Methane-driven oceanic eruptions and mass extinctions

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ABSTRACT

   Focusing on the Permian-Triassic boundary, ca. 251 Ma, I explore the possibility that mass extinction can be caused by an extremely fast, explosive release of dissolved methane (and other dissolved gases such as carbon dioxide and hydrogen sulfide) that accumulated in the oceanic water masses prone to stagnation and anoxia (e.g., in silled basins). The mechanism of the explosive release is the same as in the Lake Nyos disaster of 1986, i.e., a water-column eruption caused by the interplay of buoyancy forces and exsolution of dissolved gas. The eruption brings to the surface deep anoxic waters that cause extinctions in the marine realm. Terrestrial extinctions are caused by explosions and conflagrations that follow the massive release of methane (the air-methane mixture is explosive at methane concentrations between 5% and 15%) and by the eruption-triggered floods. This scenario accounts well for the available data, and may be relevant to other phenomena.

Keywords: mass extinctions, methane, Permian-Triassic boundary.

INTRODUCTION

   The history of life is punctuated by mass extinctions, but their causes remain obscure. Still missing is a satisfactory answer to the question posed by Raup (1991, p. 195), "Did we choose a safe planet?" Extraterrestrial causes have attracted the most attention, but "there is no reason why all catastrophes on Earth should have been induced by bolide impact. As yet we know too little about the workings of our planet to dismiss Earth-induced catastrophes" (Hallam and Wignall, 1997, p. 242). Here I explore one possible mechanism of the latter: oceanic eruption, driven by exsolution of methane dissolved in the water column.

METHANE IN THE OCEAN WATER COLUMN

   Methane, CH_4, is continuously produced beneath the ocean floor. Most of this methane is consumed by archaea and bacteria in the upper layer of sediments; the rest escapes into the overlying water column as bubbles. (For present purposes, it is immaterial whether some part of this methane flux results from dissociation of methane hydrates.) The rising bubbles diminish in size and finally disappear as methane dissolves in the seawater (Hovland et al., 1993). In a well-oxygenated (or anoxic but sulfate rich) water column, dissolved methane, as well as the sinking organic matter from the surface waters, is oxidized by microbes. But unlike the rising bubbles of methane or the sinking particles of organic matter, which can traverse the entire water column in a few days, oxygen molecules or sulfate ions can be delivered to the water column only by fluid flow (or diffusion, which is very slow). In stagnant water masses, therefore, the oxidation potential of the water column will be eventually overwhelmed by the flux of sinking organic matter, plus the flux of methane bubbles from the seafloor. There is strong evidence in the geological record that dissolved methane may escape oxidation in the water column (Thomas et al., 2002). Under such conditions, methane that dissolves in the water column will accumulate in it as time proceeds.

   Evidence of such accumulation exists both in direct measurements and in the geological record. The only long-term series of the former,

in the Cariaco Basin, shows that methane concentration in the deep waters of the basin is increasing with time, roughly linearly (Figs. 6d and 7 of Scranton et al., 2001). The microfossil carbon isotope data from the Santa Barbara Basin sediment core show that high levels of dissolved methane were present periodically in the water column (Kennett et al., 2000). This has been confirmed by a microbial-biomarker study (Hinrichs et al., 2003), and is likely to be representative of oceanic regions prone to stagnation and anoxia, such as silled basins or deep-water masses isolated by topography and Taylor columns[1]. (Such regions are likely to have sizes below the resolution of ocean circulation models used in biogeochemical studies; e.g., Hotinski et al. [2001].) The time scale of the meridional overturning circulation, $\sim 10^3$ yr, has little relevance for the water masses that do not participate in it; these can only be mixed by turbulence resulting from breaking of the internal gravity waves (ultimately due to tides and winds). The corresponding vertical (diapycnal) turbulent diffusivity K is typically $\sim 10^{-5}$ m^2 s^{-1}, and can be as low as 0.5×10^{-6} m^2 s^{-1} (Gregg et al., 2003); the latter translates into $K = 16$ m^2 yr^{-1}. This means that it may take a million years for turbulent mixing to penetrate vertically through $(Kt)^{1/2} = 4$ km (t being time). (The tracer-based estimates of the age of water masses are controversial [Wunsch, 2002] and are not used here.) In stagnant water masses, accumulation of dissolved methane may thus continue for very long times. Assuming that dissolved methane can accumulate to high concentrations, let us explore the consequences.

