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Sampling marine pore waters for Mn, Fe, U, Re and Mo: modifications on diffusional equilibration thin film gel probes

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Abstract

Pore water metal profiles are important for identifying redox horizons and understanding trace metal geochemical cycling. The challenges of pore water sampling for trace metals are minimizing disturbance, especially at the sediment-water interface, and minimizing oxidation during sampling. We are investigating diffusional equilibration in thin films (DET) probes for obtaining pore water profiles. Our goal is to use probes for redox-sensitive trace metals U, Re and Mo, in addition to Mn and Fe, in coastal marine areas. Initial solution equilibration tests and laboratory core incubation experiments suggest that equilibration times for probes in sediments are approximately 24-48 h. Control tests suggest that the incubation does not alter the redox conditions in the pore waters. Pore water profiles from cores sampled by slicing, centrifuging and filtering (in a nitrogen atmosphere) and from probes are similar.

Two modifications on the gel probe design were tested to determine their impact. (1) PVC wedges were attached to the backs of probes to increase the contact between sediments and the probe surface and to reduce the risk of forming channels along the probe surface, which might allow vertical pore water transport. Lower Fe concentrations were measured from probes without PVC wedges, but other metal profiles were similar. (2) A modified face frame was removed from the front of a probe, to reduce disturbance of the sediments during insertion and to increase the contact between the sediments and probe surface. Probes with modified face frames did not

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have increasing U and Mo concentrations with depth, whereas two of the three probes without face frames did have increasing concentrations. Increasing U and Mo concentrations at depth may be reflecting the influence of irrigating burrows and their supply of oxygen to reduced sediments, which could oxidize previously reduced metals. The distribution of burrows is heterogeneous and resulting profiles would also be expected to be heterogeneous in their response.

Differences between probe profiles and sliced/centrifuged profiles are examined to gain insight into possible sampling artifacts. Peaks in the Re sliced/centrifuged profiles suggest a large Re flux to the overlying waters, which is neither calculated from probe profiles nor measured in benthic chamber samples. It is possible that heterogeneity at the sampling site in Buzzards Bay resulted in these differences; however, it is also possible that centrifugation releases Re from pore structures that would not be measured with less intrusive sampling methods, such as gel probes or benthic chambers.

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1. Introduction

Redox-sensitive metal concentrations in sediment cores have been used to determine past changes in redox conditions (e.g. Calvert and Pedersen, 1993; François et al., 1993, 1997; Dean et al., 1994, 1997, 1999; Rosenthal et al., 1995; Crusius et al., 1996; Crusius and Thompson, 2000; Anderson et al., 1998; Adelson et al., 2001). The redox state can be identified by sediment concentrations of redox-sensitive trace metals (U, Re and Mo), which are soluble under oxic conditions but precipitate (or absorb) under anoxic conditions (Calvert and Pedersen, 1993; Morford and Emerson, 1999 and references therein). Changes in sediment metal concentrations deposited over time suggest changes in the redox conditions over that time period. Redoxsensitive metal enrichment in sediment is indicative of past reducing conditions; however, it is not yet possible to distinguish between an increase in carbon flux and a decrease in bottom water oxygen content. The use of U, Re and Mo as indicators of past depositional conditions is limited by our understanding of their geochemical cycling in present-day conditions, and the effect of diagenesis and its potential for obscuring the sedimentary signal are not well understood (e.g. U: Mangini et al., 2001).

2. Background

Uranium, Re and Mo are conservative in oxic seawater. Uranium appears to be removed from pore waters at the depth of Fe reduction (Cochran et al., 1986; Klinkhammer and Palmer, 1991; Crusius et al., 1996; Zheng, 1999), whereas Re is removed either shallower (Morford and Emerson, 1999) or at the same depth as U removal (Crusius et al., 1996). Molybdenum removal from pore waters appears to require near-anoxic (Shaw

et al., 1990) or sulfidic pore waters (Helz et al., 1996; Zheng et al., 2000). A compilation of sedimentary Mo concentrations relative to bottom water oxygen suggests that Mo authigenic enrichment in sediments occurs when bottom water oxygen is less than 10 μ M (Zheng et al., 2000).

