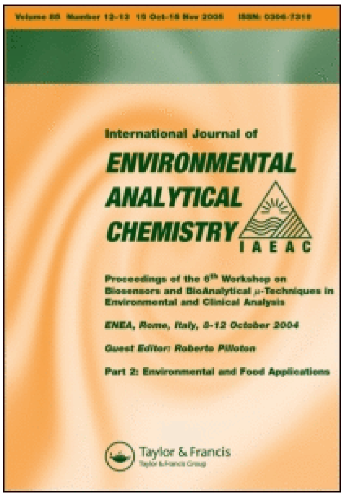

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Cesium-Labeled Phlogopite as a Tracer for in Situ Studies of Sediment Burial, Reworking, and Resuspension Rates

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CESIUM-LABELED PHLOGOPITE AS A TRACER FOR IN SITU STUDIES OF SEDIMENT BURIAL, REWORKING, AND RESUSPENSION RATES

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Phlogopite is a mica mined commercially in eastern Canada. Its major exchangeable cation, K^+, can be removed with sodium tetraphenylboron. When the K-depleted phase is soaked in CsCl (aq), it binds Cs^+, forming a new crystalline phase, CsPhlog, that contains up to 10 weight-% Cs. The new phase binds Cs^+ strongly ($K_D > 10^6$), making CsPhlog stable enough to be useful as a tracer for clay particles. We investigated the direct determination of Cs in lacustrine sediments using neutron activation analysis, X-ray fluorescence spectrometry, and radio frequency (r. f.) glow-discharge mass spectrometry. Glow discharge mass spectrometry proved insufficiently sensitive due to isobaric interferences, but the other two methods were usable at tracer levels. Activation analysis was used for routine determinations because of its superior sensitivity. Starting with CsPhlog containing a few percent Cs by weight, the observed sensitivity translated to a measurable dispersal factor of at least 10^4. We used CsPhlog deployed from a manned submersible to study sediment reworking in Lake Superior, where it behaved similarly to rare-earth oxide tracers deployed simultaneously.

KEY WORDS: Phlogopite, Cs, lacustrine sediments, sediment reworking, Lake Superior.

INTRODUCTION

Many pollutants, and some nutrients, tend to associate with particulate matter in natural water systems. Clay size particles have high surface-to-mass ratios and strong surface charges, making them effective at binding many inorganic and organic species. Studying pollutant transport often means studying the movement of clay size particles. A variety of means for doing so have reached sophisticated levels of development, especially those based on the use of naturally occurring[1-5], cosmogenic[6-10], and anthropogenic[11-16] radionuclides. Grain shape analyses, stable isotope ratios, and trace element and mineralogical signatures have also found successful application to studies of sediment transport. These methods are ubiquitous in the sedimentological literature[17,18]. All such

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adventitious tracers have the advantage of accurately reflecting the size, shape, density, and surface characteristics of the naturally occurring particles with which they are associated.

It is possible to introduce tracers into sediments deliberately, rather than using ones man and nature provide adventitiously. The literature contains relatively few examples of this strategy, but interest in the subject seems to be strong, as evidenced by a recent symposium[19]. Radioactive tracers have been added to those occurring naturally in sediments in microcosm experiments to observe bioturbation by infaunal organisms[20,21]. These studies, together with in situ observations, have led to quantitative models of sediment reworking[22–24] However, regulatory constraints may make it difficult to implement in the field any strategy based on the introduction of radionuclides into natural waters, although some examples have been reported[25,26].

Several approaches using non-radioactive tracers have also shown promise. The simplest of these consists of doping natural sediment by soaking it in a solution containing some tracer, hoping to take advantage of whatever absorption may occur[27]. This approach has the advantage of simplicity, but suffers from the drawback that the mechanism by which the tracer is bound is largely conjectural. It is difficult to foresee how tracer binding might change as conditions alter. This uncertainty could blur the distinction between dispersal of the labeled particles and simple loss of the tracer from the substrate, due, for example, to temperature or salinity changes.

