

## Phanerozoic evolution of atmospheric methane

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[1] A simple geochemical box model for the global cycle of methane ( $\text{CH}_4$ ) has been developed and applied to reconstruct the evolution of atmospheric  $\text{CH}_4$  over the entire Phanerozoic. According to the model, the partial pressure of atmospheric  $\text{CH}_4$  ( $p\text{CH}_4$ ) increased up to approximately 10 ppmv during the Carboniferous coal swamp era. This implies a maximum radiative forcing of about  $3.5 \text{ W m}^{-2}$  via  $\text{CH}_4$ . Through its radiative forcing,  $\text{CH}_4$  heated the average global surface temperature by up to  $1^\circ\text{C}$ . The elevated  $p\text{CH}_4$  values during the Permian-Carboniferous cold period may have moderated the temperature decline caused by the coeval drawdown of atmospheric  $\text{CO}_2$ . Additional runs with a global carbon model indicate that the heating induced by elevated  $p\text{CH}_4$  favored the drawdown of atmospheric  $p\text{CO}_2$  via enhanced rates of silicate weathering. Simulations with a state-of-the-art climate model reveal that the effects of atmospheric  $\text{CH}_4$  on average global surface temperature also depend on the partial pressures of  $\text{CO}_2$ . The  $\text{CH}_4$  climate effect is amplified by high background levels of atmospheric  $\text{CO}_2$  such that a coeval increase in the partial pressure of both greenhouse gases has a much stronger climate effect than previously anticipated.

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### 1. Introduction

[2]  $\text{CH}_4$  is the most abundant hydrocarbon gas in the atmosphere and plays an important role in climate regulation [Seinfeld and Pandis, 1998]. It probably was one of the greenhouse gases, emitted by methanogenic bacteria, which warmed the early Earth surface to unexpected high temperatures [Pavlov *et al.*, 2000]. Being a greenhouse gas,  $\text{CH}_4$  molecules let pass short-wave radiation, such as UV radiation but trap reflected outgoing long-wave radiation from the Earth's surface [Fogg, 2003]. Thus the troposphere gets warmer while the  $\text{CH}_4$  content increases, the direct effect of  $\text{CH}_4$  on the average global surface temperature [Lelieveld *et al.*, 1998]. Furthermore, an increase in tropospheric  $\text{CH}_4$  affects the atmospheric partial pressures of carbon dioxide ( $p\text{CO}_2$ ) and water vapor in the stratosphere and the tropospheric ozone concentration [Blake and Rowland, 1988]. These changes force additional global warming [Harvey, 1993], the indirect effect of  $\text{CH}_4$  on the average global surface temperature [Gassmann, 1994].

[3] Except for the anthropogenic emission,  $\text{CH}_4$  is emitted from waterlogged soils, by insects, out of the photic zone of the oceans and the deep seafloor, from shallow water regions of the oceans, out of lakes [Berner and

Berner, 1996], from mud volcanoes [Kopf, 2003], and during magmatic degassing [Ehhalt, 1974]. In prehuman times, wetlands, particularly swamps and peat, were the prime emitters. In times of reduced terrestrial plant coverage, mud volcanoes might have been the most important  $\text{CH}_4$  source [Kopf, 2003].

[4]  $\text{CH}_4$  both affects climate and is affected by climate. Because of the impact of atmospheric  $\text{CH}_4$  on climate [Lelieveld *et al.*, 1998] on both long and short timescales, several models for the global  $\text{CH}_4$  cycle have been developed. These include models addressing tropospheric  $\text{CH}_4$  oxidation [Jacob, 2003], modern atmospheric  $\text{CH}_4$  change [Dlugokencky *et al.*, 1998], the future evolution of atmospheric  $\text{CH}_4$  [Dickinson and Cicerone, 1986], and Precambrian  $p\text{CH}_4$  levels [Pavlov *et al.*, 2003].

[5] In this article we attempt the first detailed reconstruction of the  $p\text{CH}_4$  level over the entire Phanerozoic (570 Ma) with the main focus on biological sources. With our new model we also evaluate the possible effects of  $\text{CH}_4$  on Phanerozoic climate evolution. We show that the Phanerozoic  $p\text{CH}_4$  passes through significant changes, inducing noticeable shifts in climatic conditions.

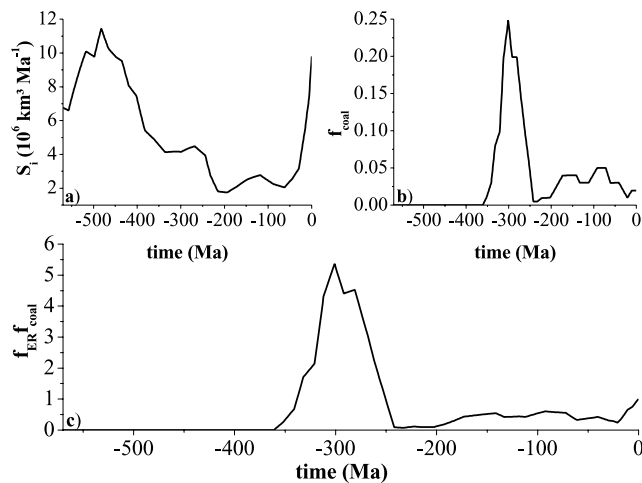
### 2. Setup of the $\text{CH}_4$ Model

[6] The box model presented in this article is built on previous models of the global carbon cycle [Wallmann, 2001a, 2004]. New parameterizations are introduced to simulate the global  $\text{CH}_4$  cycle. Hence fluxes of  $\text{CH}_4$  into the atmosphere are related to external parameters such as changes in land area, land plant coverage, organic matter burial, and volcanic/tectonic activity. A simple model of

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**Figure 1.** Changes in (a) sedimentation rate ( $S_i$ ) [Berner and Kothavala, 2001], (b) coal fraction of terrigenous sediments ( $f_{\text{coal}}$ ) [Berner, 2004], and (c) relative coal accumulation ( $f_{\text{ER}}f_{\text{coal}}$ ) derived from Figures 1a and 1b and normalized on Pliocene value (see text).

atmospheric CH<sub>4</sub> oxidation is included to calculate, finally, the  $p\text{CH}_4$  over the entire Phanerozoic and the radiative forcing (RF) induced by this greenhouse gas.

## 2.1. Sources of Atmospheric CH<sub>4</sub>

[7] Atmospheric CH<sub>4</sub> is mainly released from biological sources hosted in terrestrial anoxic environments. Our understanding of atmospheric CH<sub>4</sub> cycling is, however, to a large extent limited by a poor quantification of these and other sources.

### 2.1.1. Wetlands

[8] Wetlands are the main recent natural sources of atmospheric CH<sub>4</sub>. Direct records of the distribution of ancient wetlands are lacking. Coals are, however, formed from terrestrial plant material deposited in swamps and wetlands. Coals and coal basin sediments, which are preserved in the geological record, are thus a proxy for the abundance of methane-producing wetlands in the past.

