golden CO, April 2001, pp.43-62.

The Act requires the Secretary of Energy to establish an appropriate expert advisory panel comprising no more than 25 percent Federal membership, ensure that appropriate partnerships are formed, ensure that basic data and information are developed and widely disseminated, and ensure Federal inter-agency cooperation. Various reporting requirements are specified, including the forwarding of a National Academy of Science study of the program to Congress by September 30, 2004.

The Act also amends the Mining and Minerals Policy Act of 1970 (30 U.S.C. 1901) to include methane hydrates as marine mineral resources for the purposes therein, such as the leasing of Federal offshore mineral rights.

The Act authorizes appropriation to the Secretary of Energy of:

$ 5.0 million for fiscal year 2001,
$ 7.5 million for fiscal year 2002,
$ 11.0 million for fiscal year 2003,
$ 12.0 million for fiscal year 2004, and
$ 12.0 million for fiscal year 2005,

for a total authorization of $ 47.5 million over 5 years. Absent renewal, the Act sunsets at the end of fiscal year 2005.

Status of Appropriations

The Congress appropriates actual as opposed to authorized funds in the course of annually establishing agency-by-agency budgets. Notwithstanding previously authorized amounts, appropriated funds can vary from zero to the maximum previously authorized for that year.

For fiscal year 2001 the Department of Energy's (DOE) Office of Fossil Energy has $10 million to devote to its natural gas hydrates research program, representing the sum of funds expressly appropriated for this purpose under the Act and other funds usable for this purpose that are included elsewhere in the Office's budget. Amounts that may be appropriated for subsequent fiscal years are presently unknown.

Fiscal Year 2000 DOE Gas Hydrate Research Grants

Pursuant to its general mandate, the Office of Fossil Energy awarded four fiscal year 2000 research grants that pertained to natural gas hydrates. The University of Mississippi's Center for Marine Resources and Environmental Technology received $650,000 for a 12-month study of natural gas hydrate mounds and hydrocarbon vents in the Gulf of Mexico. The study will use a remotely controlled, multi-sensor, ocean-bottom monitoring station for continuous observation of sea floor stability.

Clarkson University received $261,944 for a 36-month project that will use a multi-phase flow laboratory to investigate the conditions that cause gas to dissociate from in-situ natural gas hydrates. Computational models will be developed to predict the rate of gas pressure buildup during drilling and the way that gas and water flow in a gas hydrate reservoir as the hydrate dissociates.

As part of a joint Department of Energy-National Science Foundation initiative to improve three-dimensional (3D) seismic images of oceanic hydrate deposits, $ 199,475 was awarded to the University of Wyoming, which will partner with the Texas Institute of Geophysics to image natural gas hydrates on the Blake Ridge off South Carolina using an array of ocean-bottom seismometers. The objective of the 36-month project is to determine the linkage between hydrate concentrations and seismic characteristics.

The Texas Bureau of Economic Geology was awarded $700,000 in support of a 2-year, $880,000 project to study gas hydrate occurrence in the Gulf of Mexico using state-of-the-art multi-component ocean bottom cable 3D seismic methods. The objective of this study is to image the sediments and their hydrate content in fine detail so as to determine how the hydrates and rock types are distributed and structurally organized, determine the pore content of the imaged hydrate-bearing sediments, and ascertain the mechanical strength of the hydrate-bearing sediments.

Fiscal Year 2001 DOE Gas Hydrate Research Grants

Through December 2000, four small proposals arising from a competition among DOE's national laboratories have been funded via the National Energy Technology Laboratory, which will coordinate the work among the laboratories.

Brookhaven National Laboratory received $75,000 to study the structure, chemical bonding, thermodynamics, and kinetics of gas hydrates and the formation thereof in both natural and synthetic samples. This project also seeks to investigate the rate of hydrate formation, to estimate the methane content of "an average hydrate," and to evaluate perflourocarbon tracers for suitability in tracking methane production.

Lawrence Berkeley National Laboratory received $200,000 for a project to integrate geology, geophysics, and gas reservoir simulation methods using enhanced numerical codes to produce geological models of four gas hydrate deposits representative of both permafrost and marine environments.

