PETM: A POSSIBLE ANALOG TO MODERN CLIMATE CHANGE/METHANE HYDRATES: MAJOR IMPLICATIONS FOR CLIMATE

DELVING INTO PAST CLIMATES

Background:

We often hear that a particular season has been the warmest or wettest on record. These temperature and precipitation records are for the instrumental period of record that extends back little more than 150 years, a relatively short time interval in Earth's history.

Earth scientists from various fields have extended our view of Earth's past climates farther back into the past through a variety of proxy indicators. One place where information about paleoclimatology, or the study of past climates, can be found is at the website maintained by <u>NOAA Paleoclimatology</u>, a branch of NOAA's National Climatic Data Center (NCDC). Data sets produced by paleoclimatologists from proxy records are archived in the World Data Center for Paleoclimatology. Interested parties may obtain these data sets, which are catalogued variously by investigator, data type or locale.

Spend some time looking at variety of topics available. For example, go to <u>Paleo Perspectives</u> and select one of the four topics: *Abrupt Climate Change, North American Drought, On Global Warming* and *On Colorado River Stream Flow.* By this point in the course, you be familiar with some of these topics. Read the story associated with a topic, such as North American Drought, to see the story that describes drought and how drought has affected society during the 20th century, or the instrumental period of record. Recall from the Supplemental in week 5, that we could describe the severity of a drought in terms of the Palmer Drought Severity Index. NCDC has extended the Palmer Drought Index across the country back to 1895, the beginning of what is considered a sufficiently dense climate-reporting network across the nation. Then continue, by reading how paleoclimatologists have assembled a variety of proxy records, such as tree rings and pollen, to extend the record of drought in various locations across North America backward over the last 2000 years. Data sets are available to those interested in working with these data.

You may also wish to go to the <u>Education and Outreach</u> page where you can view a variety of paleoclimatology slide sets prepared by experts in paleoclimatology, such as the *Resource Page on Tree Rings*, or *Coral Paleoclimatology*.

PETM: A POSSIBLE ANALOG TO MODERN CLIMATE CHANGE

Driving Questions: What is the paleoclimatic event called PETM (Paleocene-Eocene Thermal Maximum) and how was it discovered via analysis of deep sea sediment cores? Are there similarities between PETM and current anthropogenic loading of carbon dioxide in the atmosphere and ocean?

Educational Outcomes: To describe the PETM and how it was determined from the geologic records archived in deep-sea sediment cores. To examine any similarities between what

happened during the PETM and the current upward trends in atmospheric and oceanic carbon dioxide.

Objectives: After completing this investigation, you should be able to:

- Describe ways in which analyses of deep-sea sediment cores are employed in reconstructing past climates, using PETM as an example.
- Compare possible similarities between PETM and modern climate change.

Reconstructing Past Climates

The methods and findings of paleoclimatological studies are providing valuable perspectives on the present climate and climate change. Deep-sea sediment cores (sample shown in **Figure 1**) systematically acquired since the late 1960s through the Integrated Ocean Drilling Program and its predecessors, provide proxy (e.g., based on indirect evidence) climate data going back tens of thousands to hundreds of millions of years. Stable isotopes (*isotopes* are atoms of the same element with different masses because of differences in the number of neutrons in their nuclei) of oxygen and carbon are commonly used to acquire proxy climate records in paleoclimatology.



Figure 1.