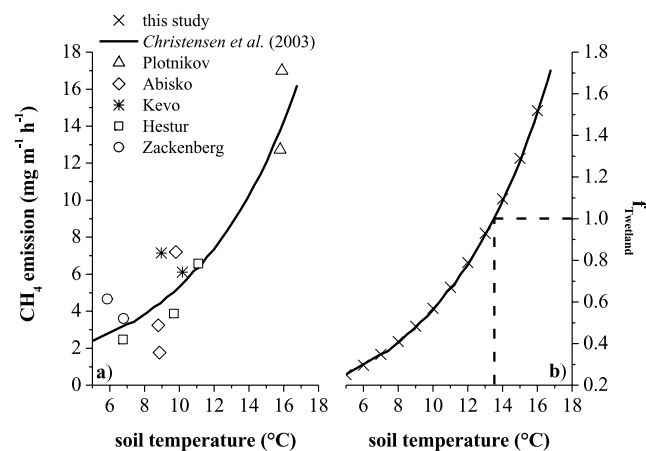
[9] Ronov [1993] investigated the abundance of terrigenous sedimentary rocks, including coal basin sediments, deposited over the various periods of the Phanerozoic and preserved until today ( $S_p$ ). These data were later updated and recompiled by W. W. Hay (personal communication, 2003) and applied by Berner and Kothavala [2001] and Berner [2004]. It should be considered that a large fraction of the initially deposited sediments was not preserved but was converted into metamorphic rocks and was lost by erosion and subduction. Previous studies on sedimentary rock cycling showed that this loss follows a simple first-order decay law [Veizer and Jansen, 1979]. Hence the initial terrigenous sedimentation rate  $S_i$  was calculated as [Wallmann, 2001a]

$$S_i = S_p e^{bt}, \quad (1)$$

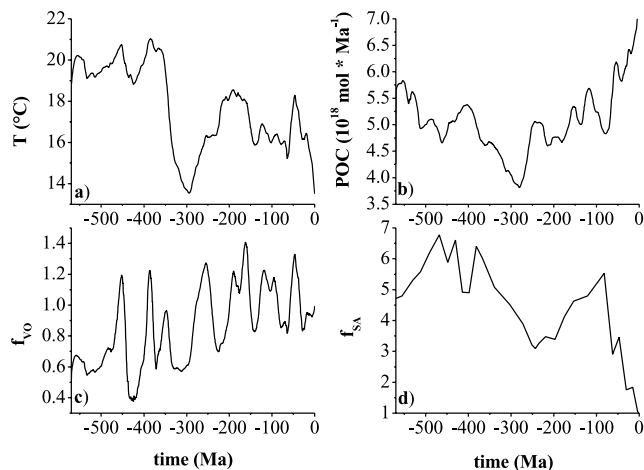
using the  $S_p$  values listed by Berner and Kothavala [2001] while the decay constant  $b$  was set to the value  $5 \times 10^{-3} \text{ Ma}^{-1}$  previously derived by Gregor [1985] and Wallmann [2001a]. A single  $b$  is appropriate to describe the loss of terrigenous sediments since the formation of coal swamps during the Carboniferous. The resulting  $S_i$  values plotted in Figure 1a were then multiplied with the fraction of terrigenous sediments deposited in coal basins (Figure 1b) taken from Berner [2004] to calculate the accumulation rate of coal basin sediments over the Phanerozoic. These values were finally normalized to the values derived for the most recent period considered in Ronov's compilations (the Pliocene) to calculate the relative change in coal basin sedimentation over the Phanerozoic ( $f_{\text{ER}}f_{\text{coal}}$ , Figure 1c). With this normalization we assume that the Quaternary sedimentation rate is close to the Pliocene value as suggested by recent studies [Clift, 2006].

[10] Christensen *et al.* [2003] investigated the CH<sub>4</sub> production in wetlands at different soil temperatures. Their data show an exponential growth in the production rate of CH<sub>4</sub> with increasing temperature (Figure 2a). We normalized this exponential dependency to the Quaternary average global surface temperature of about 13.5°C [Wallmann, 2001b] to describe the relative influence of ambient temperature on the CH<sub>4</sub> emission from waterlogged soils. We choose a simple exponential function to describe this dependency (Figure 2b). Thus the dimensionless temperature-dependent parameter ( $f_{\text{Twetland}}$ ) for CH<sub>4</sub> production in waterlogged soils can be described as

$$f_{\text{Twetland}} = 0.111 e^{0.1635 \times \text{Temp}}, \quad (2)$$



**Figure 2.** Dependency of CH<sub>4</sub> emission from waterlogged soils on ambient temperature (a) according to Christensen *et al.* [2003] and (b) normalized to the Quaternary average global surface temperature (13.5°C). An exponential function was fitted through the data to calculate the CH<sub>4</sub> emission from wetlands as a function of temperature ( $f_{\text{Twetland}}$ ). Dashed lines indicate that the equation yields  $f_{\text{Twetland}} = 1$  for the Quaternary global average surface temperature.



**Figure 3.** Changes in (a) average global surface temperature [Wallmann, 2004], (b) POC accumulation on the seafloor [Wallmann, 2004], (c) tectonic activity [Wallmann, 2004], and (d) normalized sea-covered area [Ronov, 1994] used as external forcings.

where the exponent “Temp” is the time-dependent average global surface temperature (Figure 3a) over the Phanerozoic calculated by Wallmann [2004]. For the Quaternary average global surface temperature this equation yields a value of unity so that  $f_{T_{\text{wetland}}}$  can be applied to calculate the effect of temperature change on CH<sub>4</sub> emissions from wetlands with respect to the recent temperature.

[11] The CH<sub>4</sub> production in ancient wetlands ( $F_{\text{wetland}}^{\text{CH}_4}$ ) is then calculated using the previously derived change in coal basin sedimentation ( $f_{\text{ER}}f_{\text{coal}}$ ), the parameter  $f_{T_{\text{wetland}}}$  describing the effect of temperature on the CH<sub>4</sub> release from wetlands, and the recent CH<sub>4</sub> production rate of waterlogged soils and swamps [ $F_{\text{wetland}}^{\text{CH}_4}(q)$ ]

$$F_{\text{wetland}}^{\text{CH}_4} = F_{\text{wetland}}^{\text{CH}_4}(q)f_{\text{ER}}f_{\text{coal}}f_{T_{\text{wetland}}} \quad (3)$$

The modern value is estimated to fall into the range of 55–150 Tg CH<sub>4</sub> a<sup>-1</sup> according to Seinfeld and Pandis [1998].

### 2.1.2. Insects

[12] Another important source of modern CH<sub>4</sub> is insects, mainly termites, producing 20 Tg CH<sub>4</sub> a<sup>-1</sup> [Intergovernmental Panel on Climate Change (IPCC), 2001]. Since the first appearance of insects these animals have influenced the  $p\text{CH}_4$  in the atmosphere [Grimaldi, 2001]. There are, however, a lot of uncertainties about the evolution and abundance of ancient insects and their alkane production rate. In the model we assume that termites have been the main emitter of CH<sub>4</sub> of all insects, and we couple the evolution of termites and their recent CH<sub>4</sub> emission value [ $F_{\text{termite}}^{\text{CH}_4}(q)$ ] to calculate their Phanerozoic emission rate:

$$F_{\text{termite}}^{\text{CH}_4} = f_{\text{IN}}F_{\text{termite}}^{\text{CH}_4}(q) \quad (4)$$

The evolution of termites began in the Cretaceous [Grimaldi, 2001]. Hence the parameter  $f_{\text{IN}}$  is set to zero for the Paleozoic and early Mesozoic and is increased to 1 during the Cretaceous.

