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Comparative geochemistry of cadmium, rhenium, uranium, and molybdenum in continental margin sediments

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Abstract—The concentrations of authigenic phases of Cd, Re, U, and Mo increase with depth in four 45-cm-long sediment box cores collected along the axis of the Laurentian Trough, Gulf of St. Lawrence. Average authigenic accumulation rates, estimated from element inventories, are similar to rates in other continental margin environments. Strong regional variations in sediment accumulation rate and sulfide concentration have little influence on the accumulation rates of Cd and Re. This suggests that slow precipitation kinetics controls the accumulation of Cd and Re in these sediments. The accumulation rate of authigenic U is more variable; it may be tied to the kinetics of microbially mediated U reduction and be controlled by the availability of reactive organic matter. Authigenic Mo is distinguished by a sharp subsurface concentration minimum, above which Mo cycles with manganese. Mo released to pore water upon reduction of Mn oxides diffuses downward and enriches the subsurface sediment. Mo accumulates most rapidly in the sediment with the highest sulfide content. Slow conversion of molybdate to thiomolybdate may explain the much slower Mo accumulation rate in the less sulfidic sediments. A component of authigenic Mo accumulates with pyrite in an approximately constant Mo:Fe ratio. The accumulation rate of pyrite and associated Mo is insensitive to AVS abundance. Pyrite formation may be limited by the reactivity of iron oxide minerals. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

The trace elements Cd, Re, U, and Mo are soluble in seawater and behave nutrient-like (Cd) or conservatively (Re, U, Mo) in the ocean. These elements are much less soluble in the pore water of reducing sediments, where precipitation of authigenic phases controls the solubility. The different solubility in oxic water and reducing pore water causes a net flux of these trace elements from the water column into the sediment, and this can result in considerable accumulations of authigenic phases. Because of low detrital background concentrations, the authigenic fraction can dominate in reducing sediments. For this reason, authigenic Cd, Re, U, and Mo in continental margin sediments have attracted attention as potential tracers of paleoredox conditions in sediment and water column, and of the environmental variables that control these conditions (e.g., Calvert and Pedersen, 1993; Rosenthal et al., 1995; Crusius et al., 1996; Dean et al., 1997; Morford and Emerson, 1999; Zheng et al., 2000; Nameroff et al., 2002).

A stumbling block to developing the potential of trace elements as redox tracers is that redox signals do not pass in a simple manner from the water column to the sediment but are mediated and modified by diagenesis (e.g., Shimmield and Pedersen, 1990; Gobeil et al., 1997). The rate of oxidation of sedimentary organic matter and the rate of accumulation of the

sediment are two important and related environmental variables that affect diagenesis of trace elements. Other factors being equal, the abundance and reactivity of organic matter determines the onset of sulfate reduction and sulfide production, and the rate of sediment accumulation determines the time available for sediment at a given depth horizon to interact with the water column. The oxidation rate of organic matter depends on its reactivity, which is initially high and then decreases with time as the more reactive components of the total organic matter are consumed (Westrich and Berner, 1984). One therefore expects the reactivity of buried organic matter and the rate of sulfate reduction to be more important in rapidly accumulating than in slowly accumulating sediments (Edenborn et al., 1987). The sediment accumulation rate, in addition to influencing the reactivity of the organic matter, could also be expected to control the time available for a sediment layer to accumulate trace elements from the water column. Other factors being equal, one could expect the concentration of a trace element at comparable depths below the sediment surface to be higher the slower the sediment accumulates. The interactions between sediment accumulation rate and organic matter reactivity are further complicated by the presence of benthic organisms which, by transporting particles and solutes across concentration gradients, can cause substantial recycling of trace elements between their dissolved and precipitated forms (Gobeil et al., 1997; Zheng et al., 2002).

The Laurentian Trough is a deep continental margin environment on the east coast of Canada. The bottom water in this environment has nearly constant salinity (35) and temperature (2.5–4.5°C). The sediment composition is dominated by terrestrial detrital minerals and is lithologically homogeneous and

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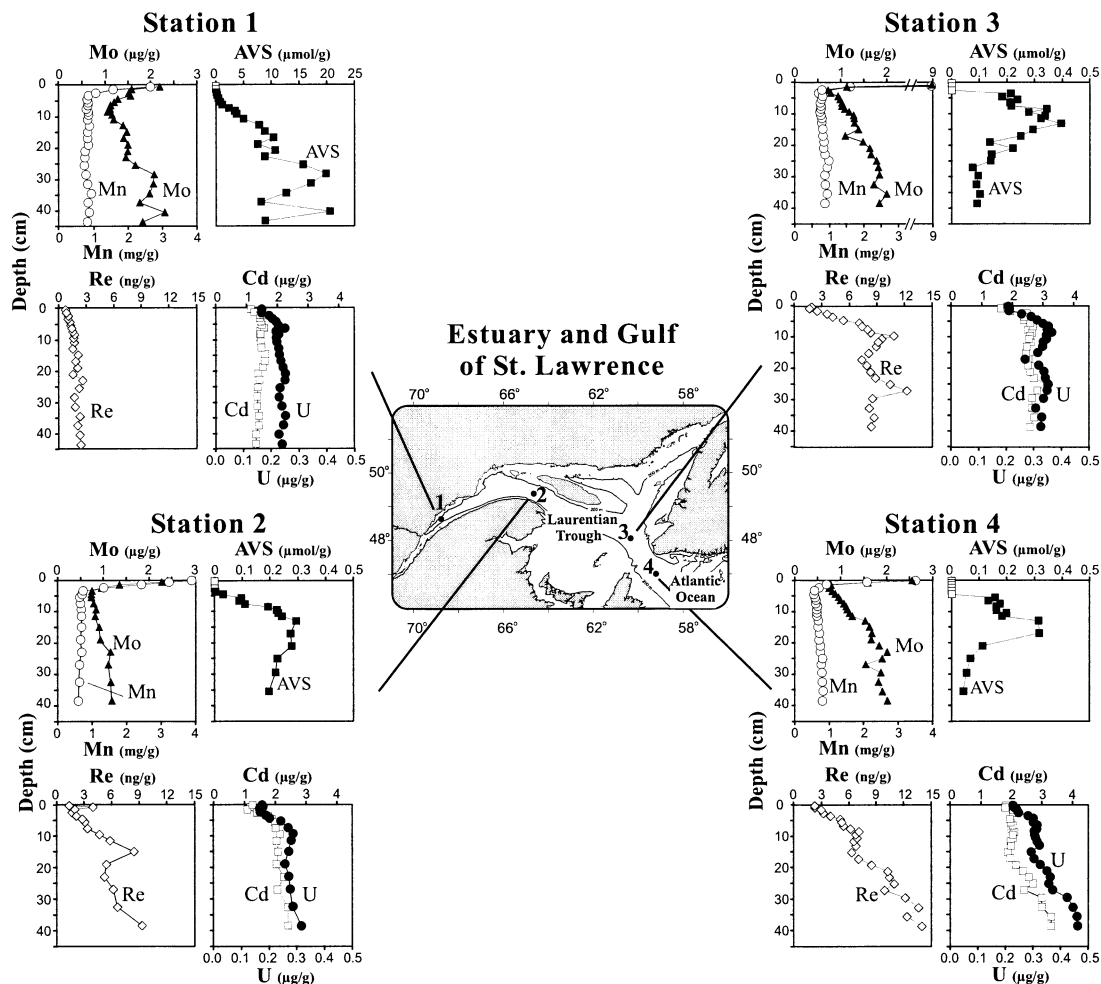