Lawrence Livermore National Laboratory received $120,000 to study the mechanical behavior of synthetic hydrates and of controlled mixtures of hydrates and sediments simulating natural occurrences, with correlation to existing laboratory and sea floor measurements. This project is primarily aimed at sea floor stability and safety.

Oak Ridge National Laboratory received $75,000 to apply its Sea-floor Process Simulator to the simulation of natural environments associated with oceanic gas hydrate deposits. This project will involve the evaluation of technologies for the discovery of hydrate deposits, the determination of the deposits' mass and energy flux, the determination of the effects of hydrates on sea floor stability, and the examination of methane recovery through dynamic flow experiments. The other national laboratories will also use this simulator in their work.

First U.S. Patent for an Integrated Hydrate Production Method Granted

On September 14, 1999, the Department of Commerce granted U.S. Patent 5,950,732 to the Syntroleum Corporation (assignee) for a "System and method for hydrate recovery." The patent covers an integrated system for the recovery of *liquid* hydrocarbons from oceanic natural gas hydrates. It includes a vessel, a vessel positioning subsystem, a recovery subsystem coupled to the vessel for the delivery of hydrates from the ocean floor to the vessel, an on-board gas-to-liquids conversion subsystem (Fischer-Tropsch process), and a liquids storage and removal subsystem. The patent also covers a method of recovering hydrates from the ocean floor. It makes 19 claims of invention in respect to various parts of the production system as well as the whole system, including the use of excess power generated by the gas conversion subsystem in the hydrate recovery subsystem.

The patented recovery subsystem utilizes a flexible and/or articulated riser which may contain a gas supply conduit and/or a liquid injection conduit and/or electrical supply cables plus a gas-lift production conduit. The riser is connected to a sea-floor-positioned "tent-like" collector unit "formed of conductive portions for creating an electrical current across the hydrates" and/or "with a plurality of heating elements" and/or "an agitator unit for stirring up the hydrates."

The Syntroleum system would likely have very limited application because it is oriented to the recovery of exposed hydrates, whereas the vast bulk of oceanic hydrates occur within the sediment column well below the sea floor. Nonetheless, it *is* the first system ever patented for oceanic natural gas hydrate recovery.

The Third International Conference on Gas Hydrates

The Third International Conference on Gas Hydrates was held in Salt Lake City, Utah in July 1999. About 370 persons attended from all regions of the globe, far in excess of the organizers' initial expectation of 100-125 attendees. Forty-seven formal papers were non-concurrently presented over four days. Ten dealt with resource characterization, 7 with global climate change, 5 with production, 8 with transportation and offshore hydrate engineering, 9 with properties of hydrates, and 8 with a miscellany of hydrate-related matters.

Ninety-six poster papers were also presented in free-form afternoon sessions. Seventeen dealt with resource characterization, 2 with climate change, 3 with transportation, 30 with general aspects of hydrate technologies, 7 with specific hydrate technologies, and 34 with properties of hydrates. This was one of those all-too-rare conferences where the poster papers were every bit as important, interesting, and challenging as the formal ones were. The vast majority of papers in both categories represented the application of science and engineering at its best. Japan will host the fourth conference in Yokohama in May, 2002.

Other National Programs

In addition to the United States and Japan, Russia, India, Norway, Germany, and Canada have now established active natural gas hydrate research programs. Cooperative efforts among them are common.

Japan

The Japanese five-year program, previously detailed in the 1998 Potential Gas Committee report, is arguably the most advanced. Beyond laboratory-based research and cooperative work with the Ocean Drilling Program, Japan's is the only program that has drilled gas hydrate research wells to-date. These efforts, which included some participation by Canada and the United States, are discussed below in the Research Drilling section.

India

At the behest of Prime Minister Atal Vajpayee, in March 1999 the Indian government charged an expert group with the task of making comprehensive recommendations regarding India's energy future. One of the recommendations offered in the resulting report was "... to tap unconventional sources of natural gas like coal bed methane, natural gas hydrates, underground coal gasification, etc."

