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Rate of growth of isolated bubbles in sediments with a diagenetic source of methane

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Abstract

Observation of bubbles in estuarine and coastal sediments indicates that bubbles at or below 10 cm depth grow on seasonal time scales (May–October). In order to determine the controls on this growth rate, we have constructed a diffusion–reaction model that accounts for the dynamics of methane formation, its diffusion through pore waters, its incorporation into a bubble, and the consequent growth of the bubble. The model produces an explicit equation for the radius of a growing bubble, $R(t)$, with time using mean parameter values and under the assumption that the mechanics of the sediment response to growth can be neglected:

$$R(t) = \left[\frac{\varphi D}{2c_g}\left\{\frac{SR_1^2}{3D} + (c_1 - c_0)\right\}t + R_0^2\right]^{1/2}$$

where φ is the porosity, D is the tortuosity-corrected diffusivity, c_g is the concentration of gas in the bubble, S is the rate of methanogenesis near the bubble, R_1 is the half-separation distance between bubbles ($R_1 \gg R$), c_1 is the ambient CH_4 concentration, c_0 is the pore-water CH_4 concentration at R, t is time, and R_0 is the initial bubble radius, if not zero. The effects of the source S and supersaturation ($c_1 - c_0$), thus, appear as separate contributing terms, and this formula can then be applied even in those cases where apparently $c_1 \approx c_0$. The model is applied to three sediments where bubbles have been previously studied, i.e., Cape Lookout Bight (USA), White Oak River (USA) and Eckernförde Bay (Germany). In all three cases, using the site-specific time-averaged parameter values, the model predicts seasonal growth rates, consistent with the observations. Furthermore, the source term dominates the rate of growth at the first of these two sites, whereas diffusion from the ambient supersaturation dominates at the German location. Real bubbles may follow a more complicated growth history than predicted by the above equation because of the mechanical properties of sediments; nevertheless, the overall growth times are concordant with ultimate diffusion control. The effects of rectified diffusion, that is, the pumping of gas into a bubble by pressure oscillations, e.g., from waves and tides, were also examined. Existing models for that process suggest that it is negligible, due to the low frequency of these types of oscillations.

Biogenic CH_4 is produced in aquatic sediments by bacterially mediated organic matter decomposition after the exhaustion of all other available oxidants (Claypool and Kaplan 1974; Martens and Berner 1974; Kuivila et al. 1989), i.e., overall,

$$2CH_2O \rightarrow CH_4 + CO_2, \quad (1)$$

where CH_2O is stoichiometric organic matter. This process can become particularly important to carbon cycling in sediments where sulfate concentrations are low, such as in brackish and freshwater systems. Escape of this gas into the overlying water and subsequently into the atmosphere appears to constitute a major source of this important ''greenhouse'' gas (Crill et al. 1991; Hovland and Judd 1992; Hovland et al. 1993).

The concentration of dissolved methane in pore waters can exceed the solubility of this gas, in which case methane bubbles can form (Martens and Berner 1974; Martens and Albert 1995) and thereafter escape the sediment by ebullition (Martens and Klump 1980; Chanton and Martens 1988; Rothfuss and Conrad 1998). Ebullition can dominate methane loss from sediments (Cicerone and Shetter 1981; Chanton et al. 1989; Crill et al. 1991). Additionally, the presence of bubbles in sediments constitutes a threat to foundation stability (Sills and Wheeler 1992) and an impediment to acoustic sensing.

In situ rates of bubble formation have not been measured. The frequent release of bubbles in some nearshore and marsh sediment suggests rapid formation, at least near the sediment-water interface or within organic matter–filled depressions and holes. However, Martens and Klump (1980) state that the deeper bubbles (>8 cm depth) at their Cape Lookout Bight site form seasonally, reaching sizes of 0.5–2 cm in diameter by late summer. Chanton et al. (1989) found bubbles throughout the year, but higher bubble inventories during the summer. Strayer and Tiedje (1978) further observed a late summer maximum in the ebullitive flux of methane from Wintergreen Lake. Outside of tropical wetlands, bubble formation deeper than a few centimeters in sediments is seasonal, i.e., during late spring and early summer, due to the

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effects of temperature on rates and seasonal inputs of metabolizable organic matter. If this latter statement is to be true, then bubbles must be able to grow to these observed sizes on a seasonal time scale.