Fig. 1. Location map and distribution patterns of AVS and total Mo, Cd, Re, and U in four cores from the Laurentian Trough, Gulf of St. Lawrence. Note the different scale for AVS on St. 1. The numerical data set is available as an electronic annex, accessible on Elsevier's Web site (<http://www.elsevier.com>).

relatively rich in organic matter (Sundby et al., 1981; Silverberg and Sundby, 1990). Oxygen penetration (maximum = 15 mm) and oxygen uptake rates of 1.4 to $4.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ do not change much throughout the channel and seem to reflect the relatively low annual rates of primary production in this region (Silverberg et al., 1987, 2000).

The sediment accumulation rate, which decreases seaward by one order of magnitude, is the principal variable along the axis of the channel (Smith and Schafer, 1999). Previous studies have shown that the lower sediment accumulation rates in the seaward portion of the Laurentian Trough favor higher concentrations of cadmium, pyrite, and arsenic (Gobeil et al., 1987; Belzile, 1988; Gagnon et al., 1995). In the present study, we examine the relationship between sediment accumulation rates and concentration and accumulation rate of authigenic phases of Cd, Re, U, and Mo. Our objective is to provide insight into the diagenesis of these elements in sulfidic continental margin sediments.

2. METHODOLOGY

Four sediment box-cores were collected at 331 to 455 m depth along the axis of the Laurentian Trough (Fig. 1). The

cores were immediately subsampled by collecting 1-cm-thick layers from the sediment surface to 10 cm depth, 2-cm layers from 10 to 28 cm, and 3-cm layers from 28 cm to the bottom of the cores. The samples were placed in acid cleaned polyethylene bottles and kept frozen at -20°C . The sampling procedure was not carried out under nitrogen atmosphere because pore water samples were not collected. Our past experience has shown that solid phase sulfides are not significantly affected by this procedure (Gobeil et al., 2002).

Acid-volatile sulfides (AVS = FeS_x with $0.9 < x < 1.5$ = amorphous FeS + mackinawite + poorly crystallized greigite) were determined on wet samples, using the protocol described by Allen et al. (1993). The sediments were acidified with hydrochloric acid, and the evolving sulfide was trapped in a sodium hydroxide solution and determined colorimetrically. The detection limit, defined as twice the standard deviation of the blank, was $0.001 \mu\text{mol g}^{-1}$. The analytical precision, determined by replicate analysis ($n = 5$) of one sample, was 10% at a concentration of $0.2 \mu\text{mol g}^{-1}$.

Sediment subsamples were freeze-dried, homogenized by grinding, and completely digested in a microwave oven with a mixture of HNO_3 and HF according to the protocol of McLaren

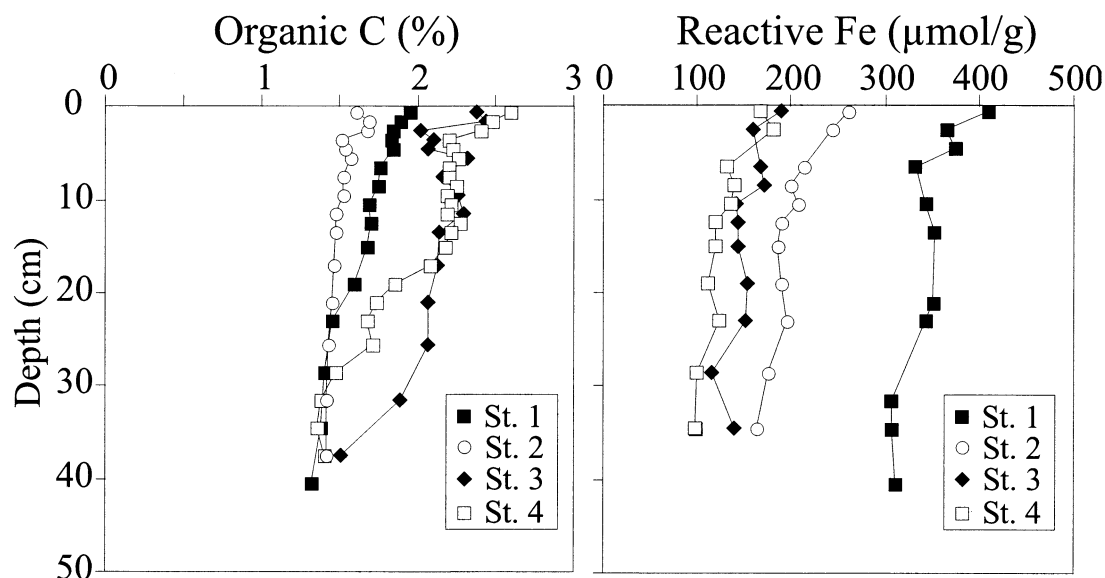


Fig. 2. Distribution of organic carbon (% d.w.) (a) and reactive Fe ($\mu\text{mol g}^{-1}$ d.w.) (b) in four sediment cores from the Laurentian Trough.

