Model for the Distribution of Sulfate Reduction and Methanogenesis in Freshwater Sediments

Derek Lovley, University of Massachusetts - Amherst
Michael J Klug

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Model for the distribution of sulfate reduction and methanogenesis in freshwater sediments†

DEREK R. LOVLEY* and MICHAEL J. KLUG
Michigan State University, Kellogg Biological Station, Hickory Corners, Michigan 49060

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Abstract—A model, based on the in situ physiological characteristics of methanogens and sulfate reducers, was developed to describe the distribution of methanogenesis and sulfate reduction in freshwater sediments. The model predicted the relative importance of methane production and sulfate reduction in lakes of various trophic status and generated profiles of sulfate, acetate, methanogenesis, and sulfate reduction comparable to the profiles that are expected based on field studies. The model indicated that at sulfate concentrations greater than 30 μM a sulfate-reducing zone develops because sulfate reducers maintain acetate concentrations too low for methanogens to grow. At lower sulfate concentrations a methanogenic zone develops because the dual limitations of low sulfate concentrations and acetate consumption by methanogens prevents sulfate reducers from growing. The model and a compilation of previously published field data indicate that, within the reported range of sulfate concentrations, the relative importance of methanogenesis and sulfate reduction in freshwater sediments is primarily dependent upon the rates of organic matter decomposition.

INTRODUCTION

MICROORGANISMS ARE the primary catalysts for many diagenetic processes. Therefore, biochemical constraints influence the vertical profiles of organic matter diagenesis in aquatic sediments. Detailed consideration of microbial physiology may not be necessary when the goal of diagenetic modelling is to estimate rates of diagenesis within a specified sediment interval where one terminal metabolic pathway (e.g. sulfate reduction) predominates (BERNER, 1980). However, data on the in situ physiological characteristics of microorganisms are necessary to model the distribution of diagenetic processes when more than one pathway for organic matter decomposition is possible. Recent studies on microbial metabolism in natural anaerobic environments have begun to provide the data necessary to construct diagenetic models based on the physiological interactions of microbial communities. We designed a simplified model of sulfate reduction and methane production in freshwater sediments: i) to determine if the physiological characteristics of sediment populations of methanogens and sulfate reducers could account for the observed segregation of sulfate reducing and methanogenic zones in sediments (CAPPENBERG, 1974; REEBURG and HEGGIE, 1977; MARTENS and BERNER, 1977; WINFREY and WARD, 1983; CRILL and MARTENS, 1983; WINFREY et al., 1981; HINES and BUCK, 1982; MOUNTFORT et al., 1980; SENOIR et al., 1982; CLAYPOOL and KAPLAN; 1974), ii) to determine if a diagenetic model based on the physiological characteristics of these bacteria could describe chemical profiles in the sulfate-reducing and methanogenic zones, and iii) to investigate which factors may be important in controlling the relative importance of sulfate reduction and methanogenesis in the decomposition of organic matter in anaerobic freshwater sediments.

Model of organic matter diagenesis

Although early diagenesis of organic matter in sediments is generally modelled as a one-reaction process with one or more first-order rate constant(s), organic matter is decomposed in a multiple reaction sequence by a complex microbial food chain (BERNER, 1980). A model for carbon and electron flow in the methanogenic and sulfate-reducing zones of freshwater sediments has been developed based on in situ studies with tracers and metabolic inhibitors (Fig. 1). The model for the methanogenic zone is derived from data for freshwater sediments in which methanogenesis predominates (LOVLEY and KLUG, 1982; LOVLEY and KLUG, 1983b). In methanogenic sediments, fermentative bacteria metabolize complex organic matter primarily to acetate and H₂. Other fermentation products include short-chain fatty acids (primarily propionate and butyrate), methanol, and methylamines. Acetogenic proton-reducing bacteria metabolize fatty acids larger than acetate to H₂ and acetate. Methanogens convert the H₂, acetate, methanol and methylamines to methane.