The advisory group set a medium-term objective of establishing an effective organizational structure to facilitate progress in the National Gas Hydrates Program sponsored by the Gas Authority of India Limited. It also set a long-term objective of exploiting India's oceanic natural gas hydrate resources. For this purpose the group recommended expenditure of $47.1 million allocated among the following phases:[2]

Phase – I	Examine existing geological, geophysical data – $2.2 million
Phase – II	Acquisition and processing of seismic data – $8.4 million
Phase – III	Stratigraphic drilling, coring 3 to 5 wells -- $3.3 million
Phase – IV	Drilling and completion of 3 to 5 wells – $33.2 million

[2]Calculated at the August 6, 2000, exchange rate.

A comprehensive report has subsequently been prepared by the National Geographic Research Institute identifying the areas most suited for hydrate prospecting based on existing geological, geochemical, and seismic data. An initial gas hydrate resource map of India has also been prepared by the National Institute of Oceanography based on existing data such as bathymetry, seabed temperature, heat flows and geothermal gradient, sediment thickness, and sediment total organic carbon content. The map will be updated continuously as new data are acquired and existing information and techniques are refined.[3]

On the basis of these initial efforts two areas have been singled out for additional study. The first is to the west in the Arabian Sea off the Mumbai (Bombay) coast. The second is located to the east off Calcutta, south of the Bengal Delta.[4]

Germany

While small-scale research on gas hydrates has been conducted in Germany for many years, it has mainly been ancillary to larger investigations of either geologic structure and history or long-term climatic changes. Now, however, specific gas hydrate-directed efforts at a larger scale have been initiated for the first time.

In February 1999, a strategy paper for natural gas hydrates research was developed at a national meeting hosted by the GEOMAR Research Center. It is very similar to the one adopted by the United States.[5]

Later in 1999 the Deutsche Forschungsgemeinschaft (DFG; German Research Foundation, the central public funding organization for academic research), set an overall 10 to 15 year budget of 500 million DM (about $219 million US) for application in 13 research themes, one of which was gas hydrates research.

In 2000, the Bundesministerium für Bildung und Forschung (BMBF; Federal Ministry for Education and Research) created a "Gas Hydrates in the Geosystem R&D Center" in recognition of the important role of gas hydrates in the carbon cycle as regards sea-floor stability and particularly climatic development. Three multi-research center projects to be coordinated by the GEOMAR Research Center for Marine Geosciences (Kiel), valued at 15.4 million DM (about $7 million US), were subsequently awarded in response to a request for proposals. Over three years, this sum appears to represent about half of all presently scheduled German gas hydrate research R&D funds.

Research Drilling

Permafrost Terrain Deposits[6]

In late March 1998, a consortium of the Japan Petroleum Exploration Company (JAPEX) and Japan National Oil Corporation (JNOC)[7] and the Geological Survey of Canada (GSC) finished drilling a permafrost terrain gas hydrate research well on the crest of the Beaufort-Mackenzie Basin’s Mallik Anticline, located directly adjacent to the Beaufort Sea at Richards Island. Of the 150 wells drilled in the Beaufort-MacKenzie Basin through 1999, 27 wells encountered natural gas

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[3] *Report of the Group on India Hydrocarbon Vision - 2025* at <http://pmindia.nic.in/pminitatives/hydro.htm>.

[4] Anon. *Petro substitutes – Goa scientists step up hunt* at <http://www.indian-express.com/ie/daily/19990313/ige1305p.html>>

[5] E. Seuss and J. Thiede, eds., "Gas hydrates in the Earth’s system - A strategy for research," via the link to gashyd_eng.pdf located at http://www.kfa-juelich.de/beo/fmeeresp.htm

[6] For complete information see S.R. Dallimore, T. Uchida, and T.S. Collett, eds, *Scientific Results from JAPEX/JNOC/GSC Mallik 2L-38 Gas Hydrate Research Well, Mackenzie Delta, Northwest Territories, Canada*, Geological Society of Canada Bulletin 544, 1999.

