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## Estimates of the Possibility of Rapid Methane Warming 55 Ma Ago

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Alternation of relatively warm and cold periods in the Earth is well known from geological, geochemical, and paleoclimatic data. There are many different causes of significant changes in the global temperature of the Earth's surface: variations in the parameters of the orbit, changes in the location of continents and oceans, falling of large asteroids, mass volcano eruptions, and others. The last decade of the 20th century was marked by the beginning of discussions concerning another possible cause of long-term (in the scale of the history of human civilization) and rather fast (in the geological time scale) climatic variations. This is the so-called methane catastrophe: emission of a large amount of methane from gas hydrates concentrated in the Earth's interior. In our work, we estimate the principal possibility of rapid (during a few thousand years) greenhouse warming at the Paleocene/Eocene boundary (55 Ma ago) owing to methane emission from gas hydrates.

The fact of enormous reserves of gas hydrates in the interior of land and crust beneath the World Ocean was obviously established in 1969 by Vasil'ev, Makagon, Trebin, Trofimuk, and Chersky [1].

The estimates of the current resources of methane in the gas hydrate pools vary strongly. According to [2], the most modest estimates yield approximately  $7 \cdot 10^{14}$  kg (700 Gt) of methane with a carbon content greater than  $5 \cdot 10^{14}$  kg (500 Gt), while the most daring estimates reach 30 000 Gt of methane. The analysis performed in [2] shows that the most reliable estimates range from 1000 to 3000 Gt, including 400 Gt confined to the Arctic permafrost zone.

The phenomenon of strong and fast (in the geological sense) warming during the Early Paleocene was discovered at the beginning of the 1990s. In the world geological literature, it was called the Paleocene–Eocene Thermal Maximum (PETM) [3, 4]. This phenomenon occurred approximately 55 Ma ago. The global warming of the Earth's surface was estimated at 5–9°C.

Variations in the mean temperature of the Earth's surface over 65 Ma adopted from [5] are shown in Fig. 1, which clearly demonstrate that the phenomenon of PETM is sharply distinguished on the background of paleotemperature dynamics during the Paleocene and Eocene occupying a period of approximately 1000 ka.

According to [3], warming during PETM is associated with emission of 1500–4500 Gt of carbon into the ocean and atmosphere, which promoted a high but poorly calculated concentration of CO<sub>2</sub> in the atmosphere. The PETM phenomenon initiated global warming, vanishing and migration of species, and significant changes in the carbon and hydrological cycles, which changed the Late Paleocene realm.

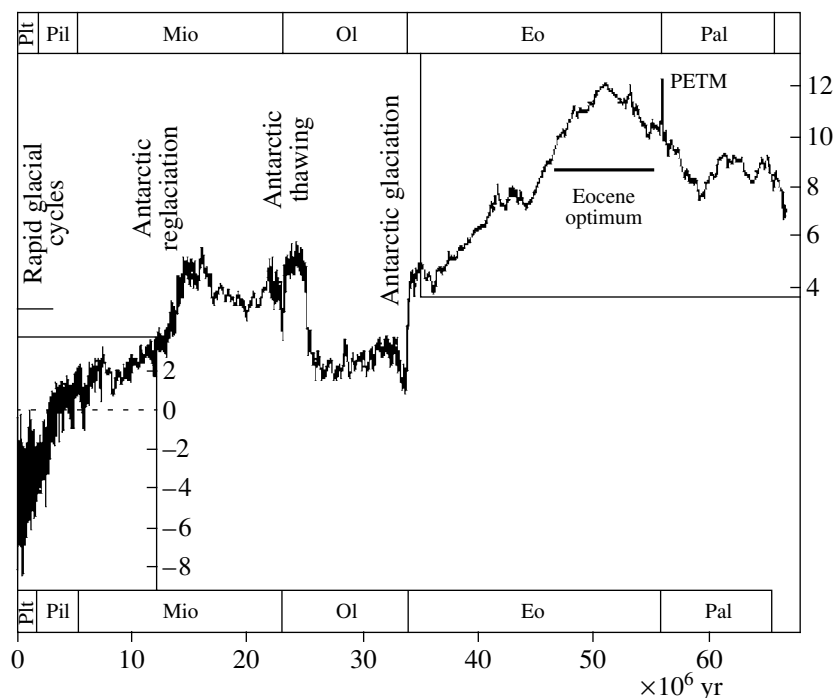
According to the carbon isotope data, the initial phase of PETM lasted 15–30 ka. This period was marked by the rapid influx of the <sup>13</sup>C-depleted carbon isotope into the ocean–atmosphere system. Later, the so-called phase of the alternating semistable state was set approximately 60 ka ago, when the <sup>13</sup>C content was close to the minimum, corresponding to the maximal content of organic carbon in the atmosphere and ocean. The final phase of PETM lasted approximately 70 ka, when the Earth system returned to the state of the Early Eocene, which in many respects was similar to the Late Paleocene [3].

