Methane hydrate in the global organic carbon cycle

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ABSTRACT

The global occurrence of methane hydrate in outer continental margins and in polar regions, and the magnitude of the amount of methane sequestered in methane hydrate suggest that methane hydrate is an important component in the global organic carbon cycle. Various versions of this cycle have emphasized the importance of methane hydrate, and in the latest version the role of methane hydrate is considered to be analogous to the workings of an electrical circuit. In this circuit the methane hydrate is a condenser and the consequences of methane hydrate dissociation are depicted as a resistor and inductor, reflecting temperature change and changes in earth surface history. These consequences may have implications for global change including global climate change.

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Introduction

Methane hydrate occurs naturally as a solid composed of rigid cages of water molecules that enclose molecules of mainly methane, often accompanied by very small amounts of ethane and carbon dioxide. The physical chemistry of methane hydrate is well understood (Sloan, 1998), and the occurrence on Earth of methane hydrate is controlled by an interrelationship between temperature, pressure, composition of the gas mixture, and ionic strength of the water (Kvenvolden, 1993). These factors limit its occurrence on Earth to: (i) oceanic sediment of continental and insular slopes and rises of active and passive margins at water depths greater than ~300 m; (ii) deep-water sediment of inland lakes and seas, also where water depths are greater than ~300 m; and (iii) polar sediment of both continents and continental shelves. Thus, methane hydrate occurs worldwide but in restricted geographic regions. An updated global inventory (Kvenvolden and Lorenson, 2001) reports on methane hydrate recovered from 19 places worldwide and 77 places where the presence of methane hydrate has been inferred from geophysical, geochemical, and geological evidence (Fig. 1). Therefore, its global distribution suggests that methane hydrate could be an important component of the global organic carbon cycle.

To be an important component in the global organic carbon cycle, however, this methane-hydrate reservoir needs to contain significant amounts of methane carbon. Unfortunately, all estimates of the methane content of methane hydrate are highly speculative, but they suggest that the methane content is very large (Kvenvolden, 1999). When naturally occurring methane hydrate was first recognized, the amount of methane in the hydrate form was thought to be ‘enormous’ (Cherskiy and Makogon, 1970). By the end of the 1980s, estimates of hydrate methane were greatly constrained when Kvenvolden (1988) and MacDonald (1990), working independently, estimated the global methane-carbon content of methane hydrate to be about 10 000 Gt, when expressed to one significant figure, giving rise to a ‘consensus’ estimate at the time.

In the 1990s revised estimates were made using the power of general circulation models (GCMs). Best estimates of 14 000 Gt (in situ model of Gornitz and Fung, 1994) and of 24 000 Gt Harvey and Huang (1995) were reported. Other global estimates made during the same period were 3000 Gt (Holbrook et al., 1996), 1 000–10 000 Gt (Dickens et al., 1997), 8000 Gt (Makogon, 1997), and 500 Gt (Ginsburg and Soloviev, 1995). Thus, the best estimates range from a low of 500 Gt to a high of 24 000 Gt of methane carbon. The ‘consensus’ value of 10 000 Gt of methane carbon in methane hydrate worldwide remains about midway between the more recently estimated extremes. Therefore, if this intermediate estimate is at all valid, then methane hydrate must be an important element in the global organic carbon cycle, because such a reservoir of methane carbon is indeed enormous when compared to the sizes of the other organic carbon reservoirs.

Organic carbon cycles

The major features of the global carbon cycle were considered in detail by Bolin (Bolin et al., 1979; Bolin, 1983, 1986). From these considerations, Fig. 2(A) was drawn (Kvenvolden, 1988) to emphasize the organic carbon portion of the global carbon cycle and the magnitude of methane hydrate reservoir relative to the other organic carbon pools. One of the striking observations from this depiction of the organic carbon cycle was that all of the organic carbon reservoirs, except one, were smaller than the reservoir of organic carbon in methane hydrate, estimated to be about 10 000 Gt of methane carbon. This value is twice as large as the fossil fuel (oil, coal, and natural gas) reservoir containing 5000 Gt of carbon.

This value of 5000 Gt deserves some scrutiny. For example, Bolin et al. (1979) provided the first estimate of >5000 Gt of fossil fuel carbon, but with time the (> ) designation was dropped (Bolin, 1983, 1986). Much earlier Hunt (1972) had estimated that the fossil fuel reservoir contained 16 000 Gt of carbon, and this value was carried into the textbook by Mason and Moore (1982). Mean-
They suggested that methane released from oceanic methane hydrate offers a plausible explanation, because the average carbon isotopic composition of hydrate methane (−60‰) provides the necessary carbon isotopic composition to lead to the negative carbon isotopic excursions. If all of this methane was utilized in affecting the carbon budget of the oceans (Dickens, 2001b), then none reached the atmosphere where its presence is required to influence global climate change. Recent evidence, however, from the terrestrial record found within the Aptian Stage of the Lower Cretaceous suggests that methane from dissociated methane hydrate may have reached the atmosphere, giving rise to a striking −5‰ excursion in δ13C as measured in vascular land-plant tissue at three localities (Jahren et al., 2001).