   Consider a water column with stable density stratification due to the temperature and/or salinity gradients. Methane carried by a rising bubble will dissolve in the surrounding water as long as the concentration of methane already dissolved in it is less than the saturation value (solubility) for the local temperature T and pressure P; here saturation means equilibrium with respect to gaseous methane at the same T and P, i.e., with respect to methane inside the bubble. The solubility of methane in seawater is low (Handa, 1990); in terms of mole fraction, solubility at $T = 25$ °C and $P = 1$ bar is $\sim 2 \times 10^{-5}$. However, solubility is nearly proportional to pressure (Henry's law), and also increases as temperature drops, so that at $T = 5$ °C and $P = 400$ bar (depth 4 km), the predicted value of solubility is 4.3×10^{-3}.

METASTABILITY AND ERUPTION

   A liquid subject to gravity and completely or partially saturated with dissolved gas is, thermodynamically, in a metastable state. Consider for clarity the case when the concentration of the dissolved gas is only slightly below saturation throughout, and thus increases downward in accordance with Henry's law. Then locally there is no tendency for the dissolved gas to exsolve (to form bubbles), in spite of the fact that nuclei are abundant in seawater. (Exsolution would lead to a slight increase in free energy: below saturation, the chemical potential of the gas species is lower in solution than in the free gas phase.) At the same

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[1]In a rotating fluid, conservation of potential vorticity leads to formation of Taylor columns over bumps or depressions, the fluid trapped inside a Taylor column either being stagnant or recirculating slowly along closed streamlines. The necessary condition for the Taylor column formation is the smallness of the Rossby number $R_o \equiv U/fL$, where U is the flow velocity scale, f is the Coriolis parameter, and L is the horizontal length scale of the obstacle. In the deep, an upper estimate of U (away from the western boundaries) is 1 cm s^{-1}; with $f = 10^{-4}$ s^{-1} and L taken as 100 km, $R_o = 10^{-3}$, so this condition is satisfied by a wide margin. Stratification counteracts the effects of rotation, leading to some reduction in the column height (Owens and Hogg, 1980).

time, the free energy of the system as a whole would be greatly reduced if most of the dissolved gas were to somehow escape from solution and collect above the liquid. (This free energy reduction is due to the fast decrease of the chemical potential of gas with a drop in pressure.) Thus, the system is in a metastable state, albeit an unusual one. Strictly speaking, this state is not an equilibrium one even locally: the increase of the solute concentration with depth causes a diffusion flux directed upward, which, given sufficient time, could bring the system into the above state of minimum free energy. However, the continuous supply of methane by the rising bubbles from the seafloor ensures that the concentration profile will remain nonuniform, slowly approaching the saturation one. Even if that supply were to cease, the diffusion time scales are so long that this path toward the global energy minimum can be ignored.

A very fast transition from this metastable state can be triggered by disturbances that displace fluid a finite distance in the vertical direction. Such disturbances may result from an earthquake, a seafloor volcano, convection currents due to geothermal heating, or an internal gravity wave. Consider a parcel of fluid that is displaced upward, and is now subject to lower hydrostatic pressure, to which corresponds a lower solubility value. As a result, the fluid in the parcel is now supersaturated with the dissolved gas, which must begin to exsolve, forming tiny gas bubbles. (If the fluid in its original position was only partially saturated, exsolution will begin after the parcel has risen through some significant distance, so in this case the initial disturbance must be sufficiently large.) The volume of the ascending parcel of fluid increases due to the formation of bubbles, making it more buoyant and accelerating its rise; this leads to further reduction in the ambient pressure, further exsolution of gas, and further increase in the volume of the parcel. This self-accelerating motion entrains the surrounding fluid; exsolution of the gas in the latter reinforces the motion. The result is a violent eruption (Kling et al., 1987; Zhang, 1996). From the initial eruption site, hydrodynamic disturbances propagate in all directions (via turbulent entrainment and/or internal gravity waves), triggering eruptions at other sites. Similarly to transitions from other metastable states (e.g., boiling of a superheated liquid), the eruption should spread quickly throughout the region of the ocean where the water column is saturated, or partially saturated, with gas.