High-resolution pore water profiles of these elements should assist in elucidating their geochemical cycling and should improve their use as paleoredox tracers. Traditional pore water separation involves slicing a sediment core, centrifuging and filtering each sample to separate pore waters from solid phase, with both sectioning and filtering under a nitrogen atmosphere. Profiles measured from these samples are used to calculate metal fluxes from the resulting concentration gradient across the sediment–water interface. However, potential artifacts from centrifugation and accidental sample oxidation could alter the profile. Disturbance at the sediment–water interface, where chemical gradients are typically at a maximum, is also difficult to minimize during overlying water removal and sampling. Techniques, such as voltammetry (e.g. Luther et al., 1998), dialysis (e.g. Carignan, 1984) and polyacrylamide gel probes (e.g. Davison et al., 1994; Fones et al., 1998), may reduce the potential for interface disturbance and oxidation artifacts, remove the need for centrifuging, and provide mm- to cm-scale information in both vertical and horizontal dimensions through multiple profiles.

We have been investigating constrained diffusional equilibration in thin films (DET) polyacrylamide gel probes for Fe, Mn, U, Re and Mo analysis. DET probes have been used to analyze Fe and Mn in both marine and lacustrine sediments (Shuttleworth et al., 1999; Zhang et al, 1999; Fones et al., 1998; Davison et al., 1991, 1994; Krom et al., 1994). Constrained DET probes have a modified design with gel sections (0.4-1 mm) separated by thin dividers, eliminating the potential for profile relaxation after sampling (e.g. Fones et al., 1998; Mortimer et al., 1998). Probe design has also included a face frame, which attaches to the front of the probe to firmly hold the gel and covering membrane in place (e.g. Davison et al., 1994; Shuttleworth et al., 1999; Krom et al., 1994).

In this study, we present verification that the probes are suitable for our elements of interest through both a solution equilibration test and a multicore incubation experiment. Two modifications on the gel probe design were tested to determine the impact of (1) the presence or absence of a PVC wedge attached to the back of the probe, and (2) the presence or absence of a modified face frame. We hypothesized that the face frame could disturb the sediments during probe insertion into the sediments and interfere with the contact between the sediments and the probe surface, while a PVC wedge could increase the contact between the probe surface that might allow vertical pore water transport. Differences between the probe profiles and the sliced/centrifuged profiles are examined to gain additional insight into other possible sampling artifacts.

3. Site description

Boston Harbor and Buzzards Bay are both shallow coastal areas on the northeast coast of the United States (Fig. 1). The sampling site in Boston Harbor is in the southeast end of the harbor and the water depth is approximately 5 m with a sedimentation rate of ~ 1.8



Fig. 1. Sampling locations in (a) Boston Harbor and (b) Buzzards Bay, on the northeast coast of the United States.

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cm year⁻¹ (Bothner et al., 1998). This site is near Nut Island, a discharge point for treated sewage effluent from 1952 to 2000, when the sewage outfall was relocated to deeper waters in Massachusetts Bay. Diverse benthic organisms are found in this area, dominated by large deposit-feeding species (Shull and Yasuda, 2001), and research done in nearby Massachusetts Bay suggests reduced bioturbation during the fall relative to the spring (Wheatcroft et al., 1994).