An alternative is to mix tracer particles of defined composition with native sediment. Reported examples of this approach include the use of fluorescent micro spheres[28] and rare earth oxide slurries[29]. The principal concerns here are the extent to which the exogenous particles mimic the degree of aggregation and hydrodynamic characteristics of the native material, and the possibility of chemical degradation or alteration.

Another strategy is the use of synthetic materials in which macroscopic physical properties, as well as the binding of the tracer, are understood and controlled. The pioneering use of this concept seems to have been made by Crickmore and Lean[25]. Later, Long[26] used ground and size-classified glass fragments to study sediment movement off Canada's Atlantic coast. The glasses used in his studies incorporated elevated concentrations of rare earth elements especially suited to activation by thermal neutrons and determination by γ-ray spectrometry. Activation prior to deployment allowed real-time observations of sediment transport by means of underwater detectors.

In this paper, we report the use of a synthetic mineral phase to study sediment reworking in fine-grained, cohesive, lacustrine sediments.

OBJECTIVES

Earlier, Krezoski[29] demonstrated a technique for deploying labeled sediment from a manned submersible, then showed that the deployment site could be revisited and cored on a tightly spaced grid. Lateral and vertical redistribution of the rare earth oxide tracers were observed by neutron activation analysis in the sectioned cores. The objectives of the work we report here were to extend this method to the use of synthetic mineral phases; to investigate alternatives to neutron activation analysis for determining tracer distribution; and to develop a tracer technique usable in marine sediments.

METHODS

Preparation of Cs-labeled phlogopite. The labeled material was prepared using the method of Komarneni and Roy[30]. We followed Scott and Reed's procedure[31] for using sodium tetraphenylboron, $Na^+[B(C_6H_5)_4]^-$, to remove exchangeable K^+ from commercially available phlogopite (Ward Supply) that we first ground to tiny flakes in a rod mill. About 20 g of the K^+-depleted phase was recovered after treating 50 g of the native material. The low yield was due principally to mechanical losses of the mineral phase during removal of the by-product, potassium tetraphenylboron, $K^+[B(C_6H_5)_4]^-$, by foam-flotation. Potassium tetraphenylborate has soap-like properties and tended to occlude very finely divided mineral matter. Soaking the K^+-depleted phase overnight in 1 M CsCl followed by three rinses in deionized water yielded a material that assayed 8% by weight Cs by X-ray fluorescence spectrometry.

X-ray fluorescence spectrometry. Determinations of Cs by X-ray fluorescence spectrometry (XRF) were performed by exciting Cs K-series X-rays with a Tb secondary fluorescer. The Tb source was in turn excited by the emanations from a W-anode X-ray tube operated at 70 kV (constant potential) and 2 – 5 mA. Radiation from the sample was filtered (0.1 mm Al) and collimated with a 8 mm dia. by 20 mm long cylindrical tungsten collimator placed 0.3 mm above the detector's Be window. X-rays were detected with a Si(Li) detector (Kevex Model 0810) shielded with 3 mm of Pb. The detector output was processed with a Kevex 0410 spectroscopy amplifier, then digitized and stored with a Canberra Model 8100 ADC/MCA. After counting for 100 - 1,000 s, the accumulated spectra were transferred to a PC-AT computer and processed with the AXIL software package[32] to obtain net intensities above background for the Cs K_α peak at 30.97 keV. Standards in the range from 0 to 10% by weight Cs were prepared by slurrying kaolinite with standard solutions of CsCl, then evaporating to dryness and regrinding in a vibratory mill. Samples and standards, 1.00 g, were mixed with purified starch powder, 1.00 g, and pressed into 25 mm diameter pellets at 10,000 psig in a steel die.

Neutron activation analysis. Sediment and standards were dried at 60°C, ground to a fine powder with a mortar and pestle, then homogenized using the classical 'cone-and-quarter' method. About 60 mg of each sample and standard were weighed into quartz tubes and sealed. Irradiation was carried out at the University of Wisconsin-Madison research reactor[33] for 2 hours at a neutron flux of 9×10^{12} neutrons $cm^{-2}s^{-1}$.