### 2.1.3. Magmatic Degassing

[13] The volcanic CH<sub>4</sub> emissions into the atmosphere by recent continental magmatic volcanism are rather small (0.8–6.2 Tg CH<sub>4</sub> a<sup>-1</sup>) [Judd *et al.*, 2002]. To calculate the volcanic CH<sub>4</sub> release over the Phanerozoic, we assume the CH<sub>4</sub> emission via volcanism to be proportional to the activity of magmatic volcanoes. Thus the recent emissions of volcanoes [ $F_{\text{volcano}}^{\text{CH}_4}(q)$ ] and the calculated trend in activity of the continental volcanoes ( $f_{\text{VO}}$ ) over time (Figure 3c) [Wallmann, 2004] give the following expression for the emission in the past:

$$F_{\text{volcano}}^{\text{CH}_4} = f_{\text{VO}}F_{\text{volcano}}^{\text{CH}_4}(q) \quad (5)$$

### 2.1.4. Plants

[14] Recent studies [Keppler *et al.*, 2006] have discovered that land plants emit substantial amounts of CH<sub>4</sub> into the atmosphere. Keppler *et al.* [2006] propose that the amount of plant-derived CH<sub>4</sub> accounts for 10–30% of the recent annual world CH<sub>4</sub> emission. The CH<sub>4</sub>-producing processes in plants remain, however, enigmatic. The plant emissions are not considered in the model since a valid parameterization of this important methane source is currently not available.

### 2.1.5. Oceans

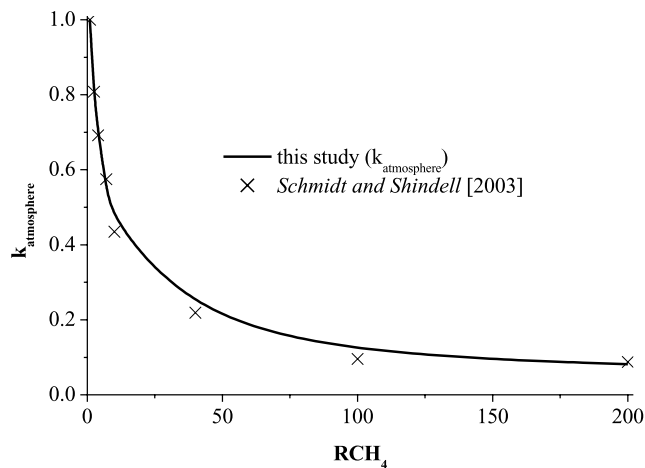
[15] Compared to the modern terrestrial emissions, the marine realm plays a minor role. The recent CH<sub>4</sub> release from the photic zone of the oceans (10–15 Tg CH<sub>4</sub> a<sup>-1</sup>) [IPCC, 2001] is mainly driven by the biogenic production in anoxic microenvironments located in “marine snow” particles sinking through the upper water column. The accumulation rate of particulate organic carbon (POC) is used to define the CH<sub>4</sub> release from sinking particles in the upper water column because the methane-generating particle flux is reflected in marine POC accumulation:

$$F_{\text{ocean}}^{\text{CH}_4} = \frac{F_B^{\text{POC}}}{F_B^{\text{POC}}(q)}F_{\text{ocean}}^{\text{CH}_4}(q) \quad (6)$$

where  $F_B^{\text{POC}}$  is the burial rate used as a proxy for biological productivity of the oceans over time (Figure 3b),  $F_B^{\text{POC}}(q)$  is the Quaternary burial rate of POC at the seafloor ( $7 \times 10^{18}$  mol C Ma<sup>-1</sup>) [Wallmann, 2003], and  $F_{\text{ocean}}^{\text{CH}_4}(q)$  is the recent CH<sub>4</sub> release from the photic zone of the oceans.

### 2.1.6. Continental Shelf

[16] Marine CH<sub>4</sub> generated in the pore space of sediments migrates toward the sediment surface, where it is oxidized by microbes or escapes through natural gas seeps as dissolved CH<sub>4</sub> or free gas. Some of this CH<sub>4</sub> is emitted into the atmosphere from shallow water environments such as marginal seas and mud flats. According to Judd *et al.* [2002], the amount of CH<sub>4</sub> released in shallow water environments is influenced by sea level change. During a falling sea level these potential CH<sub>4</sub> production areas



**Figure 4.** Decrease in loss rate of atmospheric CH<sub>4</sub> as a function of the atmospheric CH<sub>4</sub> concentration ( $k_{\text{atmosphere}}$ ) [Schmidt and Shindell, 2003].

decrease whereas transgression increases the size of shallow water environments. Thus we constrain the changing size of the shelf-bounded sources over time by simply coupling the recent CH<sub>4</sub> emission rate of these environments with the change of shelf area covered by the oceans over time and the changing rate of POC burial:

$$F_{\text{shelf}}^{\text{CH}_4} = F_{\text{shelf}}^{\text{CH}_4}(q) f_{\text{SA}} \frac{F_B^{\text{POC}}}{F_B^{\text{POC}}(q)}, \quad (7)$$

where  $f_{\text{SA}}$  is the proxy data [Ronov, 1994] for the water-covered shelf area over time normalized to the recent value (Figure 3d) and  $F_{\text{shelf}}^{\text{CH}_4}(q)$  (0.4–12.2 Tg CH<sub>4</sub> a<sup>-1</sup>) [Judd *et al.*, 2002] is the recent emission of CH<sub>4</sub> out of shallow water environments.

### 2.1.7. Mud Volcanoes

[17] Some CH<sub>4</sub> generated in the pore space of sediments is emitted during quiescent and eruptive periods from mud volcanoes, placed mainly along convergent plate margins where fluid-rich sediments accumulate [Kopf, 2002]. Mud volcanoes located on land and at shallow water depth emit substantial amounts of CH<sub>4</sub> into the atmosphere [Etiopie and Milkov, 2004]. Deep-sea mud volcanoes with a global emission rate of about 0.1 Tg CH<sub>4</sub> a<sup>-1</sup> [Wallmann *et al.*, 2006] are probably less important because CH<sub>4</sub> is almost completely oxidized near the seafloor and in the water column [Mau *et al.*, 2006]. The main controlling factor on mud volcanism is probably the rate and spatial extent of subduction and plate convergence providing the pressure gradients for fluid and mud ascent. Therefore we calculate the evolution of the CH<sub>4</sub> release from mud volcanoes for the past by using the recent CH<sub>4</sub> emission from mud volcanoes and the changing rates of subduction and organic matter accumulation:

$$F_{\text{mud}}^{\text{CH}_4} = F_{\text{mud}}^{\text{CH}_4}(q) \frac{F_B^{\text{POC}}}{F_B^{\text{POC}}(q)} f_{\text{VO}}, \quad (8)$$

where  $F_{\text{mud}}^{\text{CH}_4}(q)$  is the recent emission of CH<sub>4</sub> via mud volcanism, including both quiescent and eruptive degassing (6–9 Tg CH<sub>4</sub> a<sup>-1</sup>) [Etiopie and Milkov, 2004] and  $f_{\text{VO}}$  (Figure 3d) is the calculated tectonic/volcanic activity over the entire Phanerozoic [Wallmann, 2004].