In spite of the low solubility of methane in seawater, the total possible increase in the buoyancy of the parcel can be large. Consider a parcel that started its rise at 4 km depth, where solubility of methane is $\sim 4.3 \times 10^{-3}$. Then, if the parcel had a volume of 18 cm^3 (1 mol of water) and was saturated with methane, it contained 4.3×10^{-3} mol of dissolved methane. By the time this parcel has risen to the surface, essentially all the methane in the parcel has exsolved (solubility is $\sim 2 \times 10^{-5}$ at the surface). At the surface conditions ($T \approx 25\ °C$, $P = 1$ bar), 1 mol of any gas occupies 25×10^3 cm^3, so the total volume of methane in the parcel is ~ 108 cm^3, and the volume of the parcel, which now contains a mist of water droplets in gaseous methane, is 126 cm^3. That is, the volume of the parcel has increased by a factor of seven. Concurrent exsolution of other dissolved gases (e.g., carbon dioxide CO_2, hydrogen sulfide H_2S) will add to the effect.

A rather similar process is responsible for the most violent, explosive volcanic eruptions (called Plinian), such as eruptions of Mount Vesuvius in A.D. 79 or Mount St. Helens in 1980. These eruptions are driven by exsolution of gases (primarily water vapor) dissolved in the liquid magma.

In Lake Nyos (Cameroon), CO_2 of magmatic origin enters the water column from the bottom, at a depth of ~ 200 m. In 1986, the lake erupted, creating a gas-water fountain ~ 120 m in height (Zhang, 1996), and releasing a lethal cloud of CO_2. A water surge washed up the shore to a height of ~ 25 m. The eruption continued for several hours (Kling et al., 1987).

OCEANIC ERUPTION AS A CAUSE OF MASS EXTINCTION

The consequences of a methane-driven oceanic eruption for marine and terrestrial life are likely to be catastrophic. Figuratively speaking, the erupting region ''boils over,'' ejecting a large amount of methane and other gases (e.g., CO_2, H_2S) into the atmosphere, and flooding large areas of land. Whereas pure methane is lighter than air, methane loaded with water droplets is much heavier, and thus spreads over the land, mixing with air in the process (and losing water as rain). The air-methane mixture is explosive at methane concentrations between 5% and 15%; as such mixtures form in different locations near the ground and are ignited by lightning, explosions[2] and conflagrations destroy most of the terrestrial life, and also produce great amounts of smoke and of carbon dioxide. Firestorms carry smoke and dust into the upper atmosphere, where they may remain for several years (Turco et al., 1991); the resulting darkness and global cooling may provide an additional kill mechanism. Conversely, carbon dioxide and the remaining methane create the greenhouse effect, which may lead to global warming. The outcome of the competition between the cooling and the warming tendencies is difficult to predict (Turco et al., 1991; Pierrehumbert, 2002).

Upon release of a significant portion of the dissolved methane, the ocean settles down, and the entire sequence of events (i.e., development of anoxia, accumulation of dissolved methane, the metastable state, eruption) begins anew. No external cause is required to bring about a methane-driven eruption—its mechanism is self-contained, and implies that eruptions are likely to occur repeatedly at the same location.

Because methane is isotopically light, its fast release must result in a negative carbon isotope excursion in the geological record. Knowing the magnitude of the excursion, one can estimate the amount of methane that could have produced it. Such calculations (prompted by the methane-hydrate-dissociation model, but equally applicable here) have been performed for several global events in the geological record; the results range from $\sim 10^{18}$ to 10^{19} g of released methane (e.g., Katz et al., 1999; Kennedy et al., 2001; de Wit et al., 2002). These are very large amounts: the total carbon content of today's terrestrial biomass is $\sim 2 \times 10^{18}$ g. Nevertheless, relatively small regions of the deep ocean could contain such amounts of dissolved methane; e.g., the Black Sea alone (volume $\sim 0.4 \times 10^{-3}$ of the ocean total; maximum depth only 2.2 km) could hold, at saturation, $\sim 0.5 \times 10^{18}$ g. A similar region of the deep ocean could contain much more (the amount grows quadratically with depth[3]). Released in a geological instant (weeks, perhaps), 10^{18} to 10^{19} g of methane could destroy the terrestrial life almost entirely. Combustion and explosion of 0.75×10^{19} g of methane would liberate energy equivalent to 10^8 Mt of TNT, $\sim 10,000$ times greater than the world's stockpile of nuclear weapons, implicated in the nuclear-winter scenario (Turco et al., 1991).