Following irradiation, the samples and standards were stored for 7 days to permit short-lived activation products to decay. Each was then counted for 60 min or longer in a γ-ray spectrometry system consisting of an Ortec high purity Ge detector (resolution 2 keV FWHM and efficiency 0.3% for the 1332 keV γ ray of ^{60}Co), and a 4096 channel analyzer with an energy calibration of 0.5 keV per channel.

Peak intensities, **A**, were derived from the spectra using the GANAAS program developed by the International Atomic Energy Agency. The mass, **M**, of an element was then calculated from the appropriate peak area using the relationship:

$$M = A\,[(ke^{-\lambda D})\,(1 - e^{-\lambda I})\,(1 - e^{-\lambda C})]^{-1}$$

where λ is the radioactive decay constant, and **D**, **I**, and **C** are the times of decay, irradiation, and counting, respectively. The values of **k**, the so-called experimental activation constant, were determined by the use of suitable reference standards. In the absence of a lacustrine sediment standard reference material with certified Cs, Eu, and Sm concentrations, we prepared synthetic standards as described above under XRF, but in the concentration range from 1 – 100 $\mu g\ g^{-1}$. The isotopes of primary interest were ^{134}Cs (2.06 y, 796 keV), ^{152}Eu (12.4 y, 1408 keV), and ^{153}Sm (46.5 h, 103 keV). The precision and accuracy of the determinations were assessed by carrying out replicate measurements, and by the use of the standard reference materials S04 and NIST1633; both measures were found to be better than 10% rsd for most of a suite of 10 elements.

Glow-discharge mass spectrometry. Mass spectrometric investigations were made with a VG GloQuad quadrupole instrument, using either a Faraday cup (high current matrix peaks) or an electron multiplier (weak trace component peaks). Argon was used to support the discharge, and the discharge cell was kept at liquid nitrogen temperature to minimize molecular species.

A flat sample holder designed for use with the spectrometer's direct insertion probe was used for sediment analyses[34,35]. Samples were dried at 100°C, pressed into disks, and ionized in a glow discharge at 35 W of r.f. power. Although a stable discharge was obtained after about 5 minutes, the mass region for Cs showed several isobaric interferences. It was not possible to determine Cs quantitatively in samples or standards by this method. With the quadrupole spectrometer, resolution was equal to 1 amu. A sector mass spectrometer might resolve interfering ions and permit quantitation.

Preparation and deployment of labeled sediment. A 55 mm diameter gravity corer was used to obtain a sediment sample from near the tracer deployment site in the Isle Parisienne basin of eastern Lake Superior at a water depth of 100 m. The profundal sediments of this basin are extremely fine-grained cohesive muds that become anoxic within a few mm of the sediment-water interface (R. Cuhel, personal communication). Mean current speeds at the bottom are < 10 cm s^{-1} (N. Hawley, personal communication). The top 20 cm of the gravity core was homogenized and subsampled to provide 100 mL (~ 10 g dry weight) of wet sediment. This material was amended by the addition of 4.85 g (13.9 mmol) Sm_2O_3; 0.90 g (2.56 mmol) Eu_2O_3; and 10.0 Cs-phlogopite containing 0.8 g (6.0 mmol) Cs. On a dry weight basis, the composition of the labeled sediment with regard to Sm, Eu, and Cs was thus 1.1, 0.20, and 0.23 mmol g^{-1}, or 16.5, 3.0, and 3.1% by weight, respectively.

The sediment-tracer mixture was then frozen into the center of an ice block weighing about 5 kg, as described earlier[29]. The deployment rig incorporated a sonobuoy to aid in echo location of the site, and a small anchor weight, as shown in the sketch in Figure 1. In August, 1988, the manned submersible, Johnson-Sea-Link, deployed the tracer experiment, using the full 4 m extension of its articulated manipulator to insure locating the experiment in an undisturbed area on the bottom. Because Lake Superior is isothermal at 4°C at depths below about 20 m, little melting of the ice block occurred during the descent, and no tracer was lost. After emplacement, the ice block melted slowly and the labeled sediment settled to the interface. A short videotape of the deployment sequence is available upon request.