et al. (1995). Mn and Cd were determined by atomic absorption spectroscopy, using an air-acetylene flame for Mn and a pyrolytic graphite furnace equipped with a L'vov platform for Cd. Mo and U were determined by ICPMS using a cross-flow nebulizer. Re was analyzed with ICPMS using a flow injection system. The analyses were calibrated with standard solutions. The precision and accuracy of the analyses of Mn, Cd, Mo, and U were determined by replicate analysis ($n = 8$) of the standard reference sediments BEST-1 or HISS-1. Precision and accuracy were $> 10\%$. Due to the non-availability of a sediment standard for Re, a reference solution was prepared by dissolving rhenium metal in concentrated nitric acid (Colodner et al., 1993). The precision, expressed as the coefficient of variation of replicate analysis of one of the samples, was $> 10\%$. ^{187}Re was used for quantification rather than ^{185}Re , which can be affected by a polyatomic interference (thulium oxide).

Fe and Mo in an operationally defined pyrite fraction were determined by the method of Lord (1982) whereby the sediment is treated first with HCl, then with HF, and finally with HNO_3 . The resulting solution was analyzed for Fe by AAS and for Mo by ICP-MS. The analytical precision was $\geq 5\%$. Fe extracted from the sediments with 1 N HCl, referred to as reactive Fe, was also determined by AAS.

Organic C was determined on freeze-dried and homogenized samples with an automated CHN analyzer following Hedges and Stern (1984). The precision and accuracy of this procedure, which includes an aqueous acidification step, was $> 5\%$, based on the BCSS-1 sediment reference material.

3. RESULTS

3.1. The Sedimentary Environment

The four stations were chosen to span a range of sediment accumulation rates, determined in the Laurentian Trough with ^{210}Pb , ^{137}Cs and ^{239}Pu (Smith and Schafer, 1999). The sediment accumulation rates are $0.3 \text{ g cm}^{-2} \text{ y}^{-1}$ at St. 1, $0.09 \text{ g cm}^{-2} \text{ y}^{-1}$ at St. 2, and $0.03 \text{ g cm}^{-2} \text{ y}^{-1}$ at St. 3 and St. 4. Acid volatile sulfide (AVS), resulting from sulfate reduction, was present at all stations (Fig. 1). Station 1, with the highest sediment accumulation rate, also has the highest level of acid volatile sulfide. Maximum AVS at this site ($20 \mu\text{mol g}^{-1}$) is 50 times higher than maximum AVS at any of the three other stations. We did not measure sulfate reduction rates, but a previous study found sulfate reduction rates, integrated over the top 40 cm of the sediment column, as high as $265 \text{ nmol cm}^{-2} \text{ d}^{-1}$ at St. 1 and only $34 \text{ nmol cm}^{-2} \text{ d}^{-1}$ at a site near St. 2. This accounts for 25 and 5%, respectively, of the oxidation of the organic carbon flux to the sea floor at these sites. The low proportion of carbon oxidized via sulfate reduction at the Gulf site was attributed to low sedimentation rate and consequently long residence time of the organic matter in the surface sediment (Edenborn et al., 1987). Reactive Fe is abundant at all stations ($300\text{--}400 \mu\text{mol Fe g}^{-1}$ at St. 1 and $100\text{--}175 \mu\text{mol Fe g}^{-1}$ at St. 4, Fig. 2), and the sulfide produced is likely to be trapped as FeS. On this basis, and on the basis of measured sulfate reduction rates, we will assume that low AVS concentrations reflect low rates of sulfate reduction and low rates of carbon oxidation.

The organic carbon content, although generally decreasing with depth in each core, does not follow the regional pattern of AVS concentration. The organic carbon content decreased from St. 1 to St. 2, but increased from St. 3 to St. 4 (Fig. 2). Given that AVS is low at St. 3 and 4, it is likely that the measurement of total organic carbon includes a high background of relatively unreactive or refractory compounds. The concentration of total organic carbon in these sediments is thus a poor predictor of its reactivity.

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3.2. Total Cadmium, Rhenium, and Uranium

Within each of the four cores, the distributions of total Cd, Re, and U are similar (Fig. 1). At St. 1, the trace element

concentrations are low and, following a slow initial increase in the top few centimeters, nearly constant or slowly increasing with depth. The highest concentrations of each of these three elements were found at St. 4, increasing gradually from near the top to the bottom of the core. The profiles at St. 2 and St. 3 show pronounced concentration maxima at ~15 and 30 cm depth. Chaillou et al. (2002) reported similar increases with depth for total Cd and U in a core from a 150 m deep, organic and sulfide rich site in the Bay of Biscay. At deeper, less sulfidic sites, vertical trends were less pronounced. Zheng et al. (2002) report several examples of sediments, underlying low oxygen bottom waters, where the concentration of authigenic U increases with depth in the core.

3.3. Total Molybdenum

The vertical distribution of total molybdenum goes through a pronounced subsurface minimum. The minimum is closely aligned with the bottom of the manganese-enriched layer. Above the concentration minimum, total Mo reaches values as high as $9 \mu\text{g g}^{-1}$ and is linearly related to manganese (Fig. 3a). The average atomic Mo/Mn ratio of 0.37×10^{-3} ($r^2 = 0.80$) is within a factor of three of the Mo/Mn ratio found in oxidizing surface sediments and manganese nodules throughout the world ocean (Shimmiel and Price, 1986; Shimmiel and Pedersen, 1990). Below the concentration minimum, total Mo increases nearly linearly to the bottom of each core. A similar distribution of Mo has been observed in sediments of a Scottish loch (Malcolm, 1985) and in the Bay of Biscay (Chaillou et al., 2002).