One means of estimating the (potential) growth rate of methane bubbles in sediments is through a predictive model. This paper presents the first model for the diffusion-controlled growth of such bubbles. The model is novel in that it considers a process not normally included in bubble-growth models in other fields, i.e., a distributed source of the gas formed by in situ reaction. The validity of the model is restricted by certain assumptions, as discussed below, but the results are probably correct within an order of magnitude even if some of the more important assumptions are violated in reality. The model is applied to three sites where bubbles are known to occur and methane generation rates have been measured or can be estimated.

The model

The theory of bubble growth is of considerable interest to a wide variety of fields, including photography (Barlow and Langlois 1962), boiling (Scriven 1959), production of foams (Street et al. 1971), polymer melt devolatilization (Favelukis and Albalak 1996), manufacture of beer and soft drinks (Shafer and Zare 1991), stability of magmas and vesicule formation (Proussevitch et al. 1993), medicine (Srinivasan et al. 1999), and oil recovery (Li and Yortsos 1995). Consequently, a large body of literature surrounds this subject. However, the developments in these fields apply only partially to our topic because the source of gas is fundamentally different in sediments; that is to say, other papers assume that the gas is simply held in solution in the encircling liquid, which then acts as a passive source of either finite or infinite capacity. In a sediment, Eq. 1 actively produces gas, i.e., a distributed source constantly generates methane into the surrounding medium.

To the best of our knowledge, this latter problem with a source has not been considered previously in any application; yet, it is the crux of the sediment problem. Why? Because in many cases, e.g., Chanton et al. (1989), the surrounding pore-water dissolved-gas concentrations are not observed to be supersaturated, yet bubbles grow. Classical bubble-growth theory demands oversaturation. Below, we show that methanogenesis adjacent to the bubbles can supply the needed gas.

In developing an appropriate bubble-growth model, we need to introduce a simplified modeling context. As noted by Rosner and Epstein (1972), a full model would include consideration of nucleation, kinetics of gas adsorption, transport of the gas, and mechanical response of the sediments. Nucleation should only be a question when preexisting gas cavities are scarce, a situation we do not believe exists in clay-rich sediments with their abundant and complex surface area and past history of aerial exposure; consequently, nucleation kinetics are ignored (Jones et al. 1999). Similarly, the rate of growth of bubbles in sediments is sufficiently slow that adsorption kinetics should not be an issue. This leaves transport and mechanical controls.

Results from our experimental growth of bubbles in sediments, to be reported at a later time, indicate that sediments yield relatively rapidly to bubble formation and that the mechanical properties influence only shape, the rate of vertical movement (if any), and the details of the growth history. Therefore, we present here a model of bubble growth that highlights the effects of diffusion and production in the surrounding sediment on bubble growth. In a later section, we will also consider the possible effects of rectified diffusion, i.e., growth induced by pressure fluctuations.

In order to describe the sediment bubble system, we adopt the bubble-in-a-continuum model proposed by Wheeler (1988), wherein a bubble is a discrete gaseous entity that is embedded in a sediment–pore water continuum, as in a classical diagenetic model (Boudreau 1997). The bubble is considered to be spherical. In cases where bubbles adopt other shapes (e.g., Abegg et al. 1994), the present model is simply an approximation using a spherical bubble of equivalent volume.

Furthermore, the bubble must be relatively isolated, i.e., bubbles are a few radii apart. Given this separation and the fact that the bubbles are small compared to the vertical scale of most methane gradients, x_m, then the local environment around a bubble can be idealized as one of constant CH_4 concentration at a radial distance R_1 that is much greater than the radius of the bubble, R, but $R_1 \ll x_m$. The latter assumption reduces the problem to one that is spherically symmetric, and whereas this is an acknowledged approximation, we firmly doubt that an exact model would produce results that differ significantly from those reported below. Finally, we also ignore the other gasses found in bubbles and consequently underestimate bubble-growth rates.

The mass of a spherical bubble, m, in a sediment will change in time as gas is supplied to the growing surface of the bubble by molecular diffusion from pore waters (Epstein and Plesset 1950; Scriven 1959; Barlow and Langlois 1962), i.e.,

$$\frac{dm}{dt} = 4\pi\varphi R^2 D \left.\frac{\partial c}{\partial r}\right|_{r=R} \tag{2}$$

where t = time, r = radial direction, $\pi = 3.14159\ldots$, φ = porosity at the bubble surface, D = diffusion coefficient corrected for tortuosity, and R = radius of the bubble at time t.