Coring and subsampling. In August, 1990, the tracer deployment site was revisited in the Johnson-Sea-Link, using echo location of the sonobuoy to navigate the final 100 m. Nineteen 55 mm diameter core samples were taken within a 1.2 m radius of the deployment site. Coring was accomplished with so-called "Alvin-type" punch core tubes, using the submersible's articulated manipulator arm. The video record (available on request) showed very little disturbance of the sediment column during coring, and later visual examination of the cores showed good preservation of minor features at the sediment-water interface. The core samples were stored at 4°C, then extruded hydraulically and sectioned at 1 cm intervals. The subsamples were stored in preweighed plastic screw-cap bottles. Later, the bottles were thawed and the contents dried to constant weight at 110°C. The dried material was homogenized by grinding with a mortar and pestle prior to further subsampling for analytical determinations.

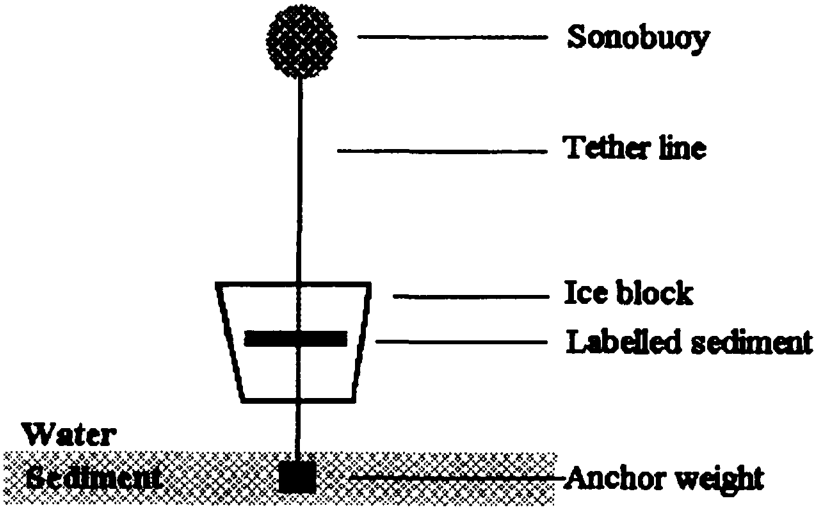

Figure 1 Cartoon showing the frozen tracer pellet immediately after deployment from the submersible.

RESULTS AND DISSUSION

Tetraphenyl borate salts can remove K^+ irreversibly from a variety of micas[31]. Generally, removal of the native cation leads to a loosening of the minerals' sheet-like structure, with an increase in the spacing between adjacent aluminosilicate layers. Phlogopite itself does not bind Cs by intercalation. The aquo Cs^+ ion is too large to enter the interlayer spacing of phlogopite's aluminosilicate sheets. The expanded structure of the K^+-depleted phase, however, does admit Cs^+, as the cartoon in Figure 2 illustrates. Komarneni and Roy[30] discovered that when this occurs, the lattice subsequently collapses slightly, trapping Cs^+. Thus, the binding of Cs^+ to the K-depleted phlogopite begins with something like simple ion exchange, but results ultimately in a new crystalline phase with a distinctive interlamellar spacing. The binding of Cs^+ is strong, with a K_D value exceeding 10^6. Cs^+ is not lost by exchange with Na^+ even at seawater salinities and above. For convenience, we will refer to this synthetic material as Cs-phlogopite. Depending on the conditions under which it is prepared and isolated, Cs-phlogopite may contain up to ~10% by weight Cs, or ~ 0.75 mmol g^{-1}.

Preliminary experiments with standards revealed that glow-discharge mass spectrometry failed to provide the necessary sensitivity for Cs determinations at tracer levels in lacustrine sediments. The poor signal-to-noise ratio in the mass region around 133 amu was due to the presence of isobaric interferences arising from the sediment matrix. These interferences were not eliminated by ashing at 500°C overnight.