The Buzzards Bay sampling site is the same location used by Martin and Sayles (1987) for their study of seasonal changes in bioturbation and irrigation, and by McNichol et al. (1988) for their study of carbon remineralization. The water depth is approximately 15 m, sediments are predominantly silty-clay (Moore, 1963) and the sedimentation rate is much slower (0.05 cm year⁻¹; McNichol et al., 1988). Stations monitored in northwestern Buzzards Bay indicate that the overlying waters are oxic throughout the year (Driscoll, 1975). Deposit-feeders dominate in the sediments, accounting for 70–90% of the benthic fauna (Sanders, 1958). During the early summer, average bioturbation rates are 17 cm² year⁻¹, approximately three times larger than winter bioturbation, and summer irrigation was found to extend to at least 20 cm (Martin and Sayles, 1987). Past studies have found the carbon flux to the sediment–water interface ranged from 620 to 850 µmol cm⁻² year⁻¹ (McNichol et al., 1988), and benthic chamber data from a deployment in April 2001 indicate the carbon flux was 410 µmol cm⁻² year⁻¹ (Morford et al., in preparation).

4. Analytical method

4.1. Gel probe preparation

A gel mix of acrylamide monomer (6% solution) and bis-acrylamide cross-linker (0.8% solution) is combined with tetramethylethylene diamine (TEMED), the catalyst, and ammonium persulfate (10% solution), the polymerization initiator, to make the polyacrylamide gel. All of the aforementioned solutions are Fisher electrophoresis grade. The gel solution is poured into an acrylonitrile butadiene styrene (ABS) mold $(17.5 \times 4 \text{ cm}; \text{ purchased from DGT Research})$, which was modified to have openings ranging from 0.3 cm at the top to 1 cm at the bottom (Fig. 2). The high depth resolution at the top of the probe aids in identifying the steep gradients at the sediment-water interface. The probe is hydrated in Milli-Q water (18.2 M Ω) for 24 h, to remove excess catalyst and initiator. The resulting gel contains >90% water. The monomer and cross-linker content was optimized to provide a gel composition that was not prone to swell out of the mold during hydration. Gels made with low monomer content coupled with bis-acrylamide as cross-linker have metal diffusion coefficients similar to diffusion through water and behave similarly to gels made with agarosederivative cross-linker (Zhang and Davison, 1999), which is also commonly used (e.g. Fones et al., 1998).

The probe face is covered with a 0.1-µm polycarbonate membrane, which reduces potential contamination from sediments. After hydration, the probe may have a PVC wedge attached to the back or a modified face frame attached to the front. The PVC



Fig. 2. Cross-section drawing of a modified probe on its side. Openings are 0.3 cm (top), 0.5 cm (middle) and 1 cm (bottom). Typically three to five small sections are left in the overlying water during the incubation to identify the overlying water concentration. The PVC wedge on the back is thicker on the top (2 cm) and narrower on the bottom (0.1 cm), to increase the contact between the probe and the sediments. After the openings are filled with polyacrylamide gel, the probe is covered with a 0.1-µm membrane. A modified face frame can then be attached to the probe face. The bottom of the frame was removed to minimize sediment disturbance during insertion.

wedge is thicker at the top (2 cm) and narrower at the bottom (0.1 cm) to increase the contact between the probe face and the sediments. The face frame was modified, with the bottom section removed and the penetrating edges angled, to reduce the disturbance of the sediments during insertion. The membrane is securely wrapped around the probe face and attached on the back of the probe with tape, to ensure that sediment does not come into direct contact with the gel. When the PVC wedge is attached with nylon screws to the probe, the membrane is secured between the probe and the wedge, providing additional security against direct sediment contact with the gel sections. The probe is then placed in an electrolyte solution (NaCl/MgSO₄, approximately 33 ‰), and deoxygenated by bubbling with nitrogen for 72 h prior to use. Probe exposure to oxygen is minimized (<10 s) during insertion into the core, to reduce authigenic formation of oxides due to entrained oxygen, which is especially critical for elements that oxidize quickly (e.g. Fe: Sung and Morgan, 1980; U: Cochran et al., 1986; Anderson et al., 1989). Gel sections are removed from the probe and placed in preweighed microcentrifuge vials, and the vials are reweighed to determine the sample size. Gel sections range from 80 to 280 mg. Dilute nitric acid (5%, Fisher Optima grade) is added to the vials and they are again reweighed to calculate a dilution factor, which was adjusted for the gel size to be approximately 20-fold. Gel section sampling from the probe occurs in a laminar flow hood. Probes and PVC backs are soaked in 2 N HCl for several days and then soaked for several more days with Milli-Q water prior to use.