### 2.1.8. CH<sub>4</sub> Release

[18] In our model the overall prehuman CH<sub>4</sub> emission into the atmosphere is thus given as (equations (2)–(8))

$$F_{\text{release}}^{\text{CH}_4} = F_{\text{mud}}^{\text{CH}_4} + F_{\text{volcano}}^{\text{CH}_4} + F_{\text{ocean}}^{\text{CH}_4} + F_{\text{shelf}}^{\text{CH}_4} + F_{\text{wetland}}^{\text{CH}_4} + F_{\text{termite}}^{\text{CH}_4}. \quad (9)$$

## 2.2. Sinks of Atmospheric CH<sub>4</sub>

[19] The main destruction of CH<sub>4</sub> reaching the modern atmosphere takes place in the troposphere (360–530 Tg CH<sub>4</sub> a<sup>-1</sup>) [Seinfeld and Pandis, 1998] because more than 80% [Sudo *et al.*, 2002] of the cleaning power of the atmosphere is housed in its lower 16 km [Budyyko *et al.*, 1987]. A minor part of atmospheric CH<sub>4</sub> is consumed within soils.

### 2.2.1. CH<sub>4</sub> Oxidation in the Atmosphere

[20] Some of the reactants in the reaction chain of CH<sub>4</sub> destruction are formed in the troposphere, e.g., NO [Jacob, 2003]; some others, e.g., O<sub>3</sub>, one of the main agents in tropospheric chemistry [Wang *et al.*, 1998], move from the stratosphere into the troposphere [Schultz *et al.*, 1999]. There are two types of triggers for the whole reaction chain of CH<sub>4</sub> destruction/oxidation: One is the solar flux, which triggers the photolytic reactions, and the other one is the radicals, which affect the chain reaction. The reaction chain for the production of the oxidizing agents is very complex and is discussed by Seinfeld and Pandis [1998]. The main oxidizing agents removing CH<sub>4</sub> from the atmosphere are hydroxyl radicals (OH) produced in these chain reactions [Dunlop and Tully, 1993]. Furthermore, Johnson *et al.* [2001] show that the CH<sub>4</sub> destruction by OH is linked to climate since both the OH production and the reaction of OH with CH<sub>4</sub> increase with temperature. The reaction efficiency of OH with CH<sub>4</sub> as a function of the average global surface temperature can be approximated by an Arrhenius expression [Atkinson, 2003]. The net effects of climate on the atmospheric production and consumption of OH radicals are, however, poorly understood and are therefore not considered in the model.

[21] In the context of our model it is important to note that the effectiveness of the CH<sub>4</sub> oxidation by OH increases as the amount of the hydrocarbon molecules decreases [Jacob, 2003; Lawrence *et al.*, 2001]. Because of the rapid recycling rate of OH at moderate CH<sub>4</sub> levels the oxidation processes mentioned above do not significantly deplete the OH [Lelieveld *et al.*, 2002]. However, at high CH<sub>4</sub> concentrations the cleaning power of the atmosphere decreases substantially. Consequently, the atmosphere adjusts to pollution when moderate CH<sub>4</sub> emissions prevail, while CH<sub>4</sub> accumulates in the atmosphere during times of enhanced emission.

[22] The loss of CH<sub>4</sub> from the atmosphere ( $F_{\text{atmosphere}}^{\text{CH}_4}$ ) normalized to the preindustrial loss [ $F_{\text{loss}}^{\text{CH}_4}(q)$ ] is proportional

**Table 1.** RCH<sub>4</sub> as Function of the Net Release of Methane Normalized to the Prehuman Value

Net Release	RCH <sub>4</sub>
0	0
0.1	0.1
0.5	0.5
1	1
2	2.5
3	4.5
4	7.548
5	12.3
6	18.5
7	25.8
8	35.2
9	49.6
10	76.1
12	129.4
15	180.9
20	250.4

to the atmospheric content of methane (RCH<sub>4</sub>) and a kinetic constant ( $k_{\text{atmosphere}}$ ), which also depends on RCH<sub>4</sub>:

$$\frac{F_{\text{atmosphere}}^{\text{CH}_4}}{F_{\text{loss}}^{\text{CH}_4}(q)} = k_{\text{atmosphere}} \text{RCH}_4. \quad (10)$$

[23] *Schmidt and Shindell* [2003] applied atmospheric chemistry modeling to quantify the exponential decrease in atmospheric OH abundance and CH<sub>4</sub> oxidation caused by increasing  $p\text{CH}_4$  (Figure 4). Figure 4 shows the decreasing tropospheric oxidation with increasing atmospheric RCH<sub>4</sub>. We fitted a third-order exponential term to the model results of *Schmidt and Shindell* [2003] to define a kinetic constant for atmospheric CH<sub>4</sub> oxidation depending on the prevailing atmospheric CH<sub>4</sub> level:

$$k_{\text{atmosphere}} = 0.07925 + 0.61712e^{-\frac{\text{RCH}_4}{5.43812}} + 0.62564e^{-\frac{\text{RCH}_4}{0.41025}} + 0.35927e^{-\frac{\text{RCH}_4}{39.436}}. \quad (11)$$

[24] The RCH<sub>4</sub> parameter appearing in this equation gives the  $p\text{CH}_4$  in the atmosphere normalized to the preindustrial value (0.7 ppmv). We further assume that the preindustrial loss [ $F_{\text{loss}}^{\text{CH}_4}(q)$ ] and the preindustrial emission (225 Tg CH<sub>4</sub> a<sup>-1</sup>) [*Schmidt and Shindell*, 2003] are balanced.

### 2.2.2. Oxidation Within Soils

[25] A small part (1–10%) [*Lelieveld et al.*, 1998] of the atmospheric CH<sub>4</sub>, mainly the CH<sub>4</sub> in the soil air and/or in the air near the Earth's surface, is decomposed by soil organisms. These microorganisms live in the humus-rich and aerated part of soils. The humus layer is formed by land plants. Hence the methane oxidation rate in soils was much lower prior to the advent of land plants.