The gradient on the left-hand side of Eq. 2 must be calculated from the solution to the gas conservation (diagenetic) equation in the sediment, i.e.,

$$\frac{\partial c}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D \frac{\partial c}{\partial r}\right) + S \tag{3}$$

where S = source of methane at radial distance r and time t. Given that the bubbles are sufficiently small compared to the overall gradient in CH_4 with depth, then S is treated as a local constant; we will return to the implications of this assumption later. In writing Eq. 3 we have also omitted the advection term, due to inertial effects and burial; neither should be important to a bubble that grows slowly.

In principle, both D and S, as well as some other parameters given below, are time dependent as a result of seasonal effects, i.e., primarily due to variations in temperature. In-

clusion of such time dependence precludes the derivation of a simple explicit equation for bubble growth, without adding fundamentally important new chemistry or physics to the model. We have therefore chosen to treat these parameters as constants, employing estimated average values over the growth period.

An additional assumption is that the gradient near the bubble can adjust on a time scale that is short compared to the typical time for the growth of a bubble. The time scale for diffusive adjustment is given by Einstein's relation, i.e., $t = L^2/(2D)$, where L is the distance in question. For a bubble, L is of the order of the bubble radius (0.1–0.5 cm) and D is of the order of 10^{-5} cm^2 s^{-1}. The calculation indicates that the diffusive gradient can adjust on a time scale of a few days at most. In comparison, we have already cited evidence for seasonal growth scales for bubbles. This means that the time-dependent term in Eq. 3 can be ignored, i.e.,

$$\frac{d}{dr}\left(r^2 D\frac{dc}{dr}\right) = -r^2 S \tag{4}$$

This type of pseudo–steady-state model is commonly invoked in other papers on bubble modeling, some of which are cited above.

As appropriate boundary conditions for Eq. 4, the concentration at the bubble surface, c_0, is in equilibrium with that in the bubble, c_g, i.e.,

$$c_g = Kc_0, \tag{5}$$

where K is Henry's Law constant (obtained from Wiesenburg and Guinasso 1979) divided by the gas constant and the absolute temperature, and the concentration at some large distance, R_1, from the bubble is known,

$$c(R_1) = c_1. \tag{6}$$

With these conditions the solution of Eq. 4 for the gradient at $r = R$ is

$$\left.\frac{dc}{dr}\right|_{r=R} = -\frac{RS}{3D} + \frac{1}{R^2}\left(\frac{R_1 R}{R_1 - R}\right)\left[c_1 - c_0 + \frac{S}{6D}(R_1^2 - R^2)\right] \tag{7}$$

By assumption, however, $R_1 \gg R$, so that Eq. 7 simplifies to

$$\left.\frac{dc}{dr}\right|_{r=R} \approx \frac{R_1^2 S}{6DR} + \frac{[c_1 - c_0]}{R} \tag{8}$$

Substitution of Eq. 8 into Eq. 2 generates the relation

$$\frac{dm}{dt} = 4\pi\varphi RD\left[\frac{SR_1^2}{6D} + (c_1 - c_0)\right] \tag{9}$$

Equation 9 can be further simplified by noting that the mass of the gas in a spherical bubble bears a simple relation to its radius, i.e.,

$$m = \frac{4}{3}\pi c_g R^3 \tag{10}$$

A final crucial, and perhaps controversial, assumption must be made at this point; c_g is treated as a constant in time and space. In a small bubble the gas density is almost certainly homogeneous, but time invariance of c_g is more problematic. The latter requires that the contribution of the surface tension, i.e., $2\sigma/R$ where σ is the surface tension, is small compared to the external pressure of the sediment medium. Given the magnitude of the hydrostatic and lithostatic pressures in sediments, 1–2 atm (10^5 N m^{-2}), and surface tension values of the order of 0.07 N m^{-1}, at least for gas-water interaction, the assumption is justified. Gas-solid surface tensions may be considerably higher, but would need to be several orders of magnitude greater to have an effect. Constant c_g is widely assumed in the gas-bubble literature (e.g., Szekely and Martins 1971; Jones et al. 1999).

With constant c_g, Eqs. 9 and 10 produce

$$\frac{dR^2}{dt} = \frac{\varphi D}{2c_g}\left[\frac{SR_1^2}{3D} + (c_1 - c_0)\right] \tag{11}$$

which readily integrates to generate an equation for the change in radius of the bubble with time,

$$R(t) = \left[\frac{\varphi D}{2c_g}\left\{\frac{SR_1^2}{6D} + (c_1 - c_0)\right\}t + R_0^2\right]^{1/2} \tag{12}$$

where R_0 is the initial radius of the bubble, chosen as zero in all subsequent calculations in order to maximize the growth time estimates. By comparison, the equation for bubble growth from a solution that acts as a passive source is (Scriven 1959)

$$R(t) = \left[\frac{\varphi D(c_1 - c_0)t}{2c_g} + R_0^2\right]^{1/2} \tag{13}$$

The additional term on the right-hand side of Eq. 12 is the growth from the distributed source of CH_4 in the sediment that surrounds the bubble. Thus, even if c_0 approaches the value of c_1 to the point where the difference cannot be calculated, e.g., Chanton et al. (1989), the growth can still be calculated with our new equation provided there is a source S.