4.2. Sediment core slicing/centrifuging

Sediment cores for slicing/centrifuging were obtained with 10.7-cm-diameter polycarbonate core liners and were processed at approximately in situ temperatures, either dockside (January, Boston Harbor sampling) or in a 4 °C cold lab (May, Buzzards Bay sampling). Sectioning and filtering (N₂-flushed 0.45- μ m Acrodisc filters) occurred in a nitrogen atmosphere in a glove bag. Centrifuging was done at approximately 10,000 rpm for 10-15 min. Subsamples of pore water were split for nitrate+nitrite, ammonium, silica (syringes and filters Milli-Q washed) and trace metals (syringes and filters 2 N hydrochloric acid washed) (data presented in Morford et al., in preparation). Trace metal samples were acidified with concentrated nitric acid (Optima Fisher grade). Sample depths from 0 to 5 cm were determined by completely filling scintillation or centrifuge vials and calculating the sample interval by volume. This is most complicated at the sediment-water interface, where an uneven and complex relief makes it difficult to uniformly sample across the entire surface to an even depth. Boston Harbor had 0.3-cm resolution from 0 to 1.6 cm and 0.5-cm resolution below, whereas Buzzards Bay had 0.3-cm resolution from 0 to 1.4 cm and 0.5-cm resolution from 1.4 to 4 cm. This method might also result in smearing of the profile since sediment along the wall of the core liner cannot be discarded; however, sharp peaks in the surface samples from the trace metal profiles suggest this is not a major concern. The cores from Buzzards Bay were further sectioned in 1- and 2-cm slices deeper than 4 cm.

4.3. Pore water analysis

Trace metal samples were measured on the Woods Hole Oceanographic Institution high resolution inductively coupled plasma-mass spectrometer (Finnigan). We use a modified method based on Rodushkin and Ruth (1997) for measuring Mn, Fe, U, Re and Mo in a 20-fold-diluted seawater matrix.

5. Results

5.1. Accuracy and precision

Replicate measurements (n=46) of a standard seawater solution (CASS-4, Nearshore seawater for trace metals, National Research Council Canada) over months of analysis indicate that the instrumental method precision as determined by the relative standard deviation (standard deviation/mean × 100) for a 20-fold seawater dilution is < 10% for Mo and U, and < 11% for Re and Mn. The average concentrations for Mo and Mn are within certified 95% confidence ranges, U is 15% below its information value (not certified) and Re is not certified. Replicate gel section measurements on one day of analysis of all metals yielded a method precision of 4% or better (n=4).

5.2. Bottle equilibration results

Initial experiments involved placing seven probes in an electrolyte solution (NaCl/MgSO₄, approximately 33%) spiked with Mn, Fe, U, Re and Mo to determine the equilibration time in solution. Individual probes were removed over time (t=3, 6, 9, 12, 24, 35 and 48 h) and several (four to five) gel sections from each probe were analyzed for trace metals and compared to replicate measurements of the solution (Fig. 3). After 6 h, average Mn and Fe gel concentration are within one standard deviation of replicate measurements of the solution (n=7), and Re, U and Mo gel concentrations are 10–12%





Fig. 3. Gel probes were placed in an electrolyte solution spiked with Mn, Fe, U, Re and Mo, individually removed over time and sampled (four to five sections from each probe). Horizontal lines and error bars represent the measured solution concentration (n=7). Two gel sections (identified on the figure with parentheses) had anomalously low (t=6 h) and high (t=12 h) concentrations and were not considered further.

greater than their measured solution concentrations, blank gel sections incubated in Milli-Q were either similar to dilute nitric acid (Mo, Re) or < 0.2 nM (U), suggesting that contamination from gel material is not the cause of the higher gel concentrations relative to the solution, and the direct cause is still unknown. However, pore water samples from sliced/centrifuged cores and gel probes are similar, suggesting that the offset from the solution equilibration experiment is not a concern for core/probe comparisons.