[7] As backed by the Japanese Ministry of International Trade and Industry (MITI).

hydrate deposits which in the majority of cases (15) are known to be associated with underlying conventional hydrocarbons.[8]

The Mallik structure is a southeast-trending anticline truncated by large-scale listric down-to-the-basin faults. Drilled in 39 days at a location 328 feet distant from the Mallik L-38 well which was drilled and abandoned by Imperial Oil in 1972, the JAPEX/JNOC/GSC Mallik 2L-38 research well reached a total depth of depth of 8,281 feet. It fully penetrated the permafrost zone in the interval from 0 to approximately 2,100 feet, the anticline's laterally continuous and approximately 20 square mile gas hydrate zone in the interval from 2,494 to 3,836 feet, and the immediately underlying 5-foot-thick free-gas zone. The hydrate and free-gas zones occur in the Late Eocene/Oligocene age Kugmallit Sequence which primarily consists of deltaically deposited coarse-grained sandy sediments with fine-grained silty sediment interbeds in the upper portion and infrequent gravel interbeds in the lower portion where most of the hydrate is located.

Well logging included a high resolution laterolog (deep and shallow resistivity log), an induction log, a sonic log, a neutron log, a gamma ray log, and full wellbore imaging. A vertical seismic profile was also obtained. Within the 693-foot-thick hydrate zone the well logs indicated that 361 feet of hydrate-bearing sediment were encountered. Core runs were made in the 2,940 to 3,123 foot interval using four different types of core barrels. Average core recovery was 42 percent.[9]

The encountered gas hydrate was predominantly Structure I hydrate occurring as fine grains (less than 2 millimeters, or 0.07 inch, in diameter) which filled the pore spaces within framework-supported sands and pebbly sands. Rare thin veins and clasts (1 to 2 millimeters, or up to 0.07 inch, thick) or nodules up to 0.5 millimeter (0.02 inch) in diameter were also observed, while the largest observed manifestation consisted of 2-centimeter (0.8 inch) diameter nodules forming the matrix of a granular sand at a depth of 2,995 feet. The composition of most gas samples was pure methane, although some samples contained up to 2 percent propane and/or carbon dioxide. The isotopic composition of the gas indicated a thermogenic origin. The porosities of the hydrate zone sediments averaged 34 percent, while the gas hydrate saturations averaged 64 percent. Assuming that the hydrate zone is laterally continuous, the surrounding square mile contains about 366 billion cubic feet of methane.

A delay of 8 days beyond the intended operations schedule owing to a combination of adverse weather and mechanical/electrical problems resulted in cancellation of the planned production testing. However, the two closed-chamber production tests conducted earlier by Imperial Oil in the neighboring Mallik L-38 well, which had very similar porosity and gas hydrate saturation within the hydrate zone, showed (a) little gas flow from the tested hydrate zone interval, presumably owing to very low permeability of the gas hydrate-filled pore structure, and (b) a potential for high production rates from the underlying free-gas zone.

A larger research consortium plans to drill a second gas hydrate test well on the Mallik structure in January to March 2002. Flow testing is the principal objective. As this is being written, the consortium consists of JNOC and its subsidiaries, the Geological Survey of Canada, the United States Geological Survey, the U.S. Department of Energy, and GeoForschungsZentrum-Potsdam (GFZ; "GeoResearchCenter"). It appears likely that other entities will join the consortium by the spud date, possibly including one or more industry firms.

[8] J. Majorowicz and P. Hannigan, "Stability Zone of Natural Gas Hydrates in a Permafrost-Bearing Region of the Beaufort-Mackenzie Basin: Study of a Feasible Energy Source," *Natural Resources Research*, v. 9, no. 1, March 2000.

[9] The experimental core barrel designed to retrieve *in situ*-pressured samples unfortunately failed to seal properly.

Oceanic Deposits

On November 19, 1999, under contract to Japan National Oil Corporation on behalf of itself, the Japanese Ministry of International Trade and Industry (MITI), and a consortium of 10 other firms,[10] the semi-submerisble drilling vessel *M. G. Hulme, Jr.* began gas hydrate research drilling operations in about 3,100 feet of water in the western Nankai Trough approximately 37 miles off Honshu's Omae Zaki peninsula.