Deep sea sediment core showing the onset of the PETM as an abrupt change from light to dark sediment. [American Museum of Natural History]

Of particular interest has been the comparison between temperatures and carbon dioxide concentrations in the reconstruction of past climates. The main reason is that some past climatic episodes exhibit similarities to the modern-day rapid increases in the flux of carbon into our atmosphere and ocean. The **Paleocene-Eocene Thermal Maximum (PETM**), occurring early in the

Cenozoic Era (65.5 million years ago to the present) near the transition from the Paleocene to the Eocene Epoch, was a geologically brief period of widespread and extreme climatic warming that was associated with massive atmospheric greenhouse gas input into Earth's climate system. The estimated magnitudes of these carbon releases are comparable to releases due to human activity at the present time and expected this century. The PETM serves as a reference showing the effect of a rapid increase of fossil carbon into the atmosphere, although it is dwarfed by comparison to the present rate of CO_2 releases into Earth's atmosphere. The onset of PETM was marked with

temperatures increasing by several Celsius degrees, at least 5 C° (9 F°) during a time period of between 1000 and 10,000 years. The mass of increased carbon was sufficiently large to lower the pH

of ocean waters, driving widespread dissolution of seafloor carbonates. The geologic record also shows that between 100,000 and 200,000 years passed for the ocean to fully recover from the PETM through natural carbon sequestration (removal) processes. That time scale is similar to a forecast of the time which will be required for the modern-day ocean to return to its pre-industrial age condition. [Intergovernmental Panel on Climate Change (IPCC), *Climate Change 2007: The Physical Science Basis Report,* pp. 442-443, and the National Academies' *Understanding Earth's Deep Past: Lessons for Our Climate Future* (2011), pp, 69-71]

1. Figure 2 depicts the PETM as a temperature spike of several Celsius degrees that took place approximately [(40)(50)(56)] million years before present. [Note that in Figure 2 the most ancient time is to the right and the most recent is to the left, that is, the direction of time is from right to left.]

Much of what is known about the PETM is from the study of the stable isotopes of oxygen and carbon obtained from deep-sea sediment cores. From cores that include fossils composed of calcite

(CaCO₃), determinations of the proportions or ratios of carbon isotopes (^{13}C : ^{12}C) or oxygen

isotopes (¹⁸O:¹⁶O) can be made. The ratios of these isotopes vary depending on physical conditions and species involved. Because organisms build their shells in isotopic equilibrium with the seawater in which they live, they reliably record history that can be read to reconstruct past climates.

For a detailed overview of the employment of stable isotopic analysis in paleoceanography, go to the Consortium for Ocean Leadership's *Abrupt Events of the Past 70 Million Years* at *http://www.oceanleadership.org/education/deep-earth-academy/educators/classroom-activities/undergraduate/abrupt-events-of-the-past-70-million-years-evidence-from-scientific-ocean-drilling/*. There, click on "Download Abrupt Events".

Page 2 of this Deep Earth Academy's overview describes how evaporation of seawater and build-up of land ice during glacial climatic episodes results in seawater that is enriched in [(¹⁸0) (¹⁶0)]. Therefore, ocean microfossils that lived during those glacial episodes have calcite shells with relatively higher proportions of ¹⁸O compared with those ocean microfossils that lived during interglacial climatic episodes.

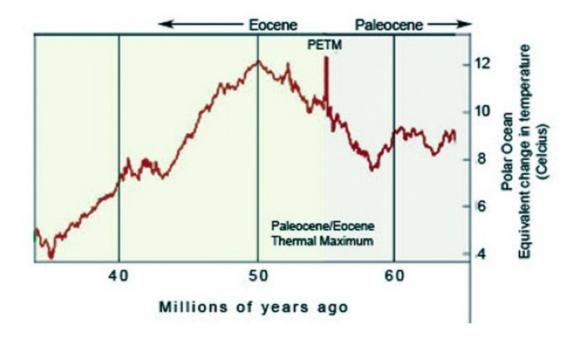


Figure 2. Temperature change curve showing PETM spike. [Mongabay.com. Rhett A. Butler-San Francisco, CA. 1999-2008]

3. From the discussion in item 2 above, it can be inferred that the oxygen isotope ratio (¹⁸O:¹⁶O) is a proxy for [(*temperature*)(*glacial ice volume*)(*both of these*)].