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[2]Fuel-air explosives are used in weapons of enormous destructive power, comparable to tactical nuclear weapons; the list of potential fuels includes methane (GICHD, 2001). It is not obvious that the methane-air mixture will detonate spontaneously (weapons have detonators); still, the deflagration front may accelerate to very high speeds, and pressures of ~ 5 bar may result (Dorofeev, 2002). The likelihood of the deflagration-to-detonation transition increases with the size of the gas cloud (Bradley, 1999; Dorofeev, 2002); the latter can be very large in the case of oceanic eruption. In detonation, the combustion zone is preceded by a shock wave, moving with velocity ~ 2 km s^{-1}; pressures of ~ 30 bar can be produced.

[3]Integrating the solubility (Handa, 1990) over the water column yields the maximum mass of methane, per unit area of horizontal cross section, that can dissolve in a water column of depth H. (The depth must not be too small because the mixed surface layer, ~ 100 m, while supersaturated with respect to methane in the atmosphere, will remain far below saturation with respect to methane in the bubbles.) The result is, approximately, σH^2, with $\sigma \approx 0.64$ g m^{-4}; e.g., for $H = 4$ km, $\sigma H^2 \approx 10^7$ g m^{-2}. The maximum amount of dissolved methane in a deep basin of area A can be calculated as $\sigma H^2 A$, where H is the root-mean-square value of the depth.

PERMIAN-TRIASSIC BOUNDARY

At the time of the Permian-Triassic boundary, large regions of the ocean were anoxic and possibly stagnant (Kajiwara et al., 1994; Wignall and Twitchett, 2002), so large amounts of dissolved methane could accumulate in the water column. The boundary is characterized by the following: (1) rapid simultaneous mass extinctions in marine and terrestrial realms (Jin et al., 2000; Twitchett et al., 2001), the "extreme rapidity" of the extinctions suggesting a catastrophic cause (Jin et al., 2000); (2) equally rapid die-off of terrestrial vegetation (Ward et al., 2000); (3) a sharp peak in the atmospheric concentration of carbon dioxide (Fig. 3 of Retallack, 2002); (4) a drastic negative sulfur isotope excursion (Kajiwara et al., 1994); (5) in some locations, the presence of fullerenes (Chijiwa et al., 1999; Becker et al., 2001) or of metallic and glassy microspherules (Jin et al., 2000); (6) a strong abrupt negative carbon isotope excursion (Jin et al., 2000; Krull et al., 2000; Twitchett et al., 2001; Sephton et al., 2002); more precisely, several such excursions in succession (Krull et al., 2000; de Wit et al., 2002); (7) in New Zealand's Maitai Group, these carbon isotope excursions are associated with breccia within a sandstone formation, which is "largely devoid of fossils," and was interpreted as a "massive event deposit." "Dominance of poorly sorted sediment, . . . load casts, flame structures, and rip-up clasts suggest rapid mass emplacement" (Krull et al., 2000). In South Africa's Karoo basin, the boundary is overlain by an "anomalously nonfossiliferous event bed" of mudrock, and/or marked by accumulations of extraformational clasts and large logs of fossilized wood (Hancox et al., 2002).

The present hypothesis accounts well for all of the items listed here. In particular, the sulfur isotope excursion could have resulted from sudden massive mixing in the ocean (Kajiwara et al., 1994). The origin of fullerenes has been debated, and their very presence questioned; it is known, however, that fullerenes form during combustion of methane (Siegmann et al., 1996). Similarly, the microspherules could have been produced from mineral dust in the high-temperature zone of the methane flame; their close analogues are found in combustion products of fossil fuels (Cisowski, 1990).

Release of the isotopically light methane would have resulted in a negative carbon isotope excursion (Krull et al., 2000; de Wit et al., 2002). The die-off of land plants in the ensuing conflagration would have led to destabilization of soil and a drastic increase in delivery of terrestrial carbon to the ocean (Ward et al., 2000), another possible source of a negative carbon isotope excursion (Sephton et al., 2002). Both sources would likely have contributed (to the extent depending on the location), so in the geological record the carbon isotope excursions may precede the extinctions (Jin et al., 2000), follow the extinctions (Twitchett et al., 2001; Sephton et al., 2002), or both (de Wit et al., 2002). The event deposits could have been produced by the eruption-triggered floods.