5.3. Core incubation and PVC wedge tests

Six 10.7-cm-diameter cores were retrieved from Boston Harbor in January 2001, and two cores were immediately sectioned. The other four cores were transported to a cold lab (4 °C) where they were continuously bubbled with air and overlying water was exchanged every 5-6 h with recovered bottom waters from the site. One core was incubated without probes as a control on the incubation method. Six probes were inserted into the other three

Insubstign time (b)	Cara	BVC healt attack
Incubation experiment and PVC wed	lge details for cores collected in Janu	ary 2001 from Boston Harbor

Incubation time (h)	Core	PVC back attached?
8	А	No
16	В	Yes
24	С	No
48	А	Yes
73	С	No
97	В	Yes

All probes were used without face frames.

Table 1

cores, with two probes in each core facing the core center and with the maximum separation possible to minimize disturbance. The distance between probes was also greater than the calculated 2-cm separation required for minimizing equilibration times and keeping the pore waters effectively undepleted (Harper et al., 1999). All probes were without face frames. Three of the six probes had PVC wedges attached on the probe back (Table 1). The probes were removed after different equilibration times and after the final probe was removed, the control core was sliced and centrifuged, similar to the first two processed cores.

The two initially sliced/centrifuged cores were compared to the control core, to ensure that the incubation did not alter the pore water profiles. The trace element data (Fig. 4) suggest that the element profiles are very similar among the three cores. The only exceptions are higher U concentrations in the control core from 1 to 2 cm and higher Re concentrations from 1 to 4 cm (5–10 pM).

Three probes with PVC backs were incubated and sampled at 16, 48 and 97 h, while three probes without PVC backs were incubated and sampled at 8, 24 and 73 h (Fig. 5). The three metal profiles from the probes without PVC backs are more scattered for Mn and



Fig. 4. Sliced/centrifuged pore water trace element profiles for the two initially processed cores and the control core processed at the conclusion of the incubation experiment from Boston Harbor. Arrows denote seawater concentrations (U = 14 nM: Ku et al., 1977; Re = 39-45 pM: Anbar et al., 1992; Colodner et al., 1993; Mo = 105 nM: Collier, 1985).



Fig. 5. Gel probes were inserted into sediment cores from Boston Harbor (January 2001). The top row of profiles were probes with PVC wedges attached (t=16, 48, 97 h), while the bottom row of profiles were probes without PVC wedges (t=8, 24, 73 h). The letters in parentheses represent the core identification. Dashed horizontal lines represent the sediment-water interface, whereas arrows denote seawater concentrations (see Fig. 4 caption).

Fe, and Fe concentrations are also lower. Uranium, Re and Mo profiles are similar for probes with and without PVC backs. The probe incubated 48 h with a PVC back is very similar to the two initially sliced/centrifuged cores (Fig. 6).



Fig. 6. Sliced/centrifuged pore water trace element profiles for the two initially processed cores and the metal profile from the gel probe incubated 48 h with a PVC wedge attached to the back of the probe. Arrows denote seawater concentrations (see Fig. 4 caption).

Probes either had no face frame or a modified face frame attached to the probe front			
Incub	ation time (h)	Core	Modified face frame attached?
	25	В	Yes
	25	В	No
	25	D	No
	49	D	Yes
	49	C	Yes
	49	С	No

Modification included removing the bottom of the frame and angling the inserting edges to minimize sediment disturbance during insertion. Cores were collected in May 2001 from Buzzards Bay. All probes had PVC wedges attached to the probe backs.