Figure 3, reported in the IPCC *Climate Change 2007, The Physical Science Basis,* p. 443, shows detected changes in carbon and oxygen isotope ratios, and percentage of calcium carbonate saturation, before, during, and after the PETM event. Note the time scale in this Figure 3, in

megannum (Ma), a unit of time equal to one million (10^6) years, with the most ancient to the left and most recent to the right. The direction of time is from left to right.

In Figure 3, stable isotopes of oxygen and carbon in samples were measured by comparing the ratios of ${}^{13}C$: ${}^{12}C$ and ${}^{18}O$: ${}^{16}O$ relative to those in a known standard. These "del" values (δ) are reported in units of parts per thousand (‰).

- 4. Examine the top graph in Figure 3. Isotopic studies of bottom-dwelling foraminifera fossils recovered from deep-sea sediment cores from sites described in the Figure 3 caption show that with the onset of PETM there was a rapid [(*increase*)(*decrease*)] in the carbon isotope δ (del) value (note scale on left increases upward). This is indicative of a large increase in the concentration of the atmospheric greenhouse gases carbon dioxide (CO₂) and methane (CH₄).
- 5. The middle panel has scales for two different measures. Note that the oxygen isotope δ (del) scale on the left increases downward, while the water temperature scale on the right increases upward. The middle panel shows that a relatively rapid decrease in oxygen isotope δ values was associated with a dramatic [(*increase*)(*decrease*)] in seawater temperature of approximately 5

Celsius degrees.

- 6. The bottom panel in Figure 3 reports the percentage of calcium carbonate (CaCO₃) in solution in seawater compared to the amount if the liquid were saturated with CaCO₃. The third panel shows that during the period prior to and the period after the PETM event, ocean waters at the two depths measured (4.8 km and 2.6 km) were approximately [(0%)(50%) (90%)] saturated with calcium carbonate (CaCO₃).
- 7. Under the full impact of PETM, the ocean waters at those depths were approximately [(0%) (50%) (90%)] saturated with CaCO₃. This condition, brought on by the ocean's absorption of carbon dioxide, lowered seawater pH (increased acidity) and caused widespread dissolution of seafloor carbonates.

How did the PETM happen? The IPCC states that, "Although there is still too much uncertainty in the data to derive a quantitative estimate of climate sensitivity from the PETM, the event is 'a striking example of massive carbon release and related extreme warming."" [*Climate Change 2007, The Physical Science Basis,* p. 442]

Summary: The similarities between the PETM and the comparable current increases in atmospheric and oceanic carbon makes the PETM an analog worthy of study as we face climate change.

The possible sources of such a large mass of carbon could be from the release of methane (CH_4) from decomposition of hydrate deposits in seafloor sediments, CO_2 from volcanic activity, or oxidation of organic-rich sediments. In **Part B** of this investigation, we will explore gas hydrates as components of Earth's climate system.

Optional: To view an approximately 8-minute video entitled **PETM: Unearthing Ancient Climate** *Change*, go to *http://www.amnh.org/sciencebulletins/?sid=e.f.PETM.20081126&src=l*. This American Museum of Natural History Science Bulletin presentation describes the work of paleontologists, paleobotanists, soil scientists and other researchers in Wyoming's Bighorn Basin as they reconstruct how climate, plants, and animals changed during the PETM.