[26] *Berner and Kothavala* [2001] reconstructed the rise and evolution of vascular land plants over the Phanerozoic. These nondimensional data ( $f_{\text{AN}}$ ) and the recent uptake of CH<sub>4</sub> by soil organisms ( $F_{\text{soil}}^{\text{CH}_4}(q) = 30\text{--}40$  Tg

CH<sub>4</sub> a<sup>-1</sup>) [*King and Schnell*, 1994] are used to calculate the time-dependent CH<sub>4</sub> oxidation rate ( $F_{\text{soil}}^{\text{CH}_4}$ ) in the model:

$$F_{\text{soil}}^{\text{CH}_4} = F_{\text{soil}}^{\text{CH}_4}(q)f_{\text{AN}}. \quad (12)$$

### 2.2.3. Loss of Atmospheric CH<sub>4</sub>

[27] CH<sub>4</sub> is decomposed because of oxidation processes in the atmosphere and within soils. Because of physical transport processes [*Ehhalt*, 1974], such as the Hadley circulation and eddy diffusion (together <60 Tg CH<sub>4</sub> a<sup>-1</sup>), the reduction in the CH<sub>4</sub> inventory located in the lower atmosphere is not resolved in our model because of the lack of information on the atmospheric circulation processes in the Phanerozoic. We include this transported CH<sub>4</sub> mass (7–11% of total destroyed CH<sub>4</sub>) [*Lelieveld et al.*, 1998] in the total recent chemical destruction processes of about 392–578 Tg CH<sub>4</sub> a<sup>-1</sup> [*Seinfeld and Pandis*, 1998]. The destruction of CH<sub>4</sub> in the lower and upper atmosphere via the atmospheric cleaning power ( $F_{\text{atmosphere}}^{\text{CH}_4}$ ) and the uptake by soil organisms ( $F_{\text{soil}}^{\text{CH}_4}$ ) (equations (10) and (12)) can thus be described as

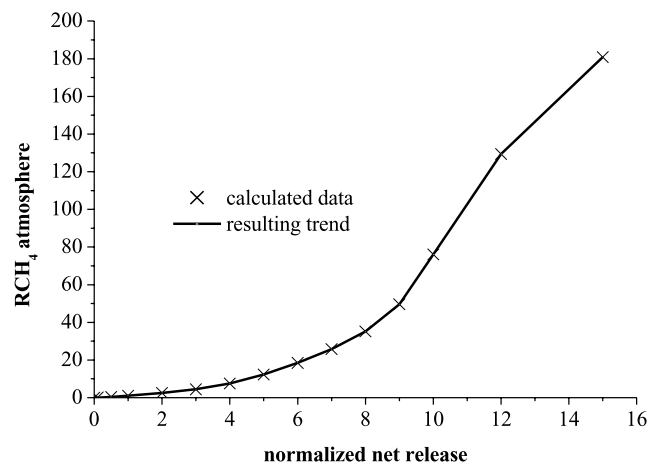
$$F_{\text{loss}}^{\text{CH}_4} = F_{\text{soil}}^{\text{CH}_4} + F_{\text{atmosphere}}^{\text{CH}_4}. \quad (13)$$

## 2.3. Budget of Atmospheric CH<sub>4</sub>

[28] On the basis of the terms above (equations (9) and (13)) the changing inventory of CH<sub>4</sub> in the atmosphere over the Phanerozoic can be calculated as

$$\frac{dM\text{CH}_4}{dt} = F_{\text{release}}^{\text{CH}_4} - F_{\text{loss}}^{\text{CH}_4}, \quad (14)$$

where  $F_{\text{release}}^{\text{CH}_4}$  is the total release of CH<sub>4</sub> into the atmosphere and  $F_{\text{loss}}^{\text{CH}_4}$  is the consumption of atmospheric CH<sub>4</sub>. Because of the fast consumption rate [*Jacob*, 2003] and the resulting short lifetime of CH<sub>4</sub> in the atmosphere [*Sudo et al.*, 2002], almost all of the released CH<sub>4</sub> gets decomposed. Thus the



**Figure 5.** Atmospheric RCH<sub>4</sub> as a function of methane net release normalized to the preindustrial net release (compare Table 1).

**Table 2.** Parameter Values and Fluxes of Methane Considered in the Box Model<sup>a</sup>

Parameter	Description	Reference	Value
$p\text{CH}_4(p)$	preindustrial partial pressure of CH <sub>4</sub> , ppmv	Raynaud et al. [1993]	(0.7)
$F_B^{\text{POC}}(q)$	Quaternary POC accumulation, 10 <sup>18</sup> mol Ma <sup>-1</sup>	Wallmann [2004]	(7)
$F_{\text{soil}}^{\text{CH}_4}(q)$	Quaternary CH <sub>4</sub> consumption of soils, 10 <sup>18</sup> mol Ma <sup>-1</sup>	IPCC [2001]	(2.37)
$F_{\text{termite}}^{\text{CH}_4}(q)$	Quaternary CH <sub>4</sub> release out of digestive tracks of insects, 10 <sup>18</sup> mol Ma <sup>-1</sup>	IPCC [2001]	(1.25)
$F_{\text{mud}}^{\text{CH}_4}(q)$	Quaternary CH <sub>4</sub> release out of mud volcanoes, 10 <sup>18</sup> mol Ma <sup>-1</sup>	Etioppe and Milkov [2004]	0.37–0.56 (0.56)
$F_{\text{shelf}}^{\text{CH}_4}(q)$	Quaternary CH <sub>4</sub> release out of shallow water environments, 10 <sup>18</sup> mol Ma <sup>-1</sup>	Ehhalt and Heidt [1973]	0.0436–0.873 (0.473)
$F_{\text{volcano}}^{\text{CH}_4}(q)$	Quaternary CH <sub>4</sub> release out of terrestrial volcanoes, 10 <sup>18</sup> mol Ma <sup>-1</sup>	Judd et al. [2002]	0.0499–0.387 (0.387)
$F_{\text{ocean}}^{\text{CH}_4}(q)$	Quaternary CH <sub>4</sub> release out of the photic zone of the oceans, 10 <sup>18</sup> mol Ma <sup>-1</sup>	IPCC [2001]	0.623–0.935 (0.935)
$F_{\text{wetland}}^{\text{CH}_4}(q)$	Quaternary CH <sub>4</sub> release out of wetlands, particularly swamps, 10 <sup>18</sup> mol Ma <sup>-1</sup>	Seinfeld and Pandis [1998]	3.43–9.35 (7.5)
$p\text{CH}_4(q)$	Quaternary partial pressure of CH <sub>4</sub> , ppmv	Raynaud et al. [1993]	(0.355)
$p\text{CO}_2(q)$	Quaternary partial pressure of CO <sub>2</sub> , ppmv	Berner and Berner [1996]	(230)

<sup>a</sup>Parameter values and fluxes applied in the standard case are given in parentheses.

atmospheric CH<sub>4</sub> amount ( $F_{\text{release}}^{\text{CH}_4} - F_{\text{loss}}^{\text{CH}_4}$ ) is in a quasi steady state:

$$\frac{dM\text{CH}_4}{dt} = 0, \quad (15)$$

$$F_{\text{release}}^{\text{CH}_4} - F_{\text{soil}}^{\text{CH}_4} - k_{\text{atmosphere}} F_{\text{loss}}^{\text{CH}_4}(q) R\text{CH}_4 = 0. \quad (16)$$

Solving for RCH<sub>4</sub> results in

$$R\text{CH}_4 = \frac{F_{\text{release}}^{\text{CH}_4} - F_{\text{soil}}^{\text{CH}_4}}{k_{\text{atmosphere}} F_{\text{loss}}^{\text{CH}_4}(q)}. \quad (17)$$