The paleogeography of the Permian may have led to development of a large number of stagnant anoxic regions, and thus to accumulation of very large amounts of dissolved methane. The unusual severity of the Permian-Triassic extinction may have been a result of chance as several different oceanic locations erupted in succession.

SOME IMPLICATIONS AND CONJECTURES

At any oceanic location where a methane-driven eruption occurs once, similar eruptions are likely to occur repeatedly, roughly periodically. (Whether a particular oceanic location is prone to eruptions would be determined by paleogeography and seafloor topography, which change on time scales of tens of millions of years, and by the ocean circulation pattern, which may change very quickly.) A crude estimate of the eruption periodicity can be obtained by using the water-column saturation time[4]. The quasi-periodic eruptions would provide sources of cyclicity in the geological record on the time scales from, perhaps, tens of thousands of years to a few million years. The larger, less frequent eruptions at great depths could cause global extinctions that define stratigraphic boundaries, and significant climate changes. The smaller, more frequent eruptions at intermediate depths could lead to regional extinctions[5], and could also influence the global climate.

The effect of a methane-driven eruption on climate could be drastic. Global warming is an obvious possibility; global cooling could result as well, if a large eruption produced a global cloud of smoke and dust particles in the upper atmosphere. Some versions of the nuclear-winter scenario predict cooling so strong that continental glaciation could be triggered (Monin and Shishkov, 2000). While these predictions remain controversial, a large methane-driven oceanic eruption entails energy release so much greater than that in the nuclear-winter scenario (by a factor of $\sim 10^3$ to 10^4) that it may be capable of triggering continental glaciation. The subsequent eruptions, with no smoke or dust coming from the ice-covered land, would be more likely to result in global warming due to the greenhouse effect, and could terminate the glaciation. This could explain, e.g., why glacial deposits of the Proterozoic are bracketed by negative carbon isotope excursions (Kaufman et al., 1997). Anbar and Knoll (2002) argued that the Proterozoic ocean was globally anoxic and sulfate poor; the eruptions could then be global and enormously powerful.

The ice-core record for the past 420 k.y. shows a jump in the atmospheric concentration of methane at each glacial termination; the jump coincides with the start of rapid melting of the Northern Hemisphere ice sheets (Petit et al., 1999). These methane jumps are so sharp and pronounced that they became a standard means of synchronizing the ice-core records from Antarctica and Greenland (e.g., Monnin et al., 2001; Morgan et al., 2002). Simultaneously with the methane jump, CO_2 jumps as well (Monnin et al., 2001). Perhaps these glacial terminations were caused by (smaller scale) methane-driven oceanic eruptions. In addition to providing the mechanism of abrupt warming, this would explain both the sharpness of the methane jumps and the methane-CO_2 synchronism. A causal role for methane in deglaciations was suggested some time ago (see Nisbet, 2002); Severinghaus et al. (1998), however, argued against it. Their interpretation of the data was challenged (Nisbet, 2002), and the question remains open.

Assuming the present hypothesis survives scrutiny, large-scale efforts will be required to prevent future eruptions.

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[4]Neglecting both consumption and production of methane in the water column, the saturation time is $(\sigma/J)H^2$, where J is the flux of methane from the seafloor. At some locations there is practically no flux, while at others it can be as high as ~ 2 kg m^{-2} yr^{-1} (Suess et al., 1999). The best estimates for the average value of J range from 4.7 to 38 g m^{-2} yr^{-1} (Hovland et al., 1993), with the geometric mean 13 g m^{-2} yr^{-1}. Using the latter yields $\sigma/J \approx 5 \times 10^{-2}$ yr m^{-2} = 0.5×10^5 yr km^{-2}. The saturation time, uncertain by at least a factor of 3 in either direction, is then 0.5×10^5 yr for $H = 1$ km, and 0.8×10^6 yr for $H = 4$ km.

[5]A number of smaller-scale eruptions may have occurred after the acquisition of language by humans and inspired the flood myths, common all over the world except Africa. See, in particular, Diodorus Siculus 5.47.3–5. *The Epic of Gilgamesh* (XI, 96–112) describes the land set ablaze, "shattered like a [clay] pot", plunged into darkness, and flooded. In Genesis 7:11, "All the fountains of the great deep burst forth . . . ", etc.

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