Determination of Cs in sediments by XRF proved feasible. A linear calibration plot was obtained for Cs concentrations between 750 and 10,000 μg g^{-1}, where

$$\text{Cs, } \mu g\ g^{-1} = \{(\text{Cs } K_\alpha, \text{ counts } s\text{–}^1) + 0.343\}/6.78 \times 10^{-4}$$

and

$$r = +\ 0.997$$

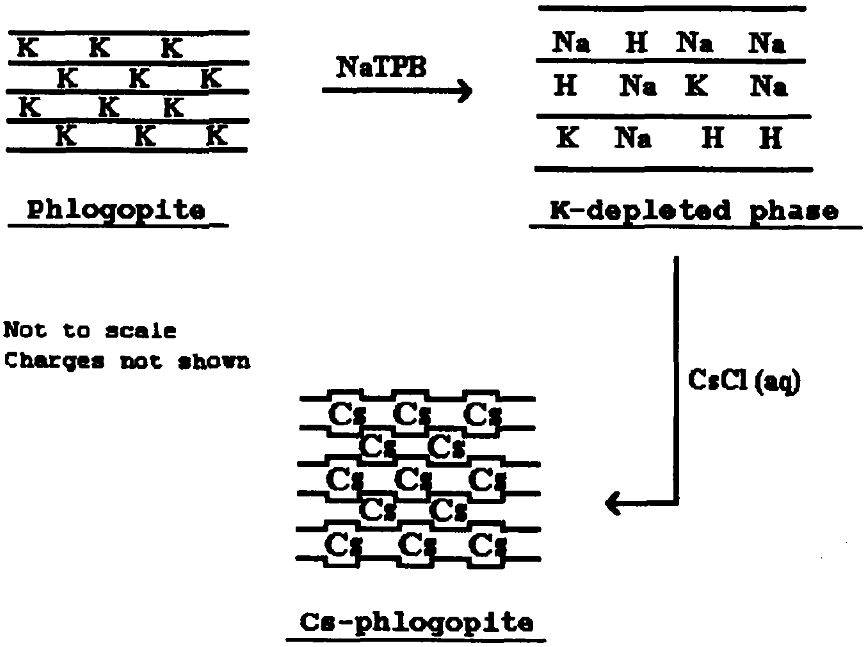

Figure 2 Cartoon representing the preparation of the Cs-labelled phase from native phlogopite with sodium tetraphenylboron, NaTPB.

However, under our experimental conditions, the detection limit was only about 100 μg g^{-1}. The major limitation on sensitivity was the inefficiency of the Si(Li) detector for 30 keV photons. With a high purity Ge detector, one would expect at least an order of magnitude increase in sensitivity. Nonetheless, XRF was useful for determining the Cs content of Cs-phlogopite, where the Cs concentration was too high to make neutron activation analysis convenient. This technique might also find application in situations where much greater amounts of labeled sediment were to be used.

Neutron activation analysis is the method of choice for determining trace elements that have high neutron capture cross-sections and produce activation products with appropriate decay characteristics[37].

This is the case for Sm, Eu and Cs. In many sediments, background concentrations of these elements are ≈ 1 μg g^{-1} or less. Because absolute detection limits for Sm, Eu and Cs by NAA are less than 1 μg, sensitivity is more than adequate for our purposes even for samples of less than 1 g. Once a tracer has dispersed to background levels, no additional information can be gained. In the present case, that limit was reached after dispersal by a factor of about

$$(3.1 \text{ g Cs}/100 \text{ g sediment})/(1 \times 10^{-6} \text{ g Cs}/ 1 \text{ g sediment}) = 3 \times 10^{4}$$

Figures 3, 4, and 5, and Table 1, show the results of NAA determinations of Sm, Eu, and Cs in sediments from around the dispersal site two years after deployment. We were unable to locate standard reference materials of lacustrine sediments in which the concentrations of Sm, Eu, and Cs were certified. Therefore, quantitation was based on the use of a series of standards prepared by doping kaolinite with various amounts of these elements. This procedure could have introduced some bias.