Considering a steady state also for the Quaternary methane cycle,

$$F_{\text{loss}}^{\text{CH}_4}(q) = F_{\text{release}}^{\text{CH}_4}(q) - F_{\text{soil}}^{\text{CH}_4}(q), \quad (18)$$

RCH<sub>4</sub> can be calculated as

$$R\text{CH}_4 = \frac{\text{net release}}{k_{\text{atmosphere}}}, \quad (19)$$

where “net release” is defined as the net release of methane into the atmosphere normalized to the Quaternary value:

$$\text{net release} = \frac{F_{\text{release}}^{\text{CH}_4} - F_{\text{soil}}^{\text{CH}_4}}{F_{\text{release}}^{\text{CH}_4}(q) - F_{\text{soil}}^{\text{CH}_4}(q)}. \quad (20)$$

Equation (19) is analytically unsolvable because of the exponents in the term  $k_{\text{atmosphere}}$  (see equation (11)). Thus we solved this term numerically (Table 1 and Figure 5) with Mathematica 5.0. The normalized CH<sub>4</sub> concentration in the atmosphere is then calculated as a function of the net release (Figure 5):  $(F_{\text{release}}^{\text{CH}_4} - F_{\text{soil}}^{\text{CH}_4}) / [F_{\text{release}}^{\text{CH}_4}(q) - F_{\text{soil}}^{\text{CH}_4}(q)] = \text{net release}$ . RCH<sub>4</sub> increases exponentially with increasing net release.

## 2.4. Climate Effects of CH<sub>4</sub>

[29] Atmospheric CH<sub>4</sub> is an important greenhouse gas and affects the average global surface temperatures by its

radiative forcing (RF in W m<sup>-2</sup>). The RF by CH<sub>4</sub> can be estimated as [Thorpe et al., 1996]

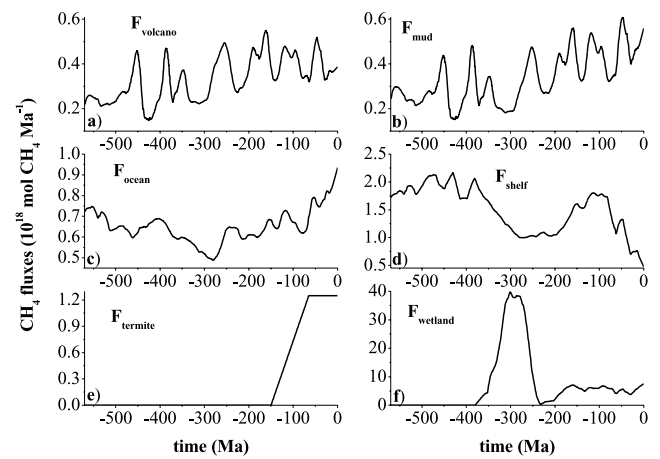
$$\text{RF} = 0.0411 \left[ \sqrt{p\text{CH}_4} - \sqrt{p\text{CH}_4(q)} \right], \quad (21)$$

where  $p\text{CH}_4$  and  $p\text{CH}_4(q)$  are the atmospheric partial pressures of CH<sub>4</sub> changing over time and the reference prehuman level (350 ppbv). In the absence of climate feedbacks the climate sensitivity parameter  $\lambda$  [0.30 K (W m<sup>-2</sup>)<sup>-1</sup>] [Seinfeld and Pandis, 1998] can be used to calculate the impact of CH<sub>4</sub> on the average global surface temperature ( $\Delta T^{\text{CH}_4}$ ):

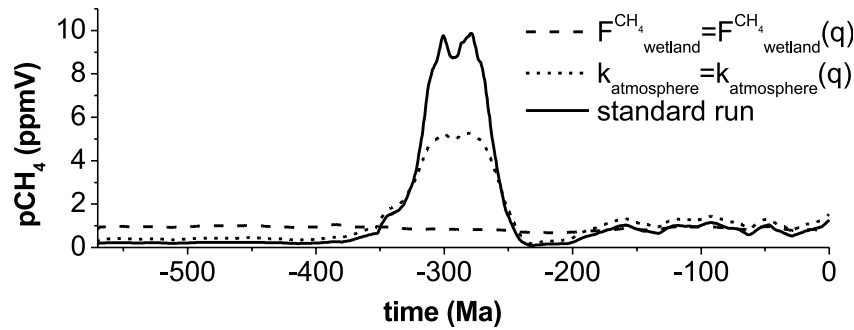
$$\Delta T^{\text{CH}_4} = \lambda \text{RF}. \quad (22)$$

## 3. Results and Discussion

[30] A standard run is produced, giving the evolution of methane-producing environments and of atmospheric CH<sub>4</sub>



**Figure 6.** Changes in CH<sub>4</sub> fluxes into the atmosphere out of (a) magmatic volcanoes on land ( $F_{\text{volcano}}$ ), (b) onshore and shallow water mud volcanoes ( $F_{\text{mud}}$ ), (c) the photic zone of the oceans ( $F_{\text{ocean}}$ ), (d) shelf zones, (e) digestive tracks of insects ( $F_{\text{termite}}$ ), and (f) wetlands ( $F_{\text{wetland}}$ ) used for the calculation of atmospheric  $p\text{CH}_4$ .



**Figure 7.** Changes in atmospheric partial pressure of methane ( $p\text{CH}_4$ ) in the standard run and in sensitivity runs with a constant kinetic loss of  $\text{CH}_4$  from the atmosphere [ $k_{\text{atmosphere}} = k_{\text{atmosphere}}(q)$ ] and with constant wetland emissions [ $F_{\text{wetland}}^{\text{CH}_4} = F_{\text{wetland}}^{\text{CH}_4}(q)$ ].

over the various periods of the Phanerozoic. Then the controls on  $p\text{CH}_4$  are evaluated by using the results of the standard run and additional model runs (sensitivity tests) with systematically varied parameter values. Table 2 shows the prehuman emission rates applied in the standard run.

### 3.1. Phanerozoic Evolution of $p\text{CH}_4$

[31] This study is the first attempt to describe the atmospheric  $\text{CH}_4$  evolution over the entire Phanerozoic. The corresponding  $\text{CH}_4$  emission trends of the individual emitters are illustrated in Figures 6a–6f. Since the advent of land plants during the Paleozoic, swamps and wetland have been the main methane emitters. However, during the early Paleozoic the marine methane-producing environments were more significant (Figures 6b–6d) because of the lower terrestrial emission rates.

[32] In the standard run the  $\text{CH}_4$  release reached the maximum value during the Carboniferous coal swamp era (Figure 6f). Consequently, the atmospheric  $p\text{CH}_4$  increased to 10 ppmv (Figure 7) during the middle Phanerozoic. The next two peaks were reached in the Cretaceous and Jurassic, with maximum contents of 1.5 ppmv approaching the  $p\text{CH}_4$  level prevailing in the modern atmosphere.

[33] The main trend in  $p\text{CH}_4$  was influenced by the appearance of vascular land plants and the subsequent spread of swamps on the continents. The first land plants flourished on the continents during the Silurian. During the following Carboniferous and Permian, large continental areas were covered by wetlands, and vast amounts of  $\text{CH}_4$  were formed in these swamps and wetlands by the microbial degradation of plant remains under anoxic conditions (Figure 6f). According to the standard run, the  $p\text{CH}_4$  was up to 28 times higher than in prehuman times and six times higher than today during the Middle Phanerozoic (Figure 7).