The pathways for the initial fermentation of organic matter in freshwater sediments in which sulfate reduction is the terminal process appear to be similar to the fermentation pattern in the methanogenic zone (LOVLEY and KLUG, 1983a, unpubl. data). This conclusion is supported by the observation that there is a similar pattern for the production of fermentation acids and methyl compounds in the sulfate-reducing zone of marine sediments (SORENSEN et al., 1981; BALBA and NEWMAN, 1982; CHRISTENSEN, 1984; KING et al., 1983; WINFREY et al., 1981).
In the presence of sufficient sulfate, freshwater sulfate reducers metabolize H₂ and acetate (Winfrey and Ziekus, 1977; Lovley et al., 1982; Lovley and Klug, 1983a) as well as other short-chain fatty acids (Smith and Klug, 1981b, unpubl. data). The metabolism of these fermentation products by sulfate-reducers has also been documented in the sulfate-reducing zone of marine sediments (Sørensen et al., 1981; Lambrech and Pfennig, 1981; Balba and Nedwell, 1982; Christensen, 1984; Winfrey and Ward, 1983; Banat and Nedwell, 1983; Banat et al., 1983; Öremland and Taylor, 1978; Abram and Nedwell, 1978). Although lactate is sometimes considered to be an important substrate for sulfate reducers, measurements of the rate of lactate production in sediments and other anaerobic ecosystems indicate that the fermentation of organic matter to lactate is minor when H₂ is maintained at low partial pressures by methanogens or sulfate reducers (Lovley and Klug, 1982 and references therein). The finding that most of the sulfate reduction in sediments can be attributed to the metabolism of volatile fatty acids and H₂ (Sørensen et al., 1981; Balba and Nedwell, 1982; Banat et al., 1981; Winfrey and Ward, 1983; Christensen, 1984) indicates that lactate, ethanol, pyruvate, long-chain fatty acids, aromatic compounds, or other substrates that sulfate reducers can potentially metabolize are not major substrates for sulfate reducers in sediments.

Methanogens metabolize methyamines in freshwater sulfate-reducing sediments (Lovley and Klug, 1983b). Methanol is probably metabolized by sulfate reducers in the sulfate-reducing zone (King et al., 1983; Banat et al., 1983) although there is some question of this conclusion (Oremland et al., 1982; Öremland and Polcyn, 1982; Lovley and Klug, 1983b). Sulfate reducers might oxidize the small amounts of methane produced from methyamines within the sulfate-reducing zone as well as methane diffusing in from the methanogenic zone. However, the potential for methane oxidation in anaerobic freshwater sediments is minor compared to total carbon metabolism even when sulfate reduction is stimulated with the addition of sulfate (Zehnder and Brock, 1980).

When the molar quantities of the various substrates are considered (Fig. 1), it is apparent that acetate and H₂ are the primary substrates available for either sulfate reduction or methanogenesis. Thus, the distribution of the sulfate-reducing and methanogenic zones can be expected to be dependent upon the competition between the microorganisms for acetate and H₂. H₂ and acetate are metabolized with sulfate reduction or methanogenesis as follows (Thauer et al., 1979).

\[
\Delta G^\circ \text{(kJ)}
\]

1. \(\text{CH}_3\text{COO}^- + \text{SO}_4^{2-} = \text{HS}^- + 2\text{HCO}_3^-\)  -47.3
2. \(4\text{H}_2 + \text{SO}_4^{2-} + \text{H}^+ = \text{HS}^- + 4\text{H}_2\text{O}\)  -151.9
3. \(\text{CH}_3\text{COO}^- + \text{H}_2\text{O} = \text{CH}_4 + \text{HCO}_3^-\)  -31.0
4. \(4\text{H}_2 + \text{HCO}_3^- + \text{H}^+ = \text{CH}_4 + \text{H}_2\text{O}\)  -135.6

The higher potential energy yield for sulfate reducers from metabolism of these substrates is translated into a higher yield of biomass per mole of substrate metabolized (Schauer and Ferry, 1980) and a higher affinity for the substrates (Lovley et al., 1982; Lovley and Klug, 1983a; Kristjansson et al., 1982; Robinson and Tiedje, 1984).