Applications

Our goal in developing the bubble-growth model, given by Eq. 12, was to determine whether the reported seasonal growth times, e.g., in Martens and Klump (1980), Chanton et al. (1989), and Strayer and Tiedje (1978), were consistent with rates dictated by transport of gas from the surrounding sediment with a gas source present. To achieve this goal we now solve Eq. 12 for the conditions at the three sites reported in these latter publications, i.e., Cape Lookout Bight, White Oak River, and Eckernförde.

Cape Lookout Bight—This site is a fully marine, small lagoonal basin on the outer bank of eastern North Carolina (*see* Martens and Klump 1980, 1984; Klump and Martens 1981). In order to apply Eq. 12, rates of methanogenesis at the appropriate depth in the sediment are needed. Crill and Martens (1986) report measured values that range from 0.17 to 0.3 mM d^{-1} for depths of 10–18 cm for the relevant time period. Other parameters in Eq. 12 are taken to be $D = 1 \times 10^{-5}$ cm^2 s^{-1}, $c_g = 70$ mM, $R_1 = \sqrt{2}$ cm, and $\varphi = 0.85$. Tortuosity, θ, is calculated as $\theta^2 = 1 - \ln(\varphi^2)$ as in Boudreau

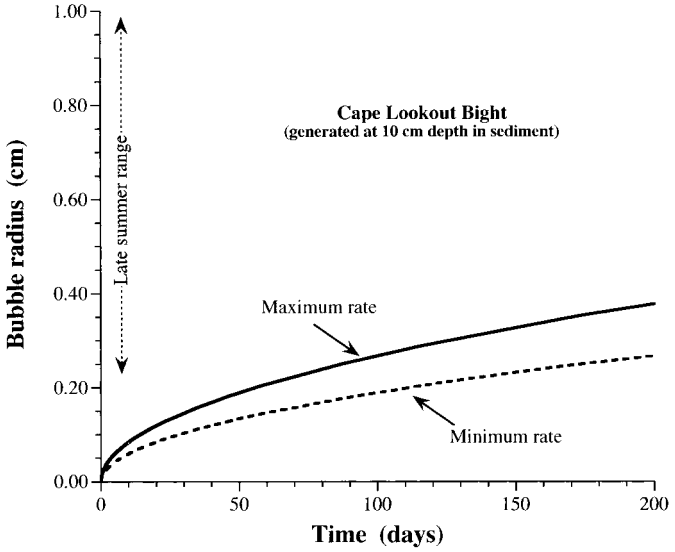

Fig. 1. Bubble size versus time as predicted by Eq. 12 for the conditions at Cape Lookout Bight, USA. Bubbles at this site reach sizes of 0.25–1.0 cm in radius by the end of the summer (October). The model is generally consistent with these observations, particularly if the larger bubbles are in part generated by bubble coalescence.

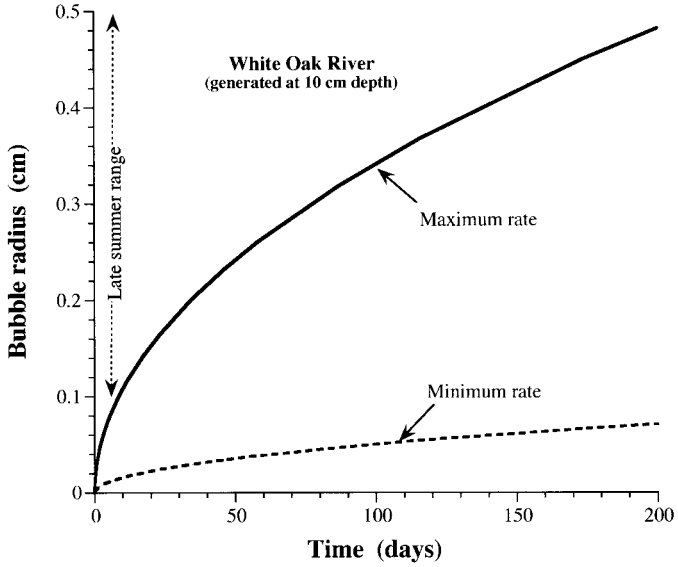

Fig. 2. Bubble size versus time as predicted by Eq. 12 for the conditions at White Oak River, USA. J. Chanton (Florida State Univ., pers. comm.) estimates the bubbles at this site are 0.1–0.25 cm in radius, completely consistent with the model results.