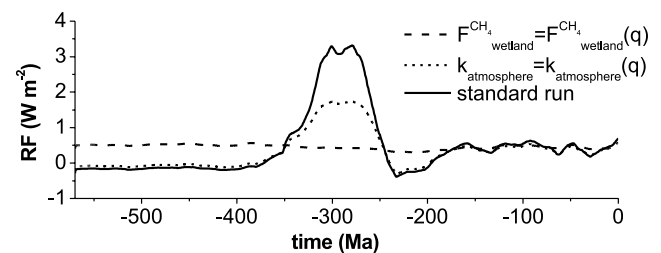
[34] The importance of the wetland source is demonstrated by an additional model run where this main emitter was maintained at the low Quaternary level over the entire model period [ $F_{\text{wetland}}^{\text{CH}_4} = F_{\text{wetland}}^{\text{CH}_4}(q)$ ]. The resulting Phanerozoic  $p\text{CH}_4$  and RF trends showed only small variations, confirming that the model output is mainly controlled by methane emissions from wetlands (Figures 7 and 8).

### 3.2. Effects of Atmospheric $\text{CH}_4$ on Average Global Surface Temperature and $p\text{CO}_2$

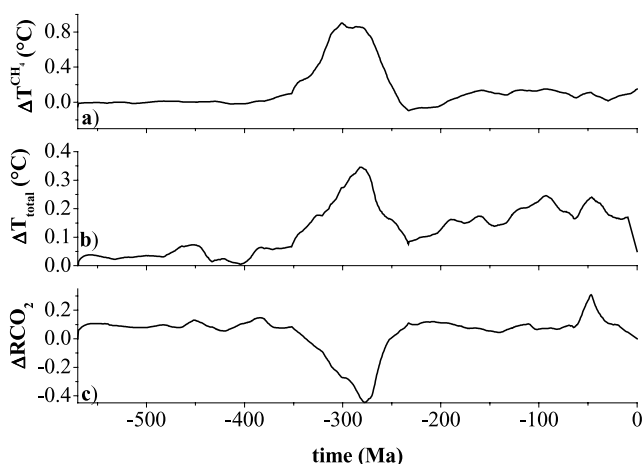
[35] During the Carboniferous coal swamp era the rising  $p\text{CH}_4$  level caused a strong positive RF (Figure 8), inducing a temperature increase of up to  $1^\circ\text{C}$  (Figure 9a). During periods of low  $\text{CH}_4$  emission the temperature effect of methane was small whereas in times with high  $\text{CH}_4$  emission rates and low atmospheric loss the effects became significant, especially during the Permian-Carboniferous coal swamp era.

[36] Additional model runs were performed with the carbon box model of Wallmann [2004] to explore the effects of  $\text{CH}_4$ -induced warming on global carbon cycling. The methane model presented in this paper was included in the  $\text{CO}_2$  model of Wallmann [2004], which also considered the  $\text{CO}_2$  produced by the oxidation of methane emitted from geological sources (volcanoes). The  $\text{CO}_2$  produced through the oxidation of biogenic  $\text{CH}_4$  wetlands is not considered since the biogenic  $\text{CH}_4$  is part of the rapid biological carbon cycle (primary production, export production, and respiration) that is not resolved by the model. The secular temperature trend was calculated by adding the methane temperature term (equation (22)) to the temperature equation of Berner and Kothavala [2001]:

$$T = \Gamma \ln \text{RCO}_2 - W_s \frac{t}{-570} + T(q) + \text{GEOG} + \Delta T^{\text{CH}_4}, \quad (23)$$



**Figure 8.** Changes in radiative forcing (RF) in the standard run and in sensitivity runs with a constant kinetic loss of  $\text{CH}_4$  from the atmosphere [ $k_{\text{atmosphere}} = k_{\text{atmosphere}}(q)$ ] and with constant wetland emissions [ $F_{\text{wetland}}^{\text{CH}_4} = F_{\text{wetland}}^{\text{CH}_4}(q)$ ].



**Figure 9.** Changes in global average surface temperature over the Phanerozoic: (a) direct temperature change due to atmospheric CH<sub>4</sub> greenhouse gas effect, (b) temperature changes calculated in the model of Wallmann [2004] considering the impacts of CH<sub>4</sub> and CO<sub>2</sub>, and (c) changes in RCO<sub>2</sub> induced by enhanced silicate weathering considering the effect of CH<sub>4</sub> on temperature.

where  $\Gamma$  gives the relation between surface temperature and RCO<sub>2</sub>, RCO<sub>2</sub> is the atmospheric partial pressure of CO<sub>2</sub> normalized to the Quaternary value (230  $\mu$ atm),  $W_s$  defines the impact of increasing solar luminosity on surface temperature, GEOG describes the effect of paleogeography on albedo and global surface temperature, and  $T(q)$  is the Quaternary average global surface temperature (13.5°C).

[37] According to this new model, the warming induced by CH<sub>4</sub> enhances the consumption of CO<sub>2</sub> via silicate weathering. RCO<sub>2</sub> decreases during periods of enhanced CH<sub>4</sub> release (Figure 9c) because the magnitude of the CO<sub>2</sub> sink, induced by accelerated silicate weathering, surpasses the CO<sub>2</sub> production caused by methane oxidation. Nevertheless, average global surface temperatures were enhanced by 0.4°C because of the high methane emissions from wetlands during the Permian and Carboniferous. The long-lasting methane emissions during this coal swamp era may have prevented a global glaciation during the middle Phanerozoic. Short pulses of methane from dissociating gas hydrates might, in contrast, reduce the  $p$ CO<sub>2</sub> level beyond a critical value and could trigger “snowball Earth” events because methane has a much smaller atmospheric residence time than CO<sub>2</sub> [Schrag *et al.*, 2002].

### 3.3. CH<sub>4</sub> Oxidation in the Phanerozoic Atmosphere

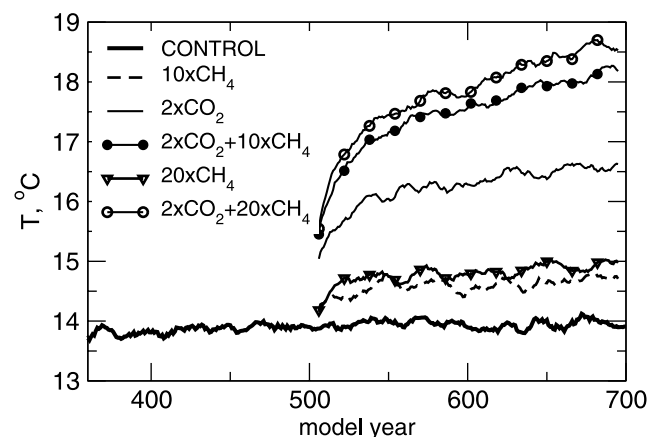
[38] The increase in atmospheric CH<sub>4</sub> caused by high CH<sub>4</sub> emissions is further amplified by the coeval decrease in the cleaning power of the atmosphere. An additional model run with a time-independent kinetic constant for atmospheric CH<sub>4</sub> loss [ $k_{\text{atmosphere}} = k_{\text{atmosphere}}(q)$ ] was performed to explore the effects of atmospheric oxidation. The high Quaternary value applied in this model run induced much lower  $p$ CH<sub>4</sub> and RF values over the Permian–Carboniferous and other periods of the Phanerozoic (Figures 7 and 8). Only during periods of very low methane emission, e.g., during the

early Paleozoic, the calculated  $p$ CH<sub>4</sub> and RF are higher than in the standard run. The strong sensitivity of the model output with respect to the kinetic constant of atmospheric oxidation confirms that the Phanerozoic evolution of atmospheric  $p$ CH<sub>4</sub> is strongly affected by the nonlinear relation between CH<sub>4</sub> emissions and atmospheric cleaning power.