**Origins of electron acceptors for metabolism**

In general, sulfate is not generated within the sulfate-reducing zone of sediments. Although some sulfate may be formed in the sulfate-reducing zone from the hydrolysis of ester sulfates, this source is not considered to support significant
rates of sulfate reduction (KING and KLUG, 1982a). Thus, sulfate must diffuse into the sulfate-reducing zone from the overlying water or sediment zone. We propose the term "external electron acceptor" to describe electron acceptors such as sulfate that are not generated within the same sediment zone in which they are consumed. Examples of other external electron acceptors are oxygen, nitrate, and ferric iron. When organic matter is in excess, the extent of metabolic processes that are dependent upon external electron acceptors is limited by the rate that the electron acceptor can flux into the sediment.

In contrast to the sulfate-reducing zone, organic matter diagenesis in the methanogenic zone is not dependent upon external electron acceptors. No electron acceptor is required for the conversion of acetate to methane (Eqn. 3). Fermentative bacteria within the methanogenic zone produce carbon dioxide, the electron acceptor for H2 conversion to methane, in excess of the methanogens' requirements. Thus, the electron acceptor for methanogenesis is an "internal electron acceptor", that is, produced at the site of methanogenesis.

Model for microbial activity

To simplify discussion, the model was based on the metabolism of acetate since acetate is the substrate for nearly 70 percent of the methane production and sulfate reduction in freshwater sediments (Fig. 1). Furthermore, preliminary results indicated that the same modelling techniques give comparable results when applied to H2 metabolism.

Uptake of acetate and sulfate in sediments follows Michaelis-Menten kinetics (SMITH and KLUG, 1981a; STRAYER and TIEDEME, 1978; LOVLEY and KLUG, 1983a). Uptake of acetate by methanogens was described by:

\[ v = \frac{V \cdot A \cdot B}{K_a + A} \]  

where \( v \) is the rate of acetate uptake, \( V \) is the maximum rate of acetate uptake per unit biomass, \( A \) is biomass, \( B \) is the acetate concentration and \( K_a \) is the acetate concentration at which \( v = 0.5 \cdot V \). The uptake of acetate by sulfate reducers was described with a multiplicative model (Ramm and Bella, 1974) and was computed as:

\[ v = \frac{V \cdot A \cdot B \times S_F \cdot S_U}{K_{S_F} + S_F + K_{S_U} + S_U} \]  

where \( S_F \) is the sulfate concentration and \( K_{S_F} \) is the half-saturation constant for sulfate uptake. The growth rate of microorganisms was computed as:

\[ \frac{\Delta B}{\Delta t} = (v \cdot Y) - (b \cdot B) \]  

where \( \Delta B \) is the increase in biomass over the time interval \( \Delta t \), \( Y \) is the yield of biomass produced per mole of acetate metabolized, and \( b \) is the mortality coefficient (the rate that biomass is lost due to the energy required for cell maintenance as well as other poorly understood factors such as grazing by predators that result in the loss of microbial biomass over time in sediments).

The parameters used in the model are listed in Table 1. The \( K_a \) and \( K_{S_F} \) estimates were from \textit{in situ} kinetic analysis of acetate and sulfate metabolism (LOVLEY and KLUG, 1983a; SMITH and KLUG, 1981a). The estimates for \( Y \), \( V \), and \( b \), which are comparable to values determined for pure cultures and enrichments of acetate-utilizing methanogens and sulfate reducers (LAWRENCE and MCCARTY, 1969; MIDDLETON and LAWRENCE, 1977; ZEHNDER et al., 1982; HUSER et al., 1982; WIDDEL and PFENNIG, 1981), were determined from a combination of experimental, thermodynamic, and kinetic considerations (LOVLEY, 1982).

Model of depth profiles

The distribution of methanogenesis and sulfate reduction in a 3 cm depth interval was modelled since this depth interval is the most active in the decomposition of anaerobic freshwater sediments (KELLEY and CHYNOWETH, 1980; KIng and KLUG, 1982b; LOVLEY and KLUG, 1982; SMITH and KLUG, 1981a). The rate of acetate production was assumed to be uniform throughout the depth interval. The water overlying the sediment was assumed to contain no oxygen or nitrate.

Sulfate flux from the overlying water was calculated from Fick's law (BERNER, 1980). The diffusion coefficient, was assumed to equal 1.5 x 10^{-5} cm^2 sec^{-1} which is the middle of the range for lake sediments in summer at 20°C (HESSLER, 1980). The sulfate concentration in the water overlying the sediment was assumed to remain constant.