(1997). In addition, because of the high rate of methanogenesis at this site, c_0 was set equal to c_1.

The predicted bubble growth from Eq. 12 is displayed in Fig. 1. The maximum rate is that obtained with the greatest rate quoted above and the minimum is for the corresponding minimum in the quoted range. Martens and Klump (1980) report bubbles of 0.25 to 1 cm radius in the late summer. Our theory predicts that the smaller bubbles would take 100 d to develop, whereas the larger ones would take over 500 d. However, many of the larger bubbles may result from the coalescence of smaller bubbles. Furthermore, S is a heterogeneous function of time and space at the scale of a bubble; our S values are those measured from larger sediment volumes (or modeled from vertical methane profiles). If S is locally very large near a growing bubble, the latter could grow substantially faster and larger than suggested by the results in Fig. 1. Finally, a larger R_1 value than we employ would generate larger bubbles on the same time scale. Overall, however, the predicted rates are consistent with the observed seasonal (April to October) growth times.

White Oak River—This site is a tidal freshwater (only slightly brackish) estuary, approximately 80 km farther southwest of Cape Lookout on the North Carolina coast; more details are provided in Martens and Goldhaber (1978) and Chanton et al. (1989). The sediments are strongly methanogenic and bubbles are abundant. Chanton et al. (1989) have measured the methane composition in the bubbles and its concentration in the pore waters to show that equilibrium existed with bulk pore-water values, i.e., $c_0 = c_1$. This is an example of a situation were the classic formula, Eq. 13, would not work.

No rates of methanogenesis are reported for the White Oak River site. However, minimum values can be estimated from the measured total flux of methane, F, from this sediment. At steady state this measured flux must be balanced by the integrated production in the sediment, i.e.,

$$F = \int_0^\infty S(x)\, dx \tag{14}$$

where x is the depth in the sediment. Note that $S(x)$ is not quite the S in Eqs. 3 and 4; the former is the actual depth-dependent rate of methanogenesis, whereas the latter is the locally averaged rate within a volume of radius R_1 from a bubble. At a given depth, they can be made equal. Assuming that $S(x)$ is approximately exponential, which minimizes the calculated rate, i.e.,

$$S(x) = S_0 e^{-\alpha x}, \tag{15}$$

where α is an attenuation obtained from fitting data, and S_0 is an initial rate, then

$$F = \frac{S_0}{\alpha} \tag{16}$$

Figure 5 in Chanton et al. (1989) reports F values from 1 to 12 moles m^{-2} yr^{-1}, whereas fitting of the observed CH_4 profiles suggests $\alpha = 0.17$–0.82 cm^{-1}. Calculated minimum and maximum values for S_0 are 5.0×10^{-7} and 3.3×10^{-5} mM s^{-1}, respectively, which imply a corresponding minimum value of S at 10 cm depth of 9.1×10^{-8} mM s^{-1} and a maximum value at 2.5 cm of 4.22×10^{-6} mM s^{-1}. The diffusivity, the porosity, and R_1 are taken to be the same as the Cape Lookout Bight example, but c_g is calculated to be lower at 52 mM. The Eq. 12–predicted growth rates for these minimum and maximum methane generation rates are illustrated in Fig. 2. The gap between the minimum and maximum rates is much larger than in the last example, but it is clear that 0.1–0.5 cm bubbles (J. Chanton,

pers. comm.) can be formed seasonally, except at the lowest rate. Chanton et al. (1989) further report that methane only makes up about 60–75% of the gas in bubbles; thus, the growth contribution from other gases means that our calculated rates are minimums and seasonal growth becomes even easier to explain.

Eckernförde Bay—Eckernförde Bay is a marine bay on the western Baltic Coast of Germany. Extensive environmental, geological, and geochemical information about this site is available in reports by Richardson (1994), and Wever (1994, 1995). The sediment becomes gassy at depth throughout a large portion of this bay. Martens and Albert (1995) report methane profiles at three stations, and in particular a station designated NRL where the pore waters become supersaturated with respect to CH_4 at a depth of about 75 cm and are gassy thereafter. The NRL site is markedly different than the two sites modeled above. NRL has an observable supersaturation, i.e., $c_1 - c_0 = 1$ mM; thus, the diffusion from ambient methane term in Eq. 12 will make a contribution, in fact the dominant contribution to growth.