The geological data evidence that during the period from 55.00 to 54.85 Ma, the <sup>13</sup>C content changed strongly in the Earth's upper layers. The maximal <sup>13</sup>C depletion in the climatic system reached 4–6 ppb. Simultaneously, the temperature of the ocean surface increased by 6–8°C according to the geological data.

The authors of [3] associate rapid global warming during the PETM period with an increase in the CO<sub>2</sub> content in the atmosphere. However, according to [3] and others, this warming could also occur owing to a sharp increase in the methane concentration in the atmosphere, which is a much stronger greenhouse gas than CO<sub>2</sub>. For example, the potential of methane global warming is considered 21 times greater than the similar potential of carbon dioxide [6].

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Variations in the mean global temperature of the Earth's surface over 65 Ma. Equivalent variations in temperature  $\Delta T$  ( $^{\circ}\text{C}$ ) were obtained from the data of station *Vostok* and from bottom sediments in the polar ocean. The figure is adopted from [5].

The authors of the present paper are aware that climatic effects of multifold increase in methane concentration in the Earth's atmosphere could be nonlinear in the sense that lifetime of methane in the atmosphere and its radiation effects would depend on its content not in the same manner as in the present conditions. However, we shall neglect this difference for simple qualitative estimates.

It is well known that the greenhouse effect caused by increased content of  $\text{CO}_2$  and  $\text{CH}_4$  is intensified significantly by positive feedback of the variations in the hydrological cycle at the surface and in the Earth's atmosphere due to the correlation of water vapor with temperature according to the Clapeyron–Clausen law. In the initial estimates, this feedback is not taken into account; i.e., the estimates given below are related to the minimal values of the greenhouse effect at any content of  $\text{CO}_2$  and  $\text{CH}_4$  in the Earth's atmosphere.

In the present conditions, the lifetime of a methane molecule in the atmosphere is approximately 10 yr. If the content of methane in the Earth's atmosphere increases many times, the lifetime of its molecule can increase significantly. According to the estimates in [4], the lifetime of a methane molecule in the atmosphere during the preindustrial period was equal to 8.4 yr, while at present it is equal to 10 yr. If the methane concentration is of the order of 100 ppm, as it could have been in the PETM period, the lifetime could exceed 40 yr.

Taking into account the increased lifetime of methane in the atmosphere and feedback related to water vapor,

one or another estimate of global warming can be reached at significantly lower methane concentrations. The potential joint influence of high concentrations of  $\text{CO}_2$  and mass emissions of methane from gas hydrates on the Late Paleocene climate are described in [4].

Let us make simple estimates of the possible greenhouse influence of high methane emissions on the Earth's climatic system. These estimates are based on the data from [6] related to radiation forcing and global warming due to increased content of the main greenhouse gases in the atmosphere (first of all,  $\text{CO}_2$  and  $\text{CH}_4$ ) from preindustrial times (the year 1750) to the end of the 20th century.

The authors of [6] (Chapter 6, Radiation forcing) give a set of simple relations for calculating radiation forcing  $\Delta F$  and the greenhouse effect  $\Delta T$  due to an increase in contents of  $\text{CO}_2$  and  $\text{CH}_4$ . Below, we present the most simple of these relations used in our work. In the calculation of the greenhouse effect of  $\text{CH}_4$ , we omitted the dependence of this effect on the variations in the concentration of nitrogen oxides, whose absorption lines overlies the lines of absorption of methane:

$$\Delta F(\text{CO}_2) = 5.35 \cdot \ln \frac{C}{C_0},$$

$$\Delta F(\text{CH}_4) = 0.036(C^{0.5} - C_0^{0.5}),$$

$$\Delta T = 0.5\Delta F.$$

Using these formulas, one can easily find that a global warming of 5 K (the lower estimate for the PETM) due solely to the increase in the methane concentration requires a concentration of 92.5 ppm. If warming is due to the increase in the concentration of carbon dioxide only, its concentration should reach 1800 ppm. Thus, in order to reach the minimal level of the PETM phenomenon, either the concentration of methane should increase more than 100 times compared to the preindustrial one or the concentration of carbon dioxide should be approximately six times greater.

Let us compare how much carbon should be supplied to the atmosphere for such increased concentrations of CO<sub>2</sub> and CH<sub>4</sub>. The molecular weight of carbon dioxide is 44 and that of methane is 16. Correspondingly, the formation of the same amount of gas requires a 2.75 times smaller amount of carbon in the case of CO<sub>2</sub> relative to the methane scenario. The necessary increase in the concentration of CO<sub>2</sub> is approximately 1500 ppm (or 90 ppm CH<sub>4</sub>); i.e.,  $C_{\text{carbon}}/C_{\text{methane}} = (1530 : 44)/(92 : 16) = 6$ .