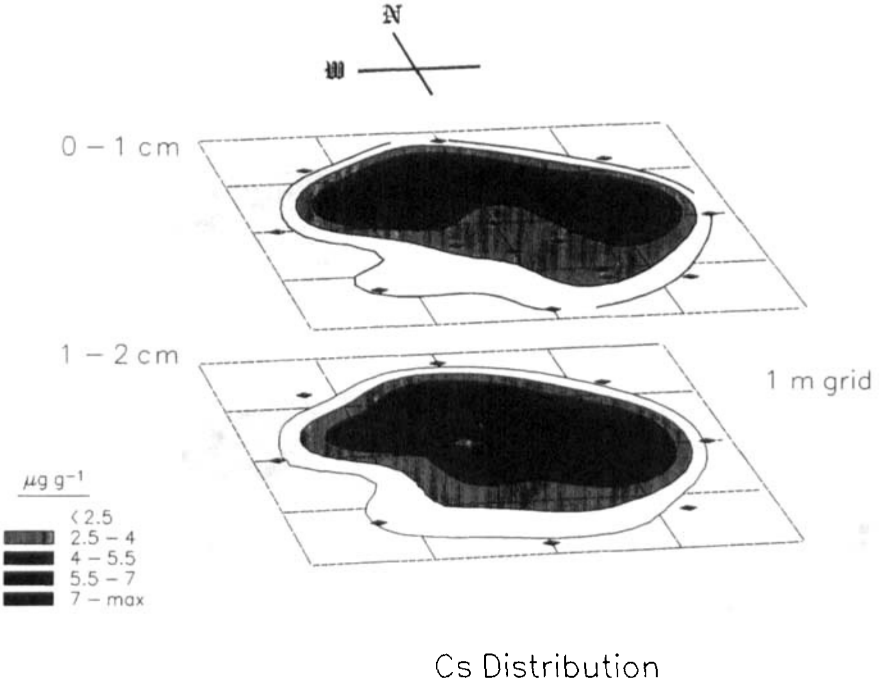

Figure 3 Isochoropleths of Cs, Eu, and Sm distribution in the 0 – 1 and 1 – 2 cm sediment layers two years after tracer deployment. The diamonds indicate locations of core samples.

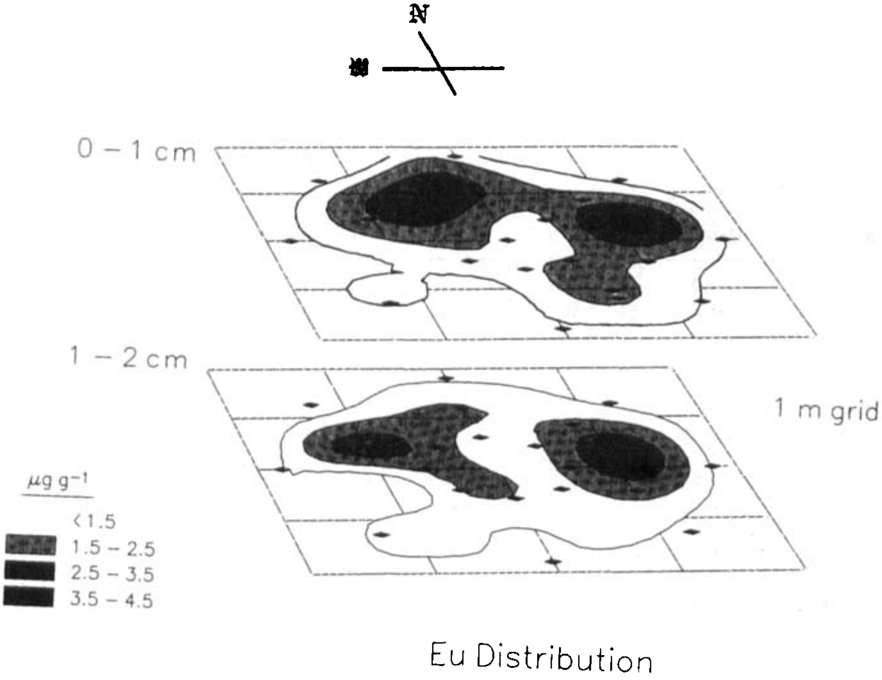

Figure 4 Isochoropleths of Cs, Eu, and Sm distribution in the 0 – 1 and 1 – 2 cm sediment layers two years after tracer deployment. The diamonds indicate locations of core samples.