Rates of methanogenesis are not measured but can be estimated with a simple, steady-state, one-dimensional diagenetic model where diffusion in the pore water is balanced by production from organic matter decay, i.e.,

$$D\frac{d^2c}{dx^2} + S_0e^{-\alpha x} = 0 \qquad (17)$$

Fitting the exponential solution to Eq. 17 to the methane data in Martens and Albert (1995), one obtains that $\alpha = 0.067 \pm 0.008$ cm^{-1} and $S_0 = 2.5 \pm 0.96 \times 10^{-6}$ mM s^{-1}. From this result, S at 80 cm can be calculated to be $1.0 \pm 0.38 \times 10^{-8}$ mM s^{-1}. As to the other parameters, D is taken as 5×10^{-6} cm^2 s^{-1}, c_g is 140 mM, and R_1 is assumed to be 3 cm.

The predicted growth rate of a bubble is given by the line in Fig. 3. Again bubbles grow to within the observed range on a seasonal time scale. (Larger bubbles may again be the result, in part, of coalescence.) The difference here is that the methane-source term in Eq. 12 contributes only 1% to this growth and most of the methane must come from the ambient store that surrounds the bubble.

Before leaving these applications, we make one final comment on our omission of sediment mechanical influences. The curves in Figs. 1–3 are smooth lines that are expected for diffusion-controlled growth. However, even if the overall rate of bubble formation is controlled by this transport process, the mechanical properties of sediments can still play an important role in causing real bubble-growth curves to deviate from the ideal. Our early experimental findings (to be reported later) indicate that sediments can respond to bubble growth by fracturing. Some preliminary work indicates that, in a fracturing medium, c_g could be 20% larger, and this would slow bubble growth. Only future research will establish the validity of this speculation.

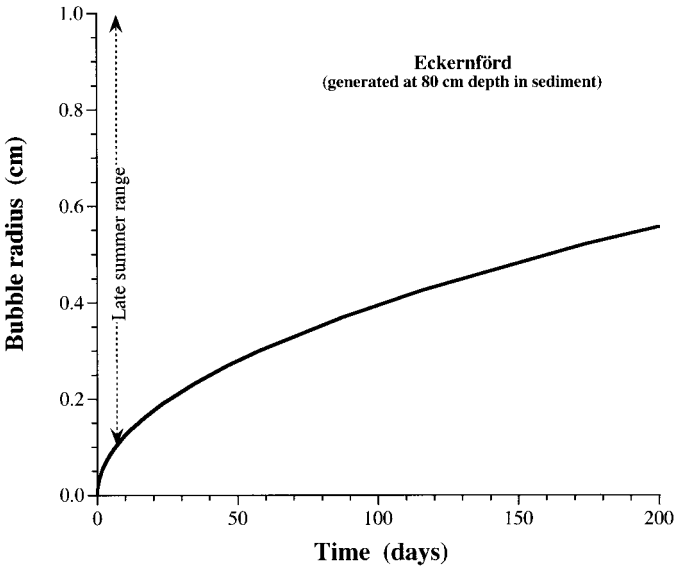

Fig. 3. Bubble size versus time at 80 cm depth as predicted by Eq. 12 for the conditions at Eckernförde Bay, Germany. Data in Abegg et al. (1994) suggests bubbles less that 1 cm in radius develop in the summer, which is again consistent with model predictions.

Rectified diffusion

Rectified diffusion describes the growth of a bubble by net gas transfer in an oscillating pressure field (Hsieh and Plesset 1961), i.e., more gas is taken into the bubble when it is expanding than is lost during compression. Because sediments are subject to an oscillatory pressure field due to passing waves and tides, rectified diffusion has the potential to add to bubble-growth rates. We explore this possibility below.

Models for rectified diffusion have been proposed by various authors, but an estimate of the magnitude of this effect can be obtained using the older and simpler theory of Hsieh and Plesset (1961). These investigators established that the simple diffusion-fed growth of a bubble was supplemented by rectified diffusion according to the formula

$$\frac{dm}{dt} = 4\pi\varphi RD(c_1 - c_0) + \frac{8\pi}{3}DRc_1\left(\frac{\Delta P}{P_\infty}\right)^2 \qquad (18)$$

where ΔP is the magnitude of the pressure fluctuations and P_∞ is the total ambient pressure at the depth of interest. The first term on the right-hand side of Eq. 18 is the classic diffusion contribution and the second term is that from rectified diffusion; growth from a source, S, is missing in this theory.