Since the uptake of substrates was defined by nonlinear equation, the steady-state distribution of processes with depth was approximated with the Euler integration technique (SPAIN, 1982). The sediment was divided into 1 mm individual layers which were assumed to be homogeneous. Sulfate flux into each layer from the overlying layer, the sulfate flux out of the layer to the next deeper layer, the amount of acetate produced, the acetate and sulfate uptake, and the growth of methanogens and sulfate reducers were calculated and updated at one minute time intervals. The model was generally run for a simulated time greater than five years. This time was sufficient to approach a steady state as indicated by insignificant changes in the rate, concentration, and biomass parameters over a modelled period of a year. Thus, the results of the depth model were not a true steady-state solution but were considered to be a close approximation and sufficient for the purposes of this study in view of the fact that the sediments that were modelled would also be expected to approach but never be at steady-state. Furthermore, as outlined in the next section, the equations for acetate and sulfate metabolism (Eqns. 5–7) could be solved: i) to compute the steady-state concentrations of acetate and sulfate within the methanogenic and sulfate-reducing zones, and ii) to predict the steady-state sulfate and acetate concentrations at which there is a shift from sulfate reduction to methane production.

RESULTS AND DISCUSSION

Segregation of sulfate-reducing and methanogenic zones

Figure 2 illustrates the vertical distribution of processes and metabolite pools that were generated from

<table>
<thead>
<tr>
<th>Table 1. Parameters for acetate uptake and growth of methanogens and sulfate reducers in freshwater sediments.</th>
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<tbody>
<tr>
<td>Parameters</td>
</tr>
<tr>
<td>Ka (M)</td>
</tr>
<tr>
<td>KSU (M)</td>
</tr>
<tr>
<td>V</td>
</tr>
<tr>
<td>b (min^{-1})</td>
</tr>
<tr>
<td>a The basis for the parameters is outlined in the text.</td>
</tr>
<tr>
<td>b moles acetate x g cells^{-1} x min^{-1}</td>
</tr>
<tr>
<td>c mg cells x mmol acetate^{-1}</td>
</tr>
</tbody>
</table>
the depth profile model for sediments with low and high rates of decomposition. The model predicted an upper zone of sulfate reduction and a lower zone of methane production as is typically observed in freshwater and marine sediments. The model indicated that sulfate reduction should predominate over methane production for depth intervals of less than one centimeter in freshwater sediments that have high rates of decomposition as has been found in field studies (Winfrey and Zeikus, 1977; Ingwersen et al., 1981; Cappenberg, 1974; Lovley and Klug, 1982; Lovley et al., 1982). However, in accordance with findings in a less productive lake (Lovley and Klug, 1983a), the model predicted that sulfate reduction can be the dominant terminal process in the upper 2 cm when the rates of organic matter decomposition are low.

The depth at which sulfate reduction declined and methane production began was associated with a marked increase in the acetate concentration (Fig. 2). An increase in acetate concentrations at the transition between the sulfate-reducing and the methanogenic zones has previously been observed in marine sediments (Sansone and Martens, 1981, 1982; Gunnarsson and Ronnow, 1982). Acetate and H2 concentrations increase when marine and freshwater sediments are artificially shifted from sulfate-reducing to methanogenic systems (Sørensen et al., 1981; Lovley et al., 1982). Reliable estimates of the acetate concentrations in the sulfate-reducing zone of freshwater sediments are not available because of the difficulties in sampling this thin zone.

However, the predicted acetate concentrations in the sulfate-reducing zone were comparable to the dissolved acetate concentrations found in the sulfate-reducing zone of marine sediments (Ansbaek and Blackburn, 1980; Balba and Nedly, 1982; Shaw et al., 1984). Acetate concentrations in the methanogenic zone fell within the wide range of acetate concentrations that have been reported for freshwater methanogenic sediments (Molongoski and Klug, 1980; Winfrey and Zeikus, 1979; Horduk and Cappenberg, 1983). Thus, the predicted increase in acetate concentration concomitant with a shift from sulfate reduction to methane production is consistent with existing data but has yet to be adequately documented in field studies on freshwater sediments.