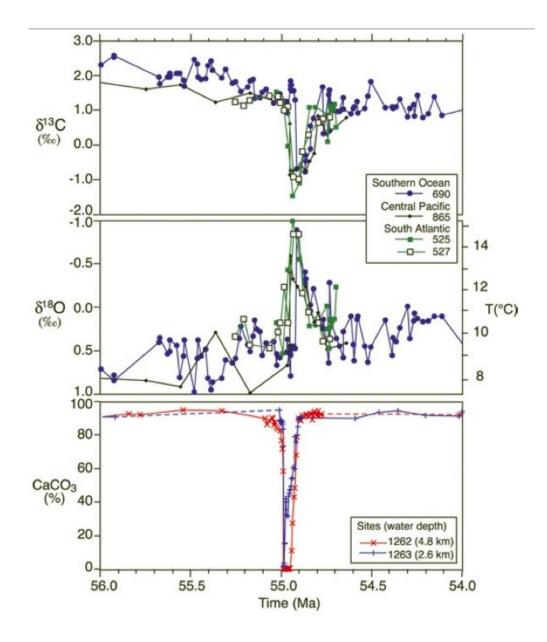


Figure 3. The PETM as recorded in benthic (bottom dwelling) foraminifera (*Nuttallides truempyi*) isotopic records from sites in the Antarctic, south Atlantic and Pacific. [IPCC, *http://www.ipcc.ch/graphics/ar4-wg1/jpg/fig-6-2.jpg*]

METHANE HYDRATES: MAJOR IMPLICATIONS FOR CLIMATE

Driving Questions: What are methane hydrates? What role might methane hydrates have played in causing the PETM (Paleocene-Eocene Thermal Maximum) and what were the possible impacts on atmospheric and ocean carbon dioxide levels? Are there similarities between PETM and current anthropogenic loading of carbon dioxide in the atmosphere and ocean?

Educational Outcomes: To describe methane hydrates and how they can impact concentrations of carbon dioxide in the atmosphere and ocean. To examine any similarities between what happened during the PETM and the current upward trends in atmospheric and oceanic carbon dioxide.

Objectives: After completing this investigation, you should be able to:

- Describe the chemical and physical characteristics of methane hydrate and its distribution in the Earth environment.
- Demonstrate how methane hydrates could be major sources of atmospheric and oceanic carbon dioxide.
- Compare possible similarities in the role of methane hydrates in atmospheric and oceanic carbon dioxide concentrations during PETM and modern climate change.

PETM and Methane Hydrates

The PETM, the abrupt warming of Earth's atmosphere and ocean and associated environmental impacts that occurred about 55.8 million years ago, was global in scale and its impact lasted for more than 100,000 years. It was likely triggered by the rapid emission of carbon dioxide (CO_2), or by methane (CH_4), which chemically reacts with oxygen to produce CO_2 (and water). Possible sources of the huge amount of carbon that was necessary for producing the PETM are not known with certainty. It could have been from the release of methane (CH_4) from decomposition of hydrate deposits in seafloor sediments, CO_2 from volcanic activity, and/or oxidation of organic-rich sediments. There is considerable scientific evidence pointing to the possibility that the release of methane from naturally occurring solid methane hydrate deposits in ocean sediments played a prime role in producing the PETM.

Figure 1 shows a sample of methane hydrate. If ignited in air, it burns, as seen in the image. Up to 170 volumes of CH_4 as a gas at 1 atmosphere of pressure can be contained in one volume of methane hydrate. **Methane hydrate** (also called methane clathrate and methane ice) belongs to a unique class of chemical substances composed of molecules of one material forming an open solid crystal lattice that encloses, without chemical bonding, molecules of another material as represented in Figure 2. Methane hydrate is a solid form of H_2O that contains methane (CH_4) molecules within its crystal

structure. It is the inclusion of sufficient methane molecules within the open cavities between water molecules that causes the stable solid structure to form (i.e., methane hydrate).



Figure 1. Burning methane hydrate. [National Research Council of Canada, NRC-SIMS]

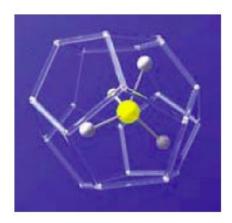


Figure 2.

Methane hydrate is a solid substance in which water molecules form an open crystalline lattice enclosing molecules of methane. [National Energy Technology Laboratory, DOE]

In Figure 2, the central molecule represents four (gray) hydrogen atoms bonded to a (yellow)
[(oxygen)(carbon)] atom. The surrounding water molecules form the crystal lattice that makes
the substance solid.