If rectified diffusion is to be important, then $(\Delta P/P_\infty)^2$ must be of order one. For typical waves on a marine coastline, ΔP is of the order of 0.01–0.04 atm, except during storms; P_∞ is of the order of 1–2 atm, so that $(\Delta P/P_\infty)^2 \approx 0.0001$–$0.001$, i.e., far from unity. The theory does not apply strictly to tidal frequencies, but the result is that at most $(\Delta P/P_\infty)^2 \approx 0.01$, and there is no significant contribution. These results were verified by employing the more complete theory of Eller (1969) to reach the same conclusion.

Conclusions

We have derived from first principles a simple predictive equation for the growth of bubbles in sediments from a distributed source of methane and the ambient oversaturation. Observations of natural bubbles at 10 or more centimeters from the sediment surface indicate that they grow on a seasonal time scale. When relevant parameter values for three studied sites are placed in the model, the predicted bubble-growth rates are indeed seasonal. This argues that diffusion of source gas must exert overall control on the growth of these bubbles; however, we note that the mechanical properties of sediments, e.g., plastic yield and fracture, may still influence the details of the growth history, i.e., bubble size versus time. On the other hand, the potential effects of rectified diffusion from waves and tides appear to be negligible.

References

ABEGG, F., A. ANDERSON, L. BUZI, A. P. LYONS, AND T. H. ORSI. 1994. Free methane concentration and bubble characteristics in Eckernförde Bay, Germany, p. 84–89. *In* T. F. Wever [ed.], Proceedings of the gassy mud workshop. Forschungs. Bundeswehr Wasserschall Geophysik.

BARLOW, E. J., AND W. E. LANGLOIS. 1962. Diffusion of gas from a liquid into an expanding bubble. IBM Journal **6:** 329–337.

BOUDREAU, B. P. 1997. Diagenetic models and their implementation. Springer Verlag.

CHANTON, J. P., AND C. S. MARTENS. 1988. Seasonal variations in ebullitive flux and carbon isotopic composition of methane in a tidal freshwater estuary. Glob. Biogeochem. Cycles **2:** 289–298.

———, ———, AND C. A. KELLEY. 1989. Gas transport from methane-saturated, tidal freshwater and wetland sediments. Limnol. Oceanogr. **34:** 807–819.

CICERONE, R. J., AND J. D. SHETTER. 1981. Sources of atmospheric methane: Measurements in rice paddies and a discussion. J. Geophys. Res. **86:** 7203–7209.

CLAYPOOL, G. E., AND I. R. KAPLAN. 1974. The origin and distribution of methane in marine sediments, p. 99–139. *In* I. R. Kaplan [ed.], Natural gases in marine sediments. Plenum.

CRILL, P. M., R. C. HARRISS, AND K. B. BARTLETT. 1991. Methane fluxes from terrestrial wetland environments, p. 91–109. *In* J. E. Rogers and W. B. Whitman [eds.], Microbial production and consumption of greenhouse gases: Methane, nitrogen oxides, and halomethanes. American Society of Microbiology.

———, AND C. S. MARTENS. 1986. Methane production from bicarbonate and acetate in an anoxic marine sediment. Geochim. Cosmochim. Acta **50:** 2089–2097.

ELLER, A. I. 1969. Growth of bubbles by rectified diffusion. J. Acoust. Soc. Am. **46:** 1246–1250.

EPSTEIN, P. S., AND M. S. PLESSET. 1950. On the stability of gas bubbles in liquid-gas solutions. J. Chem. Phys. **18:** 1505–1509.

FAVELUKIS, M., AND R. J. ALBALAK. 1996. Bubble growth in viscous Newtonian and non-Newtonian liquids. Chem. Eng. J. **63:** 149–155.

HOVLAND, M., AND A. G. JUDD. 1992. The global production of methane from shallow submarine sources. Cont. Shelf Res. **12:** 1231–1238.

———, ———, AND R. A. BURKE, JR. 1993. The global flux of methane from shallow submarine sediments. Chemosphere **26:** 559–578.

HSIEH, D.-Y., AND M. L. PLESSET. 1961. Theory of rectified diffusion of mass into a gas bubble. J. Acoust. Soc. Am. **33:** 206–215.

JONES, S. F., G. M. EVANS, AND K. P. GALVIN. 1999. Bubble nucleation from gas cavities—a review. Adv. Colloid Interface Sci. **80:** 27–50.