A further complication in comparing the predicted acetate pools with those in sediments is that a portion of the measured acetate may be unavailable for microbial metabolism (Christensen and Blackburn, 1982). However, there are no data that could be used to correct for possible differences between the measured and available acetate pool, if indeed these pools are different in freshwater sediments. For simplicity the model assumed that all dissolved acetate was available for microbial metabolism.

The model indicated that there is no methane production within the sulfate-reducing zone because methanogens were unable to grow at these depths. Microorganisms can maintain a population in the sediments over time only when there is net growth, \( \Delta B/\Delta t > 0 \), or, at steady-state conditions, when \( \Delta B/\Delta t = 0 \).
Equation 7 indicates that these conditions are met when \( v \cdot Y \geq b \cdot B \). It can be calculated from Eqns. 5 and 7 that for methanogens \( v \cdot Y \geq b \cdot B \) when the acetate concentration is 21.5 \( \mu \text{M} \) or greater (Fig. 3). Thus, in the depth profile model, there was no methane production at depths where sulfate reducers were able to maintain the acetate concentration below 21.5 \( \mu \text{M} \). Equations 6 and 7 indicate that at steady-state (\( \Delta B/\Delta t \) of the sulfate reducers = 0) sulfate-reducers can maintain the acetate concentration below 21.5 \( \mu \text{M} \) as long as the steady-state sulfate concentration is above approximately 30 \( \mu \text{M} \) (Fig. 3). Thus, in the depth profile model (Fig. 2), methanogenesis became an important diagenetic process only when the balance between the consumption and the diffusive flux of sulfate resulted in a sulfate concentration of approximately 30 \( \mu \text{M} \). This finding agrees with the observation that sulfate reduction predominates over methanogenesis in freshwater sediments with sulfate concentrations greater than 60 \( \mu \text{M} \) but methanogenesis predominates at lower sulfate concentrations (20–40 \( \mu \text{M} \)) (Lovley and Klug, 1983a; Ingvorsen et al., 1981; Winfrey and Ziekuus, 1977, 1979).

Similar calculations based on kinetic parameters for \( \text{H}_2 \) metabolism by sulfate reducers and methanogens (Lovley et al., 1982; Badzvon and Thauer, 1978; Zehnder et al., 1982) also indicated that methanogens are excluded from the sulfate reducing zone because the steady-state \( \text{H}_2 \) concentrations are too low to support the growth of methanogens. These results emphasize that the exclusion of methane production from the sulfate-reducing zone is the result of biochemical constraints on the activity of the methanogens. Physiological factors presumably also control the vertical segregation of oxygen, nitrate, iron, and manganese oxide respiration. This mechanistic explanation is preferable to the often cited (Claypool and Kaplan, 1974; Froelich et al., 1979; Atkinson and Richards, 1967; Nissenbaum et al., 1972; Mechalas, 1974) but invalid (McCarty, 1972) argument that some respiratory processes exclude others because they are more thermodynamically favorable.

Sulfate in the methanogenic zone

The model predicted that, at steady state, there should be approximately 30 \( \mu \text{M} \) sulfate in the methanogenic zone. Low concentrations of sulfate (20–40 \( \mu \text{M} \)) have been observed in the methanogenic zone of freshwater, estuarine, and marine sediments (Lovley and Klug, 1983a; Hordijk et al., 1984; Thorstenson et al., 1979; N. Simon, pers. commun.). As noted above, at steady state (\( \Delta B/\Delta t \) of methanogens = 0) methanogens maintain the acetate concentration at 21.5 \( \mu \text{M} \) (Fig. 3). According to Eqns. 6 and 7, at 21.5 \( \mu \text{M} \) acetate sulfate-reducers can only maintain a population over time (\( \Delta B/\Delta t \) of sulfate reducers \( \geq 0 \)) at sulfate concentrations greater than 30 \( \mu \text{M} \). Thus, the model suggests that the residual sulfate in methanogenic sediments is the result of metabolic constraints on the sulfate reducers; a minimum threshold concentration of sulfate is necessary to support the growth of sulfate reducers. Evidence supporting this conclusion has been reported in a pure culture study (Ingvorsen et al., 1984).