The highest subsurface Mo concentration, $3 \mu\text{g g}^{-1}$, was reached at 40 cm depth at St. 1, but Mo concentrations nearly as high were also found at St. 3 and 4. The lowest subsurface Mo levels, as well as the lowest rate of increase of Mo with depth, were found at St. 2. Unlike Cd and Re, there is not a simple relationship between the rate of increase of Mo with depth and the sediment accumulation rate, unless one disregards the data from St. 1.

3.4. Fe and Mo in the Pyrite Fraction

The vertical distribution of Mo in the operationally defined pyrite fraction is similar to the distribution of pyrite Fe, and both show a clear pattern of increasing concentrations from St. 1 to St. 4 (Fig. 4). In the pyrite fraction, the two elements are linearly correlated with an atomic Mo/Fe ratio of 0.045 to 0.062 $\times 10^{-3}$ (Fig. 3b). The steeper slope on Figure 3b was obtained by forcing the regression line through the origin.

3.5. Trace Element Accumulation Rates

Our data can be used to calculate average authigenic trace element accumulation rates by dividing the authigenic inventory of each element by the time it has taken to accumulate the sediment in each core (Table 1). The authigenic fraction of each element was estimated by subtracting the estimated detrital background concentration from the total concentration. For the detrital background we chose the lowest concentrations (Cd = $1.1 \times 10^{-3} \mu\text{mol g}^{-1}$; Re = $4.0 \times 10^{-6} \mu\text{mol g}^{-1}$; U = $6.3 \times 10^{-3} \mu\text{mol g}^{-1}$; Mo = $7.6 \times 10^{-3} \mu\text{mol g}^{-1}$) measured at

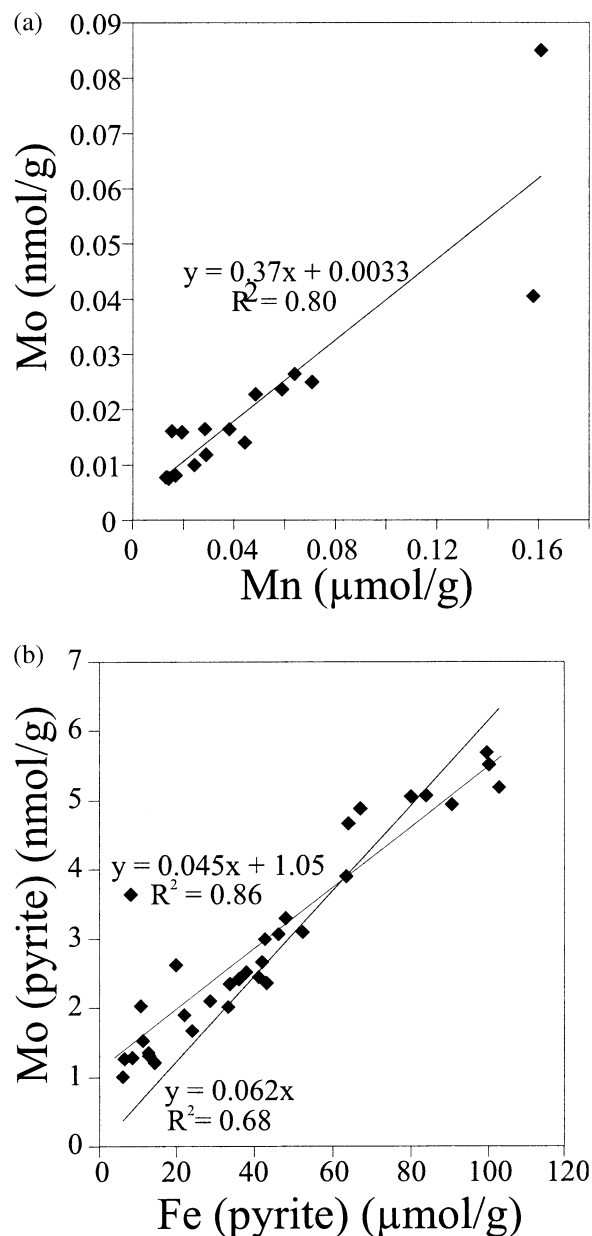


Fig. 3. The relationship between total Mo and total Mn in surface sediments (above the Mo-minimum depth) (a) and between Mo-pyrite and Fe-pyrite (b) in four cores from the Laurentian Trough, Gulf of St. Lawrence. The steeper slope in (b) was obtained by forcing the regression line through the origin.

St. 1. Mo and Fe in the pyrite fraction were included in these calculations.

The calculation of an average accumulation rate of a trace element does not assume that the accumulation rate has been constant, but it does assume that the average sediment accumulation rate over the length of the core can be represented by the radioisotope based estimates of Smith and Schafer (1999). We justify this assumption with the ^{14}C dating of a long core from St. 1 in the lower St. Lawrence estuary (St-Onge et al., 2003) which shows that the sediment at this station has been accumulating at rates similar to today's rates over the last 1000