5.4. Replicate incubations and face frame results

Table 2

Several probes were incubated for 25 and 48 h to determine the extent of heterogeneity in Buzzards Bay (May 2001). A further experiment tested the influence of modified face frames on profiles (Table 2). Six 10.7-cm-diameter cores were collected from Buzzards Bay and two cores were immediately sectioned, while four other cores were incubated at 4 °C with recovered bottom waters continuously pumped through the overlying water in each core. Three cores contained gel probes while the fourth core was incubated as the control, which was sliced and centrifuged at the conclusion of the incubation. The trace metal data from the sliced/centrifuged cores are more scattered compared to the Boston Harbor profiles, but the three profiles are similar with the exception of Mn, which has a much smaller peak at the surface in the control core (Fig. 7).

Manganese and Fe profiles from the three probes incubated without face frames are similar, whereas the profiles from the cores with modified face frames are scattered with concentrations lower by up to a factor of three (Fig. 8). Uranium and Mo profiles from



Fig. 7. Buzzards Bay sliced/centrifuged pore water trace element profiles for the two initially processed cores and the control core processed at the conclusion of the incubation. Arrows denote seawater concentrations (see Fig. 4 caption).





Fig. 8. Gel probes were inserted into sediment cores from Buzzards Bay (May 2001). The top row of profiles were probes without face frames attached, while the bottom row of profiles were probes with modified face frames. The letters in parentheses represent the core identification. Dashed horizontal lines represent the sediment-water interface, whereas arrows denote seawater concentrations (see Fig. 4 caption).

probes with modified face frames do not increase with depth, in contrast to the increases measured in probes without face frames. The small Re peaks measured at the sediment-water interface in two of the probes without face frames are not measured in any of the probes with modified face frames.



Fig. 9. Comparing gel probe profiles (t=25 h, without face frames) with the two sliced/centrifuged cores from Buzzards Bay. Arrows denote seawater concentrations (see Fig. 4 caption). Note that the small, inset figure of Re spans a smaller concentration range for the top 10 cm.

A comparison of two gel probes incubated 25 h without face frames with the two initially sliced/centrifuged cores suggests a close correlation among the four profiles for Fe, U and Mo (Fig. 9). Both probe profiles show a smaller Mn peak relative to the sliced/ centrifuged peaks, similar to the control core and results from Boston Harbor, and the surface peak for Re is substantially lower in the gel probe samples compared to the sliced/ centrifuged cores.

6. Discussion

6.1. Influence of PVC wedge and minimum core incubation time

The largest difference among probe profiles in Fig. 5 is seen in the Fe profiles. The profile from the 8-h incubation can be disregarded because this time period might have reflected incomplete equilibration, based on the solution equilibration tests (Fig. 3). Iron profiles from 24- and 73-h incubations without PVC backs have lower Fe concentrations, perhaps suggesting that vertical transport along the probe face allowed for oxygen transport, which would have oxidized $Fe_{(aq)}^{2+}$ to solid Fe oxyhydroxides. However, the effect of oxidation is not seen in the U profiles, which might also be expected to oxidize quickly (Cochran et al., 1986; Anderson et al., 1989), or Mo or Re profiles. It is more likely that the measured differences in the Fe profiles are due to heterogeneity among cores and/or the influence of microenvironments.

Multiple probes separated by 3 mm in Esthwaite Water sediment showed variable Fe peak depths and concentrations, attributed to sampling microniches and sediment pore water heterogeneity (Shuttleworth et al., 1999). Data presented in Shuttleworth et al. (1999) were from probes that did not have PVC wedges and did have face frames, which may have allowed for vertical transport along the probe face or sediment disruption during probe insertion. However, the probes equilibrated for more than 24 h in these freshwater sediments and should largely reflect concentrations towards the end of the deployment so that features due to disturbance during probe insertion would have had time to relax back to their steady-state profiles (Shuttleworth et al., 1999). The close agreement for Fe profiles between probes incubated 48 and 97 h (Fig. 5) and their close agreement with sliced/centrifuged cores (Fig. 6) suggest that PVC backs led to consistent Fe profile results, whereas the presence or absence of PVC backs does not appear to affect the U, Re or Mo profiles. In addition, the PVC backs further secure the membrane to the probe, particularly in the absence of a face frame.