Effect of rates of organic matter decomposition

The model predicted that higher rates of decomposition result in a greater overall importance of methanogenesis when the 0–3 cm zone of active decomposition is considered as a whole. As the rate of acetate production from organic matter decomposition increased, the rate of sulfate consumption in the surface sediments increased and the depth to which sulfate remained above the 30 \( \mu \text{M} \) threshold necessary for sulfate reducers to exclude methanogens decreased (Fig. 2). Sulfate profiles similar to those generated by the model have been reported for freshwater sediments with low (Lovley and Klug, 1983a) and high (Smith and Klug, 1981a; Winfrey and Ziekuus, 1977) rates of organic matter decomposition.

The partitioning of acetate metabolism between sulfate reduction and methane production in lake surface sediments as predicted by the depth profile model was
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Ible2. et al., 1984). However, the general principles that are illustrated with the model of freshwater processes are considered to be applicable to marine sediments.

CONCLUSIONS

Comparison of the results of the model with field data suggests that it is possible to model geochemical processes and chemical profiles in the sulfate-reducing and methanogenic zones of sediments from a knowledge of the physiological characteristics of the microorganisms catalyzing these reactions. The model approximated both the expected distribution of acetate and sulfate with depth as well as the distribution of methanogenesis and sulfate reduction in sediments. The model indicated that there is little methane production in the sulfate-reducing zone because the higher substrate affinity and metabolic yield of the sulfate reducers permits them to maintain the concentration of acetate (and by analogy H2) too low for methanogens to grow. However, at sulfate concentrations below a minimum threshold of approximately 30 μM, the metabolism of sulfate reducers is so sulfate-limited that methanogens are able to outcompete sulfate reducers for acetate and prevent sulfate reduction. The model indicated that as the productivity of aquatic systems increases, with the resultant increases in the rates of sediment decomposition, methanogenesis becomes a more important terminal diagenetic process because methanogens require only internal electron acceptors that are generated in excess at the site of decomposition. Sulfate reducers require an electron acceptor that is generated external to the site of sulfate reduction and thus sulfate reduction is limited by the rate of sulfate flux from the overlying water.

![Table 2. Methane production and sulfate reduction in the sediments of several lakes during summer stratification.]

<table>
<thead>
<tr>
<th>Depth Interval</th>
<th>Methane Production (μl)</th>
<th>Sulfate Reduction (μM x hr⁻¹)</th>
<th>Total Terminal Metabolism</th>
<th>% Acetate</th>
<th>Sulfate (μM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lawrence</td>
<td>1.8</td>
<td>4.6</td>
<td>6.4</td>
<td>14</td>
<td>110-130</td>
</tr>
<tr>
<td>Wintergreen A</td>
<td>6.2</td>
<td>45.2</td>
<td>51.4</td>
<td>80</td>
<td>30-280</td>
</tr>
<tr>
<td>Site B</td>
<td>26.0</td>
<td>4.0</td>
<td>30.0</td>
<td>67</td>
<td>180-290</td>
</tr>
<tr>
<td>Wintergreen B</td>
<td>24.0</td>
<td>NA</td>
<td>24.0</td>
<td>61</td>
<td>200</td>
</tr>
<tr>
<td>Wintergreen C</td>
<td>34.0</td>
<td>NA</td>
<td>34.0</td>
<td>76</td>
<td>0-100</td>
</tr>
</tbody>
</table>

*Data expressed in μoles per liter of sediment per hour.
*Based on percentage of 14CCH₄ of total 14CCH₄ and 14CO₂ produced from [2-14C] acetate.
*Sulfate in water immediately overlying the sediment.
*Data from Lovley and Klug (1982b).
*Data from Lovley and Klug (1982a), Lovley et al. (1982a, 1982b), and unpublished data from this laboratory.
*Data from Figure 6 of Windfrey and Zielke (1979).
*Data from Cappenberg (1976).
*Data not available, NA.
*Total rates of terminal metabolism calculated from reported rates of acetate turnover (Windfrey and Zielke, 1979; Cappenberg, 1976) and relative contribution of acetate metabolism to total terminal metabolism (Fig. 1).
Although limited in scope, the model presented here demonstrates the potential to predictively model some aspects of sediment geochemistry with models based on the physiological characteristics of microorganisms. An elaboration of this approach to model sediments in which organic matter is also decomposed with the reduction of oxygen, nitrate, and metals seems warranted, but the appropriate in situ data are as yet unavailable.

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