The Nankai Trough is located at the convergent margin of the Philippine and Eurasian plates where the former is subducting under the latter at an approximate 10 degree angle and a rate of about 4 centimeters (1.6 inches) per year. The trough is almost completely closed. Along its western (landward) margin lies a thick accretionary wedge (or prism) composed of turbidite trench fill primarily sourced from the Japan Alps and hemipelagic sediments sourced from the Shikoku Basin on the Philippine plate.[11] [12] Widespread occurrence of natural gas hydrates in the inner trench slope is inferred from the existence of a high-amplitude bottom simulating reflector (BSR) in the excellent seismic data that are available.[13] Several direct local confirmations of gas hydrate occurrence have been obtained in the trough by the Ocean Drilling Program (ODP) and the Japanese research drilling.

Two pilot holes were drilled to 5,249 feet, followed by the 10,827-foot-deep main research well, and then by two 4,101-foot-deep post wells. A special pressure-and-temperature-maintenance core barrel was the primary tool used to retrieve core samples in the main hole and in the second post well. For all but the first pilot hole, data were recorded from both logging-while-drilling tools (including density, neutron, dual induction, and azimuthal laterolog) and open hole wireline logging tools (including dipole shear and compressional wave slowness, laterolog, and nuclear magnetic resonance).[14] [15]

The BSR at the research site is positioned about 984 feet below the sea floor. All wells penetrated the BSR. Visible hydrates in the retrieved cores and chlorine anomalies in the interstitial waters indicate that gas hydrates are present in three discreet intervals that are located between 656 and 885 feet beneath the sea floor and range in thickness from 3 to 33 feet.[16] The hydrate occurs as intergranular pore fill in otherwise permeable sand layers which are interbedded with shales. Whereas a pre-drill modeling exercise had predicted a hydrate saturation of 10 to 25 percent,[17] preliminary post-drilling analysis

[10]Dennis Normile, "Ocean Project Drills for Methane Hydrates," *Science*, v. 286, November 19, 1999, p. 1456.

[11]Y. Aoki, et al., "Methane Hydrate Accumulation along the Western Nankai Trough," in *Gas Hydrates: Challenges for the Future*, Annals of the New York Academy of Science, v. 912, 2000, pp. 136-145.

[12]Y. Saito, et al., "Margins Source-to-Sink Experiment (Allied Site) Central Japan," at <http://web.missouri.edu/~geoscmbu/Nankai-toyama.html>.

[13]R. Matsumoto, untitled abstract, 2000 AAPG International Conference & Exhibition, at <http://aapg.confex.com/aapg/ba2000/techprogram/paper_4663.htm>.

[14]T. Uchida, et al., "Japan's Efforts to Explore Marine gas Hydrates off Tokai at the Nankai Trough and Their Occurrences," abstract, 2000 Western Pacific Geophysics Meeting, American Geophysical Union.

[15]K. Tezuka, et al., "Well Log Evaluation of Gas Hydrate Saturation in the MITI Nankai Trough Well Drilled Offshore Tokai," abstract, 2000 Western Pacific Geophysics Meeting, American Geophysical Union.

[16]A. Waseda, et al., "Origin of Methane in Gas Hydrates form the MITI Nankai Trough Well," abstract, 2000 Western Pacific Geophysics Meeting, American Geophysical Union.

[17]Y. Aoki, et al., "Methane Hydrate Accumulation along the Western Nankai Trough," *Gas Hydrates: Challenges for the Future*, Annals of the New York Academy of Sciences, vol. 912, 2000, pp. 136-145.

revealed saturations of 60 to 90 percent.[18] A pressure profile was run on the well, but flow testing was not attempted.

Increased Research Emphasis on the Environmental Implications of Gas Hydrates

Aside from their possible future energy supply potential, the role that Earth's natural gas hydrate deposits appear to have played over the long term as respects major changes of global climate has become a substantially more prominent focus of both researchers and policy-makers in the past two years. Thus far, this has happened without observable detriment to the examination of their future gas supply potential.