Within certain pressure and temperature ranges, methane hydrates form and remain stable in the Earth environment. To view methane hydrate formation and outcrops on the seafloor of the Gulf of Mexico and to answer the following questions, go to: *http://2100science.com/ Videos/Frozen_Fuel.aspx*. Click on the arrowhead in the middle of the *You Tube* screen to start the program.

2. Early in the 8-minute video and again at about 7:40 minutes into the video you can view the burning of methane hydrate. A scientific error was made in the video narration with the statement that "methane hydrate is frozen methane." Evidence that this statement is probably not true is the [(absence)(presence)] of liquid water that can be seen as the burning of methane hydrate takes place. The flames seen result from the combustion of CH₄. The loss of CH₄ molecules leads to the collapse of the crystal lattices formed by the water molecules, so solid

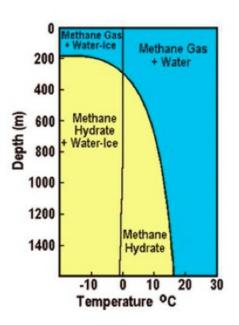
molecules leads to the collapse of the crystal lattices formed by the water molecules, so solid turns to liquid.

- 3. According to the narration (described at about 3:55), the actual seafloor observations in this video were made at a depth of [(1200)(2100)(2900)] feet.
- 4. The actual formation of methane hydrate can be seen in the video starting at about 4:50. The CH₄ entering the sampling tube in which the methane hydrate forms is in its [(*liquid*)(*solid*) (*gas*)] phase.
- 5. Methane hydrate outcrops can be viewed starting at 6:10. The existence of such outcrops is strong evidence that methane hydrate is [(*stable*)(*unstable*)] at the pressures and temperatures at that seafloor location.

Figure 3 is a methane hydrate phase diagram showing the combination of temperatures and pressures

(given as water depth in meters). In the diagram "water-ice" refers to ordinary ice. Enclosed in the yellow area are combinations of temperature and pressure at which (solid) methane hydrate can stably exist.

- 6. The solid line between yellow and blue portions of the phase diagram marks the transition between conditions under which methane hydrate can or cannot exist. It indicates that at sufficiently high pressures, methane hydrate can exist at temperatures above the melting point of ordinary ice. At about 880 m (the depth of the Gulf of Mexico seafloor where the methane hydrate outcrops were observed in the above video), the temperature could have been as high as $[(+8 \ ^{\circ}C)(+10 \ ^{\circ}C)(+12 \ ^{\circ}C)]$.
- 7. The phase diagram also shows that methane hydrate can exist at relatively shallow depths. At a temperature of 0 °C, methane hydrate could exist at water depths as shallow as about [(300 m) (400 m)(500 m)].





Methane Hydrate Phase Diagram denoting depth (i.e., pressure) and temperature at which methane hydrate can exist. Methane hydrate is a solid. [National Energy Technology Laboratory, DOE]

It should be noted that the Figure 3 phase diagram is based on interactions of pure substances. In addition to temperature and pressure, the composition of both the water and the gas are critically important when making predictions of the stability of methane hydrates in different environments.

Methane Hydrates and the 2010 Gulf of Mexico Deepwater Oil Spill:

In the Deepwater Horizon oil spill catastrophe, methane hydrate was at least implicated as the possible source of the methane gas that likely caused the explosion and fire that destroyed the Deepwater Horizon oil drilling platform. In the initial clean-up efforts, it was unquestionably

identified as responsible for thwarting the futile attempt of BP engineers to deploy an oil containment dome, acting as an upside-down funnel, to capture escaping oil and piping it to a storage vessel on the surface.

An oil containment dome was deployed on May 7-8 as one of the early attempts to cap the flow of escaping oil and natural gas (primarily composed of CH_4). It failed because the relatively low density methane hydrate that formed produced a slush that made the dome buoyant while at the same time clogging the pipe exiting at the dome's top.