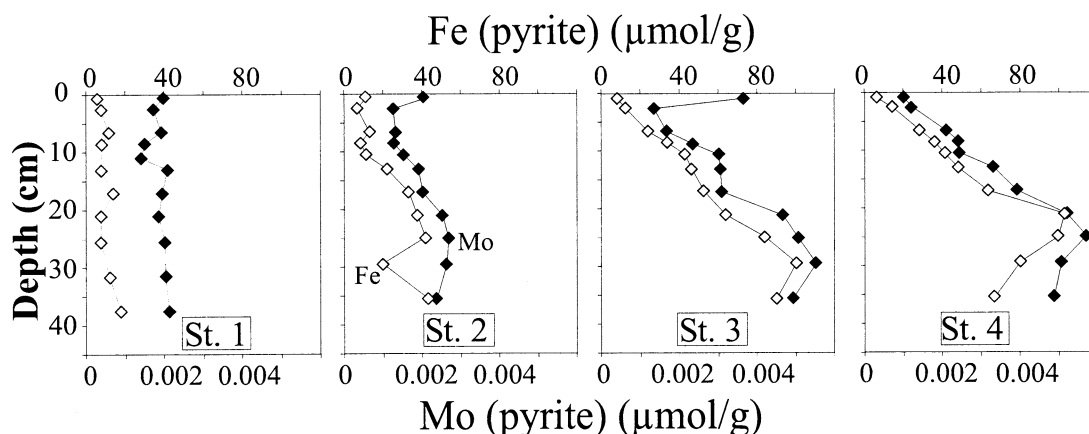


Fig. 4. The distributions of Fe and Mo in the operationally defined pyrite fraction in four sediment cores from the Laurentian Trough.

yr. We do not have similar information for St. 4, which is in the open Gulf of St. Lawrence, but we have no reason to believe that the average accumulation rate in the Gulf during the last 1000 yr has been much different from recent estimates. Using the average rate, the core at Station 4 represents 640 yr of accumulation, which is less than the time over which the sediments at St. 1 have been accumulating at a nearly constant rate. A second assumption required by our calculation is that precipitation of authigenic phases does not continue past the depth represented by the bottom of each core. Whether this is correct or not will ultimately have to be established with longer cores; if precipitation continues below 45 cm depth, the effect on our calculations is to underestimate the accumulation rates. We return to this point under “Discussion.”

The average trace element accumulation rates, obtained by dividing inventories by the time required to accumulate the inventory, are less variable than one might have expected from the larger variabilities in sediment accumulation rate and AVS concentration (Table 1). The accumulation rates of authigenic Cd and Re, and of Mo and Fe in the pyrite fraction, are similar at the four stations within a factor of 2 or less. If one ignores St. 1, the same low variability is found for the accumulation rate of authigenic U. However, the higher accumulation rate at St. 1 (~4.5 times higher than at St. 4) places U in a different category than Cd and Re. The outstanding exception to the low variability in accumulation rates is total authigenic Mo, which has been accumulating 17 times faster at St. 1 than at St. 4.

A comparison of our estimated authigenic accumulation

Table 1. Inventories and average accumulation rates of authigenic Cd, U, Re over the length of each core, and inventories and accumulation rates of authigenic Mo below the depth of the total-Mo minimum.

	St. 1	St. 2	St. 3	St. 4
Sediment accumulation rate ($\text{g cm}^{-2} \text{yr}^{-1}$)	0.3	0.09	0.03	0.03
Mass (g cm^{-2}) accumulated over the length of the core ^a	29.5	19.3	17.8	19.2
Time (yr) to accumulate sediment in each core ^b	98	214	592	640
Cd inventory ($\mu\text{mol cm}^{-2}$) ^c	0.85×10^{-2}	1.9×10^{-2}	2.6×10^{-2}	2.7×10^{-2}
Cd accumulation rate ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$) ^d	8.8×10^{-5}	8.8×10^{-5}	4.4×10^{-5}	4.4×10^{-5}
Re inventory ($\mu\text{g cm}^{-2}$) ^c	1.8×10^{-4}	5.4×10^{-4}	7.2×10^{-4}	8.9×10^{-4}
Re accumulation rate ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$) ^d	1.9×10^{-6}	2.5×10^{-6}	1.2×10^{-6}	1.4×10^{-6}
U inventory ($\mu\text{mol cm}^{-2}$) ^c	7.5×10^{-2}	7.5×10^{-2}	11×10^{-2}	14×10^{-2}
U accumulation rate ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$) ^d	7.6×10^{-4}	3.4×10^{-4}	1.7×10^{-4}	1.7×10^{-4}
Mass (g cm^{-2}) accumulated between depth of Mo-minimum and bottom of core ^a	24.9	8.90	16.7	18.4
Time (yr) to accumulate sediment below Mo-minimum ^b	83	205	562	612
Mo inventory below Mo-minimum ($\mu\text{mol cm}^{-2}$) ^c	3.7×10^{-1}	1.9×10^{-1}	1.4×10^{-1}	1.6×10^{-1}
Mo accumulation rate ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$) ^d	45×10^{-4}	9.4×10^{-4}	2.6×10^{-4}	2.6×10^{-4}
Fe (pyrite) inventory ($\mu\text{mole cm}^{-2}$)	3.4×10^2	4.6×10^2	10.2×10^2	11.4×10^2
Fe (pyrite) accumulation rate ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$)	4.0	2.3	1.9	2.0
Mo (pyrite) inventory ($\mu\text{mole cm}^{-2}$)	1.5×10^{-2}	2.1×10^{-2}	4.6×10^{-2}	5.1×10^{-2}
Mo (pyrite) accumulation rate ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$)	1.8×10^{-4}	1.0×10^{-4}	1.2×10^{-4}	1.2×10^{-4}

^a Mass (g cm^{-2}) = $\Sigma(1-\phi)\rho\Delta l$ where ϕ is the measured porosity, ρ is solid phase density (2.75), and Δl is the thickness of the individual layer analyzed.

^b Time = accumulated mass (g cm^{-2}) / accumulation rate ($\text{g cm}^{-2} \text{yr}^{-1}$).

^c Inventory = $\Sigma(\text{concentration})(1-\phi)\rho\Delta l$.

^d Average accumulation rate = inventory / time.

Table 2. A comparison of authigenic trace element accumulation rates in Laurentian Trough sediments with literature data.