An ever-growing body of evidence continues to bolster the hypothesis that massive *natural* releases of methane from natural gas hydrate deposits have had major effects on Earth's climate -- and thereby on its biota -- more than once in the geologic past. Based on high-resolution carbon isotope records obtained from benthic foraminefera tests retrieved in cores at Ocean Drilling Program (ODP) Site 690 on the Maud Rise in the South Atlantic's Weddell Sea off Antarctica[19] and at ODP Site 865 on Alison Guyot in the Equatorial Pacific,[20] Dickens, et al.,[21] hypothesized in 1997 that the mass extinction of from half to two-thirds of all benthic marine fauna which occurred at the Paleocene/Eocene boundary (55 million years before the present, or 55 Ma BP) was caused by a massive and abrupt release of methane from natural gas hydrate deposits worldwide. Neither terrestrial biota nor marine biota living near the ocean surface were affected during this event and benthic species tolerant of low oxygen levels continued to flourish while detrital shells composed of calcium carbonate dissolved. This suggests a decrease in the availability of oxygen at and near the ocean floor as well as increased acidity and therefore dissolved carbon dioxide concentration. It was found that the isotopic proportion of ^{18}O in the foraminifera tests decreased dramatically, indicating that the deep waters had warmed from 11^{o} C. to 14^{o} C. in just 1,000 years. It was also found that the organic content of rocks across the Paleocene/Eocene boundary exhibited a sudden increase of ^{12}C (so-called "light carbon") relative to ^{13}C, meaning that whatever had occurred had rapidly altered the isotopic composition of the global carbon cycle, affecting some 40 trillion tons of carbon in less than 10,000 years.[22] Inasmuch as light carbon typically has an organic origin, fossil fuel combustion is today's usual source of ^{12}C ... but this event happened 55 Ma prior to the Industrial Revolution! Carbon dioxide exhalations from volcanos or hydrothermal vents had to be ruled out as the cause because had the mantle at that time contained a proportion of ^{12}C comparable

[18] R. Matsumoto, untitled abstract, 2000 AAPG International Conference & Exhibition, at <http://aapg.confex.com/aapg/ba2000/techprogram/paper_4663.htm>.

[19] J.P. Kennett and L.D. Stott, "Abrupt deep sea warming, paleoceanographic changes and benthic extinctions at the end of the Paleocene," *Nature*, v. 353, 1991, pp.319-322.

[20] T.J. Bralower, et al., "Late Paleocene to Eocene paleooceanography of the equatorial Pacific Ocean: Stable Isotopes Recorded at Ocean Drilling Program Site 865, Allison Guyot," *Paleoceanography*, v. 10, 1995, pp. 841-865.

[21] G.R. Dickens, M.M. Castillo, and J.G. Walker, "A blast of gas in the latest Paleocene: Simulating first-order effects of massive dissociation of oceanic methane hydrate", *Geology*, v. 25, n.3, 1997, pp.259-262.

[22] Or, as some prefer to put it, a sudden decrease of ^{13}C relative to ^{12}C.

to today's level, the required exhalation rate would have been a highly unlikely two orders of magnitude larger than the average rate over the past billion years. Wetlands, then about three times more prevalent than today, also proved to be too small a source. By elimination, what was left as a possible cause was the massive decomposition of oceanic natural gas hydrates triggered by rapid warming and/or depressurization at the sea floor.

Bains, et al.,[23] subsequently provided a refined oxygen and carbon isotopic record of this event as evidenced in sediments at ODP Site 1051B (Blake Nose in the western North Atlantic off North Carolina) and ODP Site 690B (Maud Rise). Their data show multiple methane injections which approximately sum to the total injection requirement previously calculated by Dickens, separated by intervals during which the carbon cycle was in stasis. The correlation of individual injection events between the two sites further suggests that hydrate decomposition was a global rather than just a local or regional occurrence.

Katz, et al.,[24] provided additional strong evidence for this event based on a core also retrieved at ODP Site 1051 (Blake Nose) which has an unusually thick event section deposited on the lower continental slope. The core contains mud clasts which, in association with seismic evidence of sediment failure, lend credence to the sudden gas hydrate decomposition hypothesis. Approximately 55 percent of all forameniferal taxa disappeared at this site during the event, with about 60 percent of the loss occurring immediately after the carbon isotope excursion. Oxygen isotope data indicate a bottom water temperature increase on the continental slope of more than 6^{o}C. within a period of 5,000 to 7,000 years.