Thus, taking into account the different molecular weights and absorbing properties of CO<sub>2</sub> and CH<sub>4</sub>, the PETM effect caused by an increase in the concentration of CH<sub>4</sub> would require 6 times less carbon than in the case of CO<sub>2</sub>. Correspondingly, a significantly smaller emission of carbon from the Earth's interior into the atmosphere would be needed than in the case of warming due to carbon dioxide.

If we suppose that the feedback of the greenhouse effect related to water vapor 55 Ma ago was the same as in the present-day atmosphere, the overall warming caused by methane emission could be doubled. In other words, the same warming with account for the increase in the water vapor content would require a two times smaller content of methane in the atmosphere and its smaller emission from gas hydrates.

Let us estimate the principal possibility of emission of a sufficient amount of methane into the atmosphere, which is needed for rapid warming in the geological sense.

In the preindustrial time, approximately 1.85 Gt of methane was contained in the atmosphere. The present day concentration of methane is estimated at 4.6 Gt [2], while the characteristic annual supply of methane into the atmosphere is estimated at 20 Mt. In the beginning of the 1990s, the sink of methane from the atmosphere was estimated as 580 Mt/yr [2]. Taking into account the measured increase in the concentration, this gives an approximate value of 600 Mt/yr of methane transported to the atmosphere.

During the PETM period, the methane concentration should be maintained at a level of approximately 90–100 ppm. Correspondingly, its content should be at a level of 250 Gt. If we assume that the life cycle of methane is equal to 10 yr, the annual flux of methane

**Table 1.** Preindustrial (1750) C<sub>0</sub> and modern C concentrations of carbon dioxide and methane in the Earth's atmosphere, radiation forcing  $\Delta F$ , and relative warming  $\Delta T$  (based on [5])

Gas	C <sub>0</sub> , ppm (1750)	C, ppm (1998)	$\Delta F$ , W/m <sup>2</sup>	$\Delta T$ , K
CO <sub>2</sub>	278	365	1.46	0.73
CH <sub>4</sub>	0.7	1.745	0.28	0.28

into the atmosphere should be equal to 25 Gt. If the life cycle is 40 yr, the flux should slightly exceed 6 Gt.

In the modern world, the main flux of methane from the Earth's interior is natural gas production. According to British Petroleum data [7], the proven reserves of natural gas in the world by the end of 2005 were equal to 179.83 trillion cubic meters, while the annual production was 2.76 trillion cubic meters. Under normal conditions, one cubic meter of natural gas (methane) has a mass of 0.717 kg. In other words, the proven reserves of methane in the form of natural gas are approximately 130 Gt, and its annual production is approximately 2 Gt.

Table 2 presents data on the reserves and production of natural gas in the modern world. These data clearly show constant increase in the proven reserves of natural gas, and these reserves would be enough for many decades.

The reserves and production of natural gas are several orders of magnitude smaller than the reserves of methane-hydrates and possible mass emissions of methane from these gas hydrates. However, according to [8], the total content of organic carbon in the possible reserves of fossil fuel is only two times smaller than the reserves of organic carbon in gas hydrates.

The estimates presented here demonstrate that rapid (in the geological sense) methane warming is possible in principle, although it requires large fluxes of methane from the Earth's interior. Taking into account the intensification of the greenhouse effect owing to water vapor and possible prolongation of the lifetime of methane molecules in the atmosphere during the PETM, the estimates of these fluxes could be significantly smaller.

It is likely that shock emissions of methane in the geological past could trigger the process of rapid warming and, in particular, explain the leading character of some warming episodes in the Earth's history related to an increase in the concentration of carbon dioxide. According to recent studies, the increase in the concentration of methane based on paleodata usually surpasses the temperature increase.

Detailed consideration of the greenhouse phenomenon at the Paleocene/Eocene boundary requires further investigation using geological, geochemical, and paleoclimatic data with application of the modern models of climate theory.

**Table 2.** Proven reserves of natural gas and reserves/production ratio (R/P) (based on British Petroleum data [7])

Region	Resources of natural gas, tln m <sup>3</sup>			Proportion of world resources, %	R/P, yr
	1985	1995	2005		
North America	10.37	8.47	7.46	4.1	9.9
South and Central America	3.32	5.96	7.02	3.9	51.8
Eurasia	44.45	63.16	64.01	35.6	60.3
Middle East	27.67	45.37	72.13	40.1	more than 100 yr
Africa	6.16	9.93	14.39	8.0	88.3
Pacific region	7.57	10.54	14.84	8.3	41.2
World as a whole	99.54	143.43	179.85	100.0	65.1
Russia	–	–	47.82	26.7	80.0

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