Element	Accumulation rate ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$)		
	Morford and Emerson (1999) ^a	Zheng et al. (2002) ^b	This study
Mo		$5\text{--}130 \times 10^{-4}$	$2.6\text{--}45 \times 10^{-4}$
Cd	$2.1\text{--}4.9 \times 10^{-5}$		$4.4\text{--}8.8 \times 10^{-5}$
Re	$0.42\text{--}0.76 \times 10^{-6}$		$1.2\text{--}2.4 \times 10^{-6}$
U	$0.63\text{--}1.0 \times 10^{-4}$		$1.7\text{--}7.6 \times 10^{-4}$

^a Calculated as total flux into sediment with oxygen penetration ≤ 1 cm divided by total area of these sediments ($1.44 \times 10^{17} \text{cm}^2$).

^b Data from the Santa Barbara basin.

rates with literature data (Table 2) shows that the rates of Cd and Re agree within a factor of 2 or 3. Our lowest estimates for uranium accumulation agree within a factor of 3 with published values, but our highest estimate is almost an order of magnitude greater. The Mo accumulation rates fall within the range of values reported by Zheng et al. (2000) for sulfidic sediments in the Santa Barbara basin even though the oxygen levels in the bottom water there ($3\text{--}23 \mu\text{mol/L}$) are much lower than in the Laurentian Trough ($60\text{--}150 \mu\text{mol/L}$).

4. DISCUSSION

4.1. The Vertical Distribution of Authigenic Phases of Trace Elements

The most striking aspect of this data set is that the concentrations of authigenic trace elements increase with depth in the cores. For Mo, below the subsurface minimum, the vertical trend is strong at all four stations. For Cd, Re, and U the trend at St. 1 is weak, but at St. 4 the concentration of each of these element increases gradually but clearly with depth throughout the 45 cm length of the core. This is not the only data set that shows such trends. Malcolm (1985) described Mo distributions in cores from a Scottish loch that are similar to those in the Laurentian Trough. Chaillou et al. (2002) found increases with depth in authigenic Cd, U, and Mo in a core from a 150 m deep, organic and sulfide rich site in the Bay of Biscay. Crusius et al. (1996) found increasing concentrations of Re and U with depth in a core from the Japan Sea. Zheng et al. (2002) reported several examples of sediments, underlying the low oxygen bottom waters on the California margin, in which the concentration of authigenic U increases with depth.

If the kinetics of the reactions that immobilize these elements in sediments were rapid compared to downward transport in the pore water, authigenic phases should accumulate within a short distance of the source of dissolved trace elements. Since there would be no precipitation below this depth, the tracer concentration should not change further when the sediment is advected downward by the accumulation of new sediment on top. At steady state, this should give rise to constant concentrations below the depth where precipitation takes place. Since Cd, Re and U become soluble upon re-oxidation (e.g. Gobeil et al., 1987; Crusius and Thomson, 2000; Zheng et al., 2002) it is conceivable that remobilization by oxidation followed by downward diffusion could increase the concentration in the

sediment below the zone of initial precipitation. However, it is difficult to see how this mechanism could explain the gradually increasing concentration of authigenic phases all the way to the bottom of the cores. The position of the oxic-anoxic boundary in Laurentian Trough sediments is known to fluctuate vertically, but only by a few cm (Gobeil et al., 1997). Hence remobilization should be limited to the top few cm of the sediment column. Another possible explanation is that these environments have experienced a gradual change in sedimentation regime, including organic matter flux, during the last millennium, and that this allowed for greater accumulation of authigenic phases in the past. We cannot rule out this possibility, but there is no sedimentological evidence available for the St. Lawrence system to suggest that such a gradual change has been occurring. The possibility that the trends are due to gradually decreasing fluxes of trace elements into the sediment from the past to the present does not seem likely either since three of the four tracers behave conservatively in seawater.

An alternative explanation, and the one we favor, is that the rate of precipitation and accumulation of trace elements is controlled by slow kinetics. (We use the term *precipitation* loosely to include any process that immobilizes the trace elements. These processes are poorly known.) If the rate of precipitation is slow compared to transport by diffusion, authigenic phases can accumulate over a broad sediment layer below the depth where precipitation first sets in. Slow precipitation kinetics has the added attraction that it neutralizes the effects of different modes of trace element delivery to the sediment and post depositional remobilization, including that caused by bioturbation. For example, Cd and to some extent U are delivered to the sediment water interface on solid particles and released from these particles to the pore water upon burial (Gobeil et al., 1987; Zheng et al., 2002). Re is thought to be delivered by diffusion across the sediment water interface directly to the pore water (Colodner et al., 1993), and Mo is extracted or coprecipitated from seawater with manganese and released to the pore water when manganese oxides are buried and redissolved (Malcolm, 1985; Shimmield and Price, 1986). These factors are neutralized because of the different times scales of precipitation rates and fluctuations in pore water composition caused by bioturbation and by time variable remobilization of elements delivered on particles. We will now explore the evidence for slow precipitation kinetics.

4.2. Accumulation of Authigenic Cadmium, Rhenium, and Uranium

The rates of sediment accumulation, organic carbon oxidation, and sulfate reduction at the four stations in the Laurentian Trough vary by a factor of 10. Over the same stations the accumulation rates of authigenic Cd and Re, and of Fe and Mo in the pyrite fraction, only differ by a factor of 2. On the other hand, total authigenic Mo and U accumulate respectively 17 and 4 times faster at St. 1 than at the other three stations. To understand what controls the distribution and accumulation rates of these elements in continental margin sediments one has to consider both environmental factors and individual chemical properties of the elements.

The apparent insensitivity of the authigenic Cd accumulation rate to sulfide abundance is at first glance surprising in view of

the commonly held assumption that Cd is immobilized in sulfidic sediments in the form of highly insoluble CdS (e.g., Rosenthal et al., 1995). However, there is no contradiction if the rate of precipitation (immobilization) of authigenic Cd is not controlled by sulfide. If Cd exists in the pore water as organic or inorganic complexes, it may be stability of such complexes and not the abundance of sulfide that controls the CdS precipitation rate.