Additional support for the short time interval of methane injection was provided by a study of the same core conducted by Norris and Röhl.[25] Using rapid, periodic variations of iron content in the sediment column that correspond to the 21,000 year wobble of Earth's axis which causes climate and thus sediment composition to alter, they found that two-thirds of the total methane injection was released in a few thousand years or less. The abrupt release and oxidation of a large mass of methane and subsequent dispersion of the resultant carbon dioxide into various carbon reservoirs is the only known mechanism that can explain the sudden, extreme, global nature of the Paleocene/Eocene boundary carbon isotope excursion.

What ultimately caused this and similar methane releases that were or may have been involved in mass extinction events [for example, those which occurred at the Permian/Triassic boundary (251 Ma BP),[26] at the Triassic/Jurassic boundary (200 Ma BP), during the Early Jurassic Toarcian (183 Ma BP)[27], during the Early Cretaceous mid-Aptian (116 Ma BP),[28] at the Cenomanian/Turonian boundary (91 Ma BP), and at the Cretaceous/Tertiary boundary(65 Ma BP)], as well as just how frequently such events have occurred, are now the subject of intense conjecture and

[23]S. Bains, R.M.S. Corfield and R.D. Norris, "Mechanisms of Climate Warming at the End of the Paleocene," *Science*, v. 285, July 30, 1999, pp. 724-727.

[24]M.E. Katz, D.K. Pak, G.R. Dickens, and K.G. Miller, "The Source and Fate of Massive Carbon Input During the Latest Paleocene Thermal Maximum," *Science*, v. 286, November 19, 1999, pp. 1531-1533.

[25]R. Norris and U. Röhl, "Carbon cycling and chronology of climate warming during the Paleocene/Eocene transition", *Nature*, v. 401, October 21, 1999, pp.775-778.

[26]Y.G. Yin, et al., "Pattern of Marine Mass Extinction Near the Permian-Triassic Boundary in South China," *Science*, v. 289, July 21, 2000, p. 432-436. S.A. Bowring, et al., "U/Pb Zircon Geochronology and Tempo of the End-Permian Mass Extinction," *Science*, v.280, May 15, 1998, pp. 1039-1045.

[27]S.P. Hesselbo, et al., "Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event," *Nature*, v. 406, July 27, 2000, pp. 392-395.

[28]A.H. Jahren and N.C. Ahrens, "Methane Hydrate Dissociation Implicated in Aptian OAE Events," abstract, 1998 GSA Annual Meeting, Toronto, Ontario, Canada, agenda p. 23.

research.

It is likely that additional instances will be discovered in the geologic record since large volumes of oceanic natural gas hydrates have almost certainly existed since the Silurian Epoch (from 438 to 408 Ma BP), by which time terrestrial flora were abundant and humic organic detritus was therefore available to be washed into the ocean and deposited on the continentalshelves, slopes, and rises, augmenting the indigenous sapropelic source material.[29]

The possible causative mechanisms offered thus far for one or more of these events include association with Earth's precessional frequency,[30] occurrence of a very large explosive volcanic event, the non-explosive extrusion of massive flood basalts, a large bolide impact, lateral pressure equilibration of the fluids in permeable sediments, and various combinations thereof, most or all leading to slope failure and consequent unroofing of natural gas hydrate deposits located on the continental slope and rise. As Richard Kerr accurately noted, "Sorting out cause and effect in curious coincidences as old as 250 million years is going to be a challenge ..."[31]

Nonetheless, it now seems that the production of gas from oceanic natural gas hydrate deposits when and where possible would not only enhance energy supply but would also serve to progressively mitigate a long-term environmental hazard that is associated with major global consequences. Speculation along these lines has, in fact, already begun to appear in print.[32]

[29] They may even have existed in the preceding Ordovician and Cambrian Epochs inasmuch as some of the sediments deposited then have a high organic content.

[30] N. Fiet, "Calibrage temporel de l'Aptian et des sous-ètages associès par une approche cyclostratigraphhique appliquèe á la série péligique de Marches-Ombrie (Italie centrale)," Bull. Soc. géol, France, 2000, t. 171, n. 1, pp.103-113.

[31] R. Kerr, "Did Volcanoes Drive Ancient Extinctions?", Science, v. 289, August 18, 2000, pp. 1130-1131.

[32] Anon., "Blowout pits post warning," *Hart's E&P*, August 2000, p.18.