KLUMP, J. V., AND C. S. MARTENS. 1981. Biogeochemical cycling in an organic rich coastal marine basin—II. Nutrient sediment-water exchange processes. Geochim. Cosmochim. Acta **45:** 101–121.

KUIVILA, K. M., J. W. MURRAY, A. H. DEVOL, AND P. C. NOVELLI. 1989. Methane production, sulfate reduction and competition for substrates in the sediments of Lake Washington. Geochim. Cosmochim. Acta **53:** 409–416.

LI, X., AND Y. C. YORTSOS. 1995. Theory of bubble growth in porous media by solute diffusion, Chem. Eng. Sci. **50:** 1247–1271.

MARTENS, C. S., AND D. B. ALBERT. 1995. Biogeochemical processes controlling concentrations and transport of biogenic methane in organic-rich coastal sediments, p. 10–17. *In* T. F. Wever [ed.], Proceedings of the workshop on modeling methane-rich sediments of Eckernförde Bay. Forschungs. Bundeswehr Wasserschall Geophysik.

———, AND R. A. BERNER. 1974. Methane production in the interstitial waters of sulfate-depleted marine sediments. Science **185:** 1167–1169.

———, AND M. B. GOLDHABER. 1978. Early diagenesis in transitional sedimentary environments of the White Oak River estuary, North Carolina. Limnol. Oceanogr. **23:** 428–441.

———, AND J. V. KLUMP. 1980. Biogeochemical cycling in an organic rich coastal marine basin—I. Methane sediment-water exchange processes. Geochim. Cosmochim. Acta **44:** 471–490.

———, AND ———. 1984. Biogeochemical cycling in an organic rich coastal marine basin—4. An organic carbon budget for sediments dominated by sulfate reduction and methanogenesis. Geochim. Cosmochim. Acta **48:** 1987–2004.

PROUSSEVITCH, A. A., D. L. SAHAGIAN, AND A. T. ANDERSON. 1993. Dynamics of diffusive bubble growth in magmas: Isothermal case. J. Geophys. Res. **98:** 22283–22307.

RICHARDSON, M. D. 1994. Investigating the coastal benthic boundary layer. EOS Trans. Am. Geophys. Union **75:** 201–206.

ROSNER, D. E., AND M. EPSTEIN. 1972. Effects of interface kinetics, capillarity and solute diffusion on bubble growth rates in highly supersaturated liquids. Chem. Eng. Sci. **27:** 69–88.

ROTHFUSS, F., AND R. CONRAD. 1998. Effect of gas bubbles on the diffusive flux of methane in anoxic paddy soil. Limnol. Oceanogr. **43:** 1511–1518.

SCRIVEN, L. E. 1959. On the dynamics of phase growth. Chem. Eng. Sci. **10:** 1–13.

SHAFER, N. E., AND R. N. ZARE. 1991. Through a beer glass darkly. Phys. Today **44:** 48–52.

SILLS, G. C., AND S. J. WHEELER. 1992. The significance of gas for offshore operations. Cont. Shelf Res. **12:** 1239–1250.

SRINIVASAN, R. S., W. A. GERTH, AND M. R. POWELL. 1999. Mathematical models of diffusion-limited gas bubble dynamics in tissue. J. Appl. Physiol. **86:** 732–741.

STRAYER, R. F., AND J. M. TIEDJE. 1978. In situ methane production in a small, hypereutrophic, hard-water lake: Loss of methane from sediments by vertical diffusion and ebullition. Limnol. Oceanogr. **23:** 1201–1206.

STREET, J. R., A. L. FRICKE, AND L. P. REISS. 1971. Dynamics of phase growth in viscous, non-Newtonian liquids. Ind. Eng. Chem. Fundamentals **10:** 54–64.

SZEKELY, J., AND G. P. MARTINS. 1971. Nonequilibrium effects in the growth of spherical gas bubbles due to solute diffusion. Chem. Eng. Sci. **26:** 147–159.

WEVER, T. F., ED. 1994. Proceedings of the gassy mud workshop. Forschungs. Bundeswehr Wasserschall Geophysik.

———, ED. 1995. Proceedings of the workshop on modeling methane-rich sediments of Eckernförde Bay. Forschungs. Bundeswehr Wasserschall Geophysik.

WHEELER, S. J. 1988. A conceptual model for soils containing large gas bubbles. Géotech. **38:** 389–397.

WIESENBURG, D. A., AND N. L. GUINASSO, JR. 1979. Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and seawater. J. Chem. Eng. Data **24:** 356–360.

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