Dissolved Cd can indeed exist in the pore waters of the high-sulfide sediments in the Laurentian Trough to depths well below the depth where authigenic Cd begins to accumulate. In a previous study, which was carried out at a station near St. 1, dissolved Cd was found to at least 20 cm depth (Gobeil et al., 1987). A large proportion of the Cd that was dissolved in the pore water was not electrochemically active but became so upon irradiation with ultraviolet light. To explain this, it was suggested that much of the dissolved Cd was present in the pore water as polysulfide and/or organic complexes. These findings support the suggestion that the rate of authigenic Cd precipitation is not controlled by sulfide abundance.

It is well established that authigenic Re accumulates in reducing continental margin sediments, but there is not much information available about the rate of Re-immobilization in such sediments. Crusius and Thomson (2000, 2003) found that Re, and to some extent also U, remobilized at a downward-moving oxidation front in turbidities from the Madeira Abyssal Plain, was not re-immobilized immediately below the oxidation front. Instead, re-immobilized Re was found spread over a sediment layer extending 0.5 to 3 m below the oxidation front. The large spread was attributed to kinetically controlled re-immobilization, sufficiently slow to allow Re to diffuse over a distance of as much as 3 m. Indeed, (Colodner et al., 1993) reported the existence of dissolved Re in the pore waters of both oxic and anoxic sediments. Among the possible reasons for the slow re-immobilization, Crusius and Thomson (2000) suggested a multistep reduction with slow kinetics at one or more of the electron transfers from the dissolved species Re(VII) to reduced solid form Re(IV). These turbidities are not sulfidic, but our observations indicate that Re accumulation can also be kinetically controlled in sulfidic sediments.

If immobilization of Cd and Re is indeed kinetically controlled, and if the kinetics involved are slow, then the precipitation of these elements will not be limited to a narrow zone near the sediment water interface but will take place over a broader depth interval. Time then becomes an important factor in controlling the abundance of the precipitated phase: Longer times allow more precipitate to accumulate, resulting in higher concentrations of the precipitated phase. The concentration of authigenic Cd and Re tends to increase with depth in each core. At St. 1, the increase is weak, at St. 4 the increase is strong and quite regular, and at St. 2 and 3 the increase with depth is interrupted by two distinctive peaks. If the rate of precipitation of Re and Cd is slow compared to the rate with which they are supplied by diffusion, precipitated Cd and Re can have been accumulating throughout the cores. There would be no further accumulation of precipitates below the depth where supply by diffusion is balanced by loss by precipitation.

Crusius and Thomson (2000) treated the precipitation (re-immobilization) of Re in turbidities as a first order reaction and derived first order rate constants on the order of 0.1 to 0.01

yr⁻¹. For a comparison, we can obtain first order rate constants from our data if we assume that Re accumulation is insignificant below the bottom of our 45-cm cores, and that accumulation of authigenic Re becomes insignificant when 90% of dissolved Re has been removed from the pore water. The time for this to happen is 3 “half lives.” From the relationship between time and distance traveled by diffusion, $t=x^2/2D$, we can calculate the time for Re to diffuse a distance $x = 45$ cm given a diffusion coefficient $D = 10^2 \text{ cm}^2 \text{ yr}^{-1}$. This time is on the order of 10 yr. The “half life” of dissolved Re is therefore $10 / 3 = 3.3$ yr, which give a precipitation rate constant ($\ln 0.5 / 3.3$) of $\sim 0.2 \text{ yr}^{-1}$. This is similar to the rate constants calculated by Crusius and Thomson (2000).

Admitting the many uncertainties underlying these calculations, the result suggests that the assumption of insignificant accumulation of Re deeper in the sediment than the length of our cores is reasonable. Nevertheless, it would be useful to have longer cores to test this assumption experimentally. Furthermore, it would have been useful to have more precise information about the sediment accumulation rate as a function of time in these sediments. It is conceivable, for example, that the concentration peaks observed at St. 2 and 3 represent periods when sedimentation slowed down locally. Finally, we need information about mechanisms and rates of the reactions that immobilize Re and other elements in sediments.

The transport-reaction argument applies to any tracer with first order removal kinetics, so if the immobilization of Cd is controlled by slow first order kinetics, and the diffusion coefficient of the dissolved Cd species is of the same order of magnitude as for Re, accumulation of authigenic Cd would also end at 45 cm depth. The principal uncertainty is the kinetics. These considerations apply to U as well. We note that uranium accumulation is not limited to the upper part of the sediment column but has been taking place over the entire depth interval represented by our cores. High concentrations of dissolved U (up to 40 nmol/L) as well as increasing concentrations of solid phase U to the bottom of a 40-cm core from an organic rich sulfidic sediment in the Bay of Biscay have been reported by Chaillou et al. (2002).

In contrast to Cd and Re, the accumulation of U is significantly enhanced under the conditions existing at St. 1. The increased U-accumulation rate at St. 1 may not be a direct consequence of high abundance of sulfide, since U does not precipitate as a sulfide. Instead, U-immobilization (reduction of soluble U[V] to poorly soluble U[III]) can be carried out by metal reducing bacteria (Lovley et al., 1991; Fredrickson et al., 2000). The higher accumulation rate of U at St. 1 may reflect the higher rate of bacterial activity in sediments that contain more reactive organic matter. In sediments with lower abundance of organic matter, such as at St. 4, bacterially mediated precipitation of U would still be taking place, but at a lower rate, and slow kinetics would effectively control U accumulation.

4.3. Accumulation of Authigenic Molybdenum

Unlike U, Re, and Cd, the vertical profiles of Mo in Laurentian Trough sediments are distinguished by a sharp subsurface concentration minimum. A subsurface minimum in cadmium profiles, attributed to subsurface Cd release from a carrier

phase, has also been observed in these sediments, but the relative enrichment of Cd in the surface layer is weak compared to Mo (Gobeil et al., 1987). An explanation of the causes of Mo enrichment in the surface layer is beyond the scope of this paper, but we note that Mo and Mn in this layer occur in a nearly constant proportion. Evidently, a component of Mo cycles with Mn in the sediment surface layer. Mo is released to the pore water when manganese oxides dissolve (Malcolm, 1985; Shimmiel and Price, 1986). This Mo is available for diffusive transport to the deeper layers of the sediment.