To identify the appropriate incubation time, only the probes with PVC backs are compared to eliminate any variations that might be due to their absence. Manganese, U, Re and Mo profiles are similar, while the Fe peak in the 16-h probe is less than half of the other two probe profiles. The Fe profiles suggest that 16 h might have been too brief or that the system was perturbed during probe insertion and had not yet returned to steady state (Fig. 5), and that an incubation of 24–48 h is adequate for these sediments. This is consistent with the modeled equilibration times determined by Harper et al. (1997), who found that equilibration times range from 1 to 78 h to achieve 99% equilibration if the pore

waters are either resupplied by diffusion through pore waters or partially resupplied from desorption from sediment, respectively. The comparison of the two initially sliced/ centrifuged cores with the probe incubated 48 h reflects the good agreement among the profiles, suggesting that constrained gel probes are appropriate for sampling these metals (Fig. 6). The lower Mn peak in the probe profile might be reflecting the lower Mn concentrations observed in the control core and indicate that the incubation might affect Mn profiles. The small peak in Re at the surface in the probe profile suggests Re release to the overlying waters, which is consistent with, though smaller than, the flux predicted from core 2.

6.2. Influence of modified face frames on pore water profiles

The impact of modified face frames is seen in almost all of the metal profiles (Fig. 8). The face frames were modified (the bottom of the face frame was removed) to maximize the contact between the sediment and the probe face; however, it is possible that this modification increased the sediment disturbance during probe insertion by channeling the sediment against the probe surface. The lack of peaks in two of the Mn profiles and one of the Fe profiles from probes with modified face frames could reflect the longer times necessary to reestablish profiles after sediment disruption. Uranium and Mo concentrations increase with depth in probes without face frames and are similar to the sliced/centrifuged pore water profiles (Fig. 9). These measured concentration increases are consistent with a mechanism of irrigation inducing oxidative release of reduced metals from sediments (Morford et al., in preparation). The more consistent profiles measured in probes without face frames suggests minimal disturbance during probe insertion.

Both probes from core C have broad Fe peaks (Fig. 8) and are similar to the broad Fe peak measured in one of the sliced/centrifuged cores (core 1, Fig. 7). Both probes from core D show no increase in U or Mo with depth (Fig. 8), suggesting that spatial heterogeneity may also be an underlying cause for some of these observed differences. However, the different Re profiles in probes from core D at the sediment–water interface suggest either a Re flux into the sediments (with a modified face frame) or a Re flux out of the sediments (without a face frame), with the later consistent with the direction of the flux predicted from the three sliced/centrifuged cores. The Re profiles suggest that some of the difference among profiles might also be due to the modified face frame.

Spatial heterogeneity in sediment pore waters has previously been shown by DET probes (Shuttleworth et al., 1999) and specifically in the vicinity of a worm burrow using voltammetric (Luther et al., 1998) and gel probe (Mortimer et al., 1999) techniques. The inherent heterogeneity of irrigation burrows (Aller, 1990) and the lack of U and Mo increase in one profile from a probe without a face frame suggests that these probes might have sampled zones with less intense irrigation or areas not adjacent to a burrow. However, the close agreement of the three probes without modified face frames for Mn and Fe (Fig. 8) and the similar profiles measured in sliced/centrifuged cores (Fig. 9) suggest that the removal of modified face frames results in more consistent profiles.

6.3. Implications for sampling artifacts

Comparisons between DET probes and pore waters sampled by syringe are closely correlated for Fe and Mn in concentration and peak shape (Krom et al., 1994), though larger variability has been measured between DET probes and pore waters from sliced/ centrifuged cores (Fones et al., 2001). This difference could be attributable to the scale of sampling $(80-280 \ \mu l)$ of pore water from gel probe samples compared to $20-30 \ m l$ of pore water from sliced/centrifuged core samples following the sampling resolution outlined in Section 4), or to the extensive disturbance when slicing sediment and the unknown impact of centrifuging.