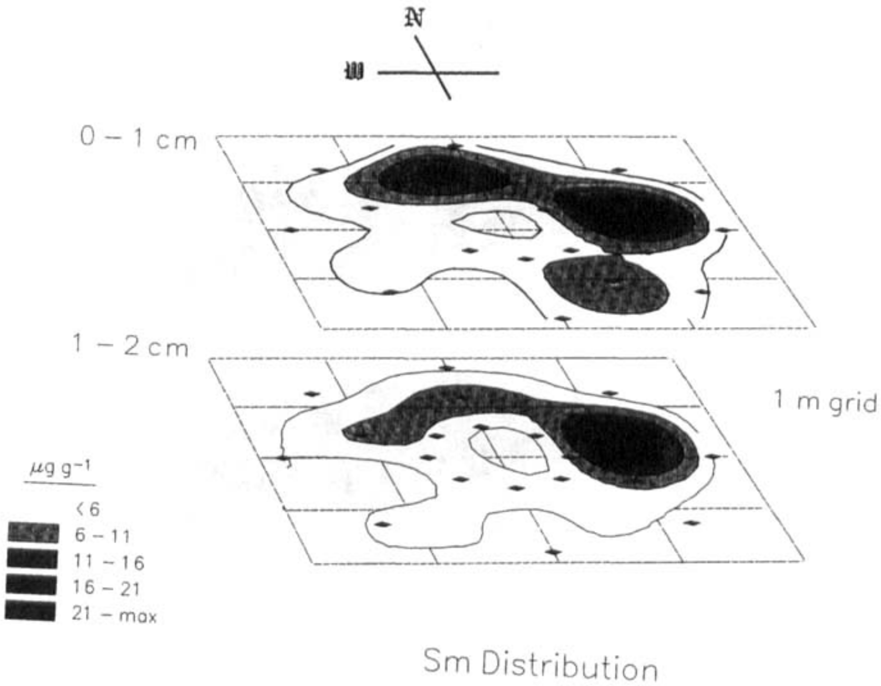

Figure 5 Isochoropleths of Cs, Eu, and Sm distribution in the 0 – 1 and 1 – 2 cm sediment layers two years after tracer deployment. The diamonds indicate locations of core samples.

Table 1 Concentrations of Cs, Eu, and Sm two years after deployment of the tracer.

Site coordinates		*Element concentration, μg^{-1}*					
		0 – 1 cm			*1 – 2 cm*		
Meters E	*Meters N*	*Cs*	*Eu*	*Sm*	*Cs*	*Eu*	*Sm*
0.6	-1.0	3.16	2.35	12.75			
0.6	-1.2	5.28	3.18	17.33			
1.0	-0.5	4.84	2.24	8.45	5.91	2.74	10.32
0.8	0.8	5.14	1.91	7.90	4.52	1.57	6.77
0.8	0.5	6.61	3.65	15.38	5.88	3.13	13.85
0.5	1.1						
0.0	1.2	5.63	2.93	11.74	6.04	2.01	7.73
-0.6	1.0	7.44	5.55	21.07			
-1.0	0.5	6.30	3.29	4.45	4.16	2.70	3.99
0.0	0.0	2.68	1.84				
0.0	0.0	4.47	2.45				
0.0	0.6				4.53	1.96	3.28
-0.6	0.0				6.79	7.75	13.17
0.6	0.0				5.41	3.06	5.60
-0.4	0.4				3.47	1.45	2.29
0.4	0.4	4.48	1.60	4.27	5.24	1.57	2.06
0.0	-0.6	4.41	4.20	10.48	3.60	1.82	2.69
-0.4	-0.4	3.23	1.51	3.27	3.92	1.34	1.75
0.4	-0.4	2.73	1.89	3.97	4.48	1.58	2.10

We did check, however, on the internal consistency of the results. Figure 6 compares the measured atom ratios Eu/Sm and Cs/Sm to the ratios in which these elements were added to the labeled sediment. Because there is considerable scatter in the data, we regressed the observed Cs and Eu concentrations on the observed Sm concentration to infer the mean ratios. With minor discrepancies, the inferred values agreed with those expected from the bulk composition of the tracer.