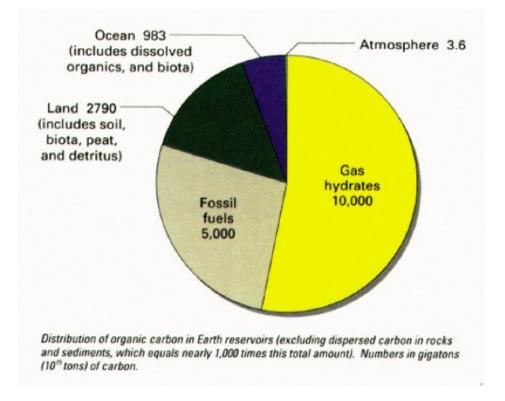
8. The Figure 3 phase diagram shows why methane hydrate formed when methane and water mixed inside the containment dome. This can be seen by plotting a point on the phase diagram at a depth of 1500 m and temperature of 5.5 °C, representing the conditions at the seafloor well site. The plot falls within the [(*blue*)(*yellow*)] portion of the phase diagram indicating stable conditions for the existence of methane hydrate.

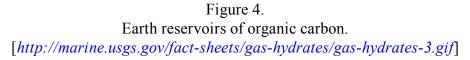
Methane Hydrates and PETM: Because the temperature and pressure ranges at which methane hydrates can exist are found throughout much of Earth's subsurface environment, it carries with it great potential to impact climate. This was as true in the past as it is now. As mentioned earlier, there is strong evidence that the release of CH_4 from methane hydrates might have been the primary

forcing agent producing the PETM. This possibility has been thoroughly treated in learning materials developed by the Deep Earth Academy at: *http://www.oceanleadership.org/wp-content/uploads/2009/06/8 petm abrupt-events.pdf*. We recommend that you examine the materials.

Global Distribution of Methane Hydrates: Figure 4 describes the distribution of organic carbon in various Earth reservoirs. Gas hydrates are primarily methane hydrates, although other molecules of similar size to CH_4 (including hydrogen sulfide, carbon dioxide, ethane, and propane) form gas hydrates.

9. The one organic carbon reservoir greater than all the other reservoirs combined is [(the ocean) (fossil fuels)(the land)(atmosphere)(gas hydrates)].

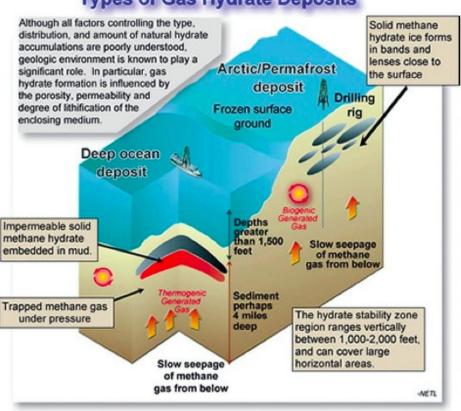




Summary: Figure 5 summarizes major aspects of methane hydrates in the Earth environment.

10. Figure 5 shows the two sources of the methane that are incorporated in the methane hydrate deposits. Biogenic generated CH₄ gas is the common by-product of bacterial ingestion of organic matter. It is considered to be the dominant source of the methane hydrate layers within shallow sea floor sediments. [(Hydrogenic)(Cryogenic)(Thermogenic)] generated CH₄ gas is produced by the combined action of heat, pressure and time on deep-buried organic material that also produces petroleum.

While not discussed here, large deposits of methane hydrates also occur in permafrost. With global warming and associated thawing of vast frozen land areas, the expectation is that significant quantities of CH_4 will be released. Their oxidation will lead to additional CO_2 , enhancing the greenhouse effect.



Types of Gas Hydrate Deposits

Figure 5. Types of gas (mostly methane) hydrate deposits. [U.S. National Energy Technology Laboratory (NETL)

http://www.earth.columbia.edu/sitefiles/image/press_room/press_releases/2009/methanehydrate_50_

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