### 3.4. Effects of Atmospheric Methane in a State-of-the-Art Climate Model

[39] Mean global temperature and methane changes in global coupled climate simulations are in general comparable to the Phanerozoic era conditions and despite other differences in boundary conditions and external forcing may serve as a demonstration of comprehensive dynamical feedbacks in a fully coupled three-dimensional climate system model. Several climate change simulations with different greenhouse gas (GHG) concentrations have been performed with the global coupled atmosphere–ocean–sea ice general circulation model ECHAM5/MPI-OM [Marshall *et al.*, 2003; Roeckner *et al.*, 2003; Semenov and Latif, 2006]. The climate change experiments were performed relative to preindustrial climate conditions with atmospheric CO<sub>2</sub> and CH<sub>4</sub> concentrations of 280 and 0.76 ppmv, respectively. Five 200 year long simulations with (instantaneously) 10 and 20 times increased  $p$ CH<sub>4</sub>, doubling of  $p$ CO<sub>2</sub>, and their combined effects (10  $\times$  CH<sub>4</sub> + 2  $\times$  CO<sub>2</sub> and 20  $\times$  CH<sub>4</sub> + 2  $\times$  CO<sub>2</sub>) were performed. The simulations started from year 500 of a long control integration (performed at the Max Planck Institute for Meteorology) [Gregory *et al.*, 2005]. The global mean surface temperature in the control simulation amounts to about 14°C.

[40] The evolution of the simulated global annual mean surface air temperature (SAT) for the different simulations is shown in Figure 10. The SAT increases (last 30 years of the perturbed experiment) range from 0.75°C to 4.6°C. The time for the climate system to adjust to the perturbation in the GHG concentrations varies from 20 to 50 years ( $e$ -folding time for the weakest, 10  $\times$  CH<sub>4</sub>, and the strongest, 20  $\times$  CH<sub>4</sub> + 2  $\times$  CO<sub>2</sub>, forcing, respectively). An estimate of



**Figure 10.** Global mean annual surface air temperatures (SAT), °C, as simulated by the ECHAM5/MPI-OM model in different climate change simulations (see legend). Eleven-year running means are shown.



the RF (top of atmosphere, first year) in the  $10 \times \text{CH}_4$  experiment is  $2.1 \text{ W m}^{-2}$ , resulting in global SAT increase of  $0.75^\circ\text{C}$ . Interestingly, the further doubling of  $p\text{CH}_4$  in the model practically does not change the global mean RF, resulting in an additional minor global SAT increase of  $0.2^\circ\text{C}$ . However, the regional differences (not shown) reach  $3.5^\circ\text{C}$  and are largest in the northern extratropics. In particular for the modern era climate conditions the simulations show a warming amplified by a factor of 4 in northern Eurasia where the largest wetlands are located. After adjustment of the SAT the SW RF significantly increases basically because of the total cloud cover decrease (about  $0.9\%/^\circ\text{C}$ ) and sea ice retreat ( $12\%/^\circ\text{C}$ ). It is apparent from Figure 10 that the SAT changes in the simulations with increased  $p\text{CH}_4$  and  $p\text{CO}_2$  together are much stronger than adding the changes from the two individual simulations. The methane effect doubles roughly under  $2 \times p\text{CO}_2$  conditions. This nonlinearity presumably arises from the water vapor feedback [Held and Soden, 2000]. However, the analysis of the spatial distribution of the SAT changes reveals that dynamical factors may also have a significant contribution. The largest temperature differences are found in the northern high latitudes in winter and are related to the sea ice changes. The latter are partly linked to changes in the large-scale ocean circulation reflected by strong surface water temperature anomalies in the Atlantic Ocean.

#### 4. Conclusion

[41] The present model describes the secular atmospheric  $p\text{CH}_4$  trend over the entire Phanerozoic and demonstrates the importance of the  $\text{CH}_4$  emission from wetlands in the past. Atmospheric oxidation is able to compensate for moderate  $\text{CH}_4$  emission rates, but with increasing pollution, methane accumulates in the atmosphere. In times of atmospheric  $\text{CH}_4$  accumulation, methane has a significant effect on average global surface temperature and  $\text{RCO}_2$ . During times of high organic matter accumulation in terrestrial environments (Permian-Carboniferous coal swamp era) the atmospheric  $p\text{CH}_4$  increases up to 10 ppmv. The high  $p\text{CH}_4$  during this period implies a maximum RF of about  $3.5 \text{ W m}^{-2}$  via  $\text{CH}_4$ , which is twice as high as the RF currently caused by anthropogenic  $\text{CO}_2$ .

[42] The model results show, conspicuously, that  $\text{RCO}_2$  did not increase in response to increasing  $\text{CH}_4$  emissions. By its radiative forcing and because of its decomposition into  $\text{CO}_2$ ,  $\text{CH}_4$  heated the average global surface temperature by up to  $1^\circ\text{C}$ . The  $\text{RCO}_2$  values were, however, substantially reduced by weathering processes which were accelerated by the  $\text{CH}_4$ -induced warming. Overall,  $\text{CO}_2$  consumption via enhanced weathering surpassed  $\text{CO}_2$  production via methane oxidation so that the atmospheric  $\text{CO}_2$  level dropped in response to enhanced  $\text{CH}_4$  emissions. As a net effect, the average global surface temperature increased by only  $0.4^\circ\text{C}$  during the Carboniferous coal swamp era.

[43] The elevated  $p\text{CH}_4$  values during the Permian-Carboniferous cold period may have moderated the cooling trend caused by the coeval drawdown of atmospheric  $\text{CO}_2$ . Both the decrease in  $p\text{CO}_2$  and the increase in  $p\text{CH}_4$

are intimately linked to the spread of land plants during the Carboniferous and Permian. The high  $\text{CH}_4$  emissions from swamps during these periods may have prevented the development of a snowball Earth state repeatedly encountered during the Precambrian prior to the advent of land plants.

[44] Simulations with a state-of-the-art climate model show that the effects of atmospheric  $\text{CH}_4$  on average global surface temperature are amplified by high background levels of atmospheric  $\text{CO}_2$ . A coeval increase in the partial pressure of both greenhouse gases thus has a much stronger climate effect than previously anticipated.

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