Although our understanding of the role of methane hydrate in global change—including global climate change—is incomplete, the circumstantial evidence available thus far is highly suggestive. Worldwide marine and terrestrial records, however, will be needed from the same intervals of geological time that all show the appropriate negative carbon isotopic excursions. Such consistency in data would seriously implicate methane hydrate as an important factor in Earth surface processes and in global change.

Tracking methane in the water column above currently dissociating gas hydrate would provide further evidence for the fate of methane in the ocean/atmosphere system. However, the fate of methane hydrate in the global methane budget is poorly understood because so little is known about how much methane from dissociating methane hydrate actually reaches that system (Valentine et al., 2001). Microbial aerobic methane oxidation in the water column (Valentine et al., 2001) and anaerobic methane oxidation in the surface sediment (Orphan et al., 2001) limit the amount of methane that enters the water and the atmosphere. However, if the rate of methane release from methane hydrate exceeds the rate of oxidation, methane from this source should reach the atmosphere, all other factors being equal, and likely affect global climate change.
Resonant circuit analogue

In order to attempt to capture in a simplistic way the possible role of methane hydrate in global change, including global climate change, the idea of methane hydrate as a capacitor (Dickens 2001a,b) is advanced further.

The role of methane hydrate in the global organic carbon cycle is visualized as being analogous to the workings of a coupled electric circuit composed of a battery, condenser (capacitor), resistor, inductor, and timer (Fig. 3). The battery is the source of methane, the condenser stores and releases methane, and the resistor and inductor represent in a crude way the possible consequences resulting from the release of methane. The clock controls the time for switching back and forth between the two circuits and is likely influenced by some feedback. While the variable

Fig. 2 (A) The global organic carbon cycle adapted from Moore and Bolin (1987) showing the addition of a compartment for the gas hydrate reservoir. Numbers are given in gigatonnes ($10^{15}$ g) of methane carbon. From Kvenvolden (1988). (B) The compartments of (A) are rearranged to show methane hydrate as a central component in the global organic carbon cycle. Units (Gt or gigatonnes) of methane carbon are the same as in (A). The methane hydrate lies within the shallow and deep biosphere, is found in the shallow lithosphere, and can occur at the interface between the lithosphere/biosphere and the hydrosphere in aquatic systems. Biochemical oxidation of hydrate methane occurs in the lithosphere/biosphere whereas photochemical oxidation occurs in the atmosphere. Vents and seeps depict the release of methane to the hydrosphere and atmosphere from non-hydrate as well as hydrate sources.
switch closes on the battery side
(opens on the inductor side) the con-
denser or methane hydrate stores
methane. Then one switch closes and
the other opens, releasing methane
from the methane hydrate condenser
to the resistor and inductor, leading to
possible interrelated consequences
such as changes in ocean chemistry,
temperature, sea level and glacial his-
tory. The coupled switches regulate
the flow of methane in the two
circuits. It is not certain yet the extent
to which the methane hydrate causes
these changes or is affected by these
changes, but the switches continue to
open and close through geological
time as methane hydrate stores and
releases methane.

There is a need to discover the
feedback controls of this system and
the directions in which they operate.
Although this representation (Fig. 3) is
simpistic and ignores possible feed-
back consequences of changing surfi-
cial conditions, it tries to illustrate the
dynamic nature of the interrelated
processes that methane hydrate can
effect. Many of these processes have
been addressed previously. For exam-
ple, McIver (1982) recognized a possi-
ble connection between gas hydrate
and submarine geohazards; Nisbet
(1990) and Paull et al. (1991) consid-
ered issues of glacial cycles, global
temperature, sea level, and climate
change; and Dickens et al. (1997)
noted changes in ocean chemistry (the
carbon isotopic record). Evidence for
an interrelationship among methane
hydrate and these various processes is
often suggestive, but not necessarily
convincing. Indeed, methane hydrate
may be a significant factor in global
changes at and near to the Earth’s
surface, but a firm understanding of its
role, as suggested in the resonant cir-
cuit analogue (Fig. 3), requires much
additional multidisciplinary research.

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Fig. 3  Electrical resonant circuit analogue for methane hydrate in the global organic carbon cycle. This simplistic drawing brings
attention to the possible interrelated consequences resulting from methane hydrate formation and decomposition throughout
geological time. The workings of the inductor, resistor and feedback circuit are analogous to the various global changes that may
be influenced by methane hydrate.


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