Higher Re concentrations were measured in the first few pore water samples relative to the overlying water concentrations for both Boston Harbor and Buzzards Bay (Figs. 6 and 9). These measurements suggest a Re flux to the overlying waters. This Re flux might be a result of a labile source at the surface that releases Re upon degradation, or a result of slow Re reduction kinetics after Re release during episodic oxidation of previously reduced sediment (Morford et al., in preparation). However, the question addressed here involves the contrast between the three cores from Buzzards Bay that suggest a much larger flux of Re to the overlying waters, and the two probe profiles that suggest a much smaller flux (Fig. 9). This distinct difference between the sliced/ centrifuged cores and the gel probes could be a result of accidental oxidation or sampling artifacts.

The gradient across the sediment-water interface in the sliced/centrifuged cores predicts a flux 7-40 times greater than the flux calculated from the probe profiles (Morford et al., in preparation). It may be questionable to compare fluxes calculated from gel probes, which potentially reflect a smaller pore water sample, to fluxes calculated from gel probes, which potentially reflect a smaller pore water reservoir. However, results from a benthic chamber obtained at approximately the same time as the cores and integrate a sediment area larger than the cores (benthic chamber=340 cm²; sediment core=92 cm²) do not show a large Re flux out of the sediments in Buzzards Bay, although the data are consistent with the smaller flux predicted by the gel probe profiles (Morford et al., in preparation). It is possible that the heterogeneity in Buzzards Bay resulted in these differences. The presence of microniches in sediments has been documented, emphasizing the variability of pore water concentrations on cm or mm scales (e.g. Luther et al., 1998; Shuttleworth et al., 1999; Mortimer et al., 1999), and the third probe without a modified face frame recorded a flux into the sediments suggesting heterogeneity at this site.

It is also possible that the probes and benthic chamber are accurately representing the benthic flux of Re from this site, whereas the sliced/centrifuged cores are reflecting a sampling artifact. If the interface was oxidized during slicing, authigenic Re in the sediments might have been oxidized and released to the pore waters, resulting in the observed peaks. However, it would be expected that other reduced elements, such as U, which is known to quickly oxidize in the presence of oxygen (Cochran et al., 1986; Anderson et al., 1989), would also have been oxidized and remobilized to the pore waters. Since U peaks at the sediment-water interface are not observed in cores from Buzzards Bay, it is not thought that oxidation of the

sediment-water interface occurred. It is possible that centrifugation released Re from microniches and pore structures that were physically enclosed. Rhenium would then not be accessible via diffusion and so would not be measured with gel probes or benthic chambers.

7. Conclusions

Polyacrylamide gel probes are promising for sampling pore waters for Mn, Fe, U, Re and Mo with minimal disturbance of the sediment-water interface, reduced chances of oxidation artifacts and no alteration due to centrifugation. Laboratory core incubations of 24–48 h appear to be sufficient for equilibration without changing the redox zones. However, Mn may be altered from its steady-state profile during the incubation, resulting in profiles with lower Mn concentrations.

The addition of PVC wedges to the backs of probes should reduce the risk of forming channels algng the probe surface, which might allow vertical pore water transport. The removal of modified face frames from the front of the probe appears to have a larger impact on metal profiles. Probes incubated with modified face frames had fewer Mn and Fe peaks and no increase in U and Mo concentrations with depth. These differences may reflect additional disturbance of the sediment during probe insertion, but with a limited number of replicates, the difference could also be attributed to sediment heterogeneity.

Differences between probe profiles and sliced/centrifuged profiles are examined to gain insight into possible sampling artifacts. Peaks in the Re sliced/centrifuged profiles suggest a large Re flux to the overlying waters, which is neither predicted from probe profiles nor measured in benthic chamber samples. It is possible that heterogeneity in Buzzards Bay resulted in these differences; however, it is also possible that centrifugation releases Re from pore structures that would not be measured with less intrusive sampling methods, such as gel probes or benthic chambers.

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