Total Mo increases to the bottom of each of the four cores. This places an important constraint on the Mo immobilization rate: it has to be sufficiently slow to allow dissolved Mo to diffuse to at least 45 cm depth. The presence of dissolved Mo to such depths and deeper in sediment pore water was observed in a Scottish loch by Malcolm (1985) who also discovered a strong association of dissolved Mo with dissolved organic matter. Chaillou et al. (2002) also report increases of both dissolved Mo and solid phase Mo with depth in cores from the Bay of Biscay. This aspect of the pore water chemistry of Mo bears a certain resemblance to the pore water chemistry of Cd.

A second aspect that distinguishes Mo from the three other trace elements is that the subsurface concentration of Mo at corresponding depths is similar at St. 1 and St. 4. Although the accumulation rate of Mo at St. 1 is nearly 20 times higher than at St. 4 (Table 1), the much longer time available for Mo accumulation at St. 4 has apparently compensated the higher accumulation rate at St. 1 to produce similar concentration levels.

The much higher Mo flux at St. 1 implies that the kinetics and/or the mechanism of Mo precipitation must be quite different under the more sulfidic conditions at St. 1. Huerta-Diaz and Morse (1992) found two different rates for Mo precipitation: high rates in the highly sulfidic sediments in the top of the cores and slower rates in the less sulfidic sediment deeper in the core. Zheng et al. (2000) proposed a link between authigenic molybdenum formation and pore water sulfide concentrations. They found an apparent threshold of 0.1 $\mu\text{mol/L}$ sulfide for the onset of the co-precipitation of a Mo-Fe-S phase and a second threshold of $\sim 100 \mu\text{mol/L}$ sulfide for Mo precipitation without Fe.

There is considerable uncertainty about the nature of precipitated/scavenged molybdenum, which reflects the complexities of Mo chemistry. For a recent review, see Erickson and Helz (2000). These authors have shown that, in sulfidic water, molybdate, the stable form of Mo in seawater, can be converted without changing the oxidation state to thiomolybdate in four successive steps, i.e., $\text{MoO}_4^- \rightarrow \text{MoS}_x\text{O}_{(4-x)}^-$ where x takes on the values 1 to 4. The rate of each successive step decreases by an order of magnitude. Thiomolybdates are more particle reactive and scavengable than molybdate and may be the initial form of Mo that becomes immobilized in sulfidic sediments. The equilibrium between molybdate and tetrathiomolybdate has a fourth order dependence on the sulfide concentration, which makes it very sensitive to small variations in sulfide. Based on this, Helz et al. (1996) proposed the existence of a sulfide "switch" whereby, during a gradual increase in sulfide, the equilibrium switches abruptly to the side of the thiomolybdate. The thiomolybdate conversion mechanism could explain both the rapid rate of Mo accumulation in the presence of high

rates of sulfate reduction/sulfide production and the slower rates where sulfide is less important.

4.4. Accumulation of Fe and Mo in the Pyrite Fraction

Morse and Luther (1999) pointed out that Mo is likely to co-precipitate with sedimentary pyrite, but that molybdate must be reduced to Mo(IV) before incorporation into pyrite. Mo incorporation in pyrite will therefore be influenced by complex redox reaction pathways, such as those described above, rather than by simple substitution. The nearly constant Mo:Fe ratio we observe in the operationally defined pyrite fraction is consistent with co-precipitation of Mo with Fe.

The abundance of AVS, a precursor for pyrite, does not seem to have much influence on the rate of pyrite accumulation, which only varies by a factor of 2 over the four stations. The conversion of AVS to pyrite can be inhibited in Fe-rich sediments where a large excess of reactive iron limits the buildup of sulfide ($\Sigma\text{H}_2\text{S}$) in the pore water by precipitating AVS. In the absence of a significant $\Sigma\text{H}_2\text{S}$ gradient, slow upward diffusion to the redox boundary and limited formation of soluble intermediate sulfur species can hinder the conversion of AVS to pyrite (Gagnon et al., 1995). An alternative pathway involves the anaerobic oxidation of sulfide by iron oxide minerals, which are abundant in many sedimentary environments (Canfield, 1989). Luther et al. (1992) have proposed that this pathway involves initially the formation of organically complexed Fe(III), which may subsequently react with sulfides. The presence of organically complexed Fe(III) in anoxic pore waters has been demonstrated by Taillefer et al. (2000) Organically complexed Fe(III) exists in the anoxic pore waters of Laurentian Trough sediments (Sundby, unpublished data).

If pyrite formation in Laurentian Trough sediments does indeed take place by this second pathway, the rate of pyrite formation is not limited by the concentration of AVS, but by the reactivity of iron oxide minerals. This can explain why pyrite and associated Mo accumulate at nearly the same rate.

5. CONCLUSIONS

1. Slow kinetics of the reactions that precipitate authigenic Cd, Re, U, and Mo exert strong influence their accumulation rates and distributions patterns in Laurentian Trough sediments.
2. The accumulation rates of authigenic Cd and Re are insensitive to variations in sediment accumulation rate and sulfide concentration and are similar to rates in other continental margin sediments. Cd precipitates likely as CdS but the rate of precipitation is not controlled by the sulfide abundance.
3. The accumulation rate of U appears to depend on the abundance of reactive organic carbon, which controls the kinetics of the microbially mediated U(V) reduction.
4. The accumulation rate of Mo is high in sediment with high sulfide concentrations and low in sediments with low sulfide concentration. The kinetics and the mechanism of Mo precipitation appear to depend on the sulfide concentration.
5. The accumulation rate of pyrite and associated Mo is independent of AVS abundance and may be controlled by the reactivity of iron oxide minerals

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