Limitations imposed by financial resources have restricted our studies so far to the top two centimeters of the sediment column. The contour plots in Figures 3, 4, and 5 were computed and drawn with AXUM software (TriMetrix, Inc.). They are intended as a guide to visualization, not as the basis for a detailed model of sediment redistribution, since contouring results in some smoothing and idealization of the data. For example, to permit closed contours to be drawn, we arbitrarily assumed that tracer concentrations became indistinguishable from background levels at radial distances beyond 1.8 m from the deployment site. This assumption may not hold in the East to North sector, where tracer concentrations were highest. It is also clear that tracer concentrations do not drop to background levels vertically at depths within the 1 – 2 cm stratum. Additional analyses of deeper layers will be necessary to determine the maximum depth of vertical mixing. The preliminary indication is that vertical mixing was both more rapid and more extensive than we expected.

CONCLUSIONS

The synthetic mineral phase, Cs-phlogopite, is a convenient means of studying local redistribution phenomena such as burial, reworking, and resuspension in fine-grained

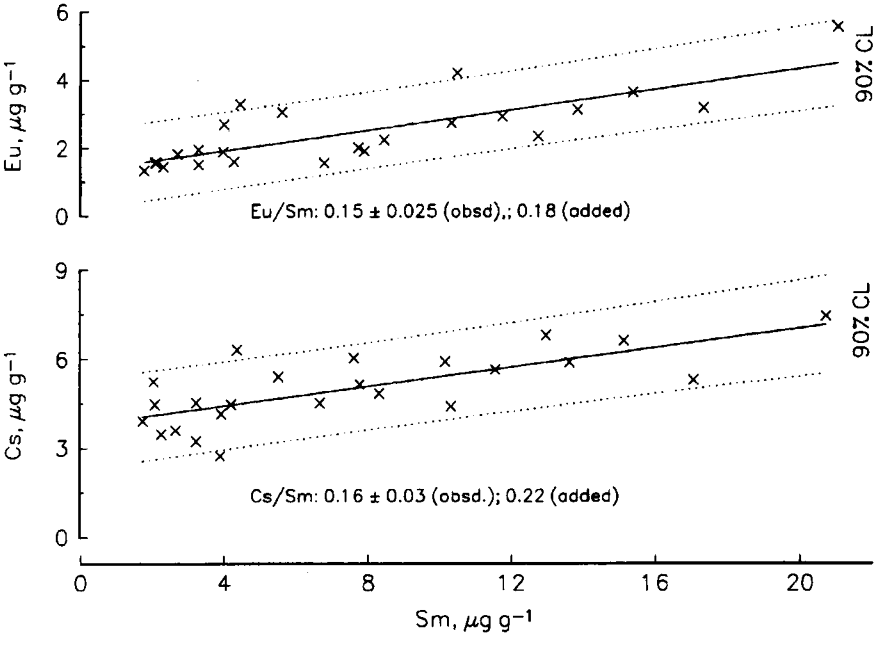

Figure 6 Linear regressions of Eu and Cs concentration on Sm concentration for all sediment samples showing that the original atom ratios in the tracer were preserved after dispersal.

sediments. Its behavior in cohesive lacustrine sediments was indistinguishable from rare earth oxide tracers added simultaneously. Cs-phlogopite is potentially applicable to much larger scale tracer experiments, and to experiments in estuarine and marine sediments. Direct determination of Cs at tracer levels in lacustrine sediments by NAA is sensitive and interference-free, as it is for Sm and Eu. X-ray fluorescence spectrometry is also applicable, but only at concentrations above 100 μg g^{-1} due to the inefficiency of Si(Li) detectors at the photon energy of the Cs K-series X-rays. Glow-discharge mass spectrometry failed in this case due to isobaric interferences the region around 133 amu. The measured atom ratios of Sm, Eu, and Cs in sediment samples showed definite scatter, but the means were close to the values computed from the composition of the tracer pellet. There was no clear evidence of differential migration among the three elements.

Using neutron activation analysis, the observeable dispersal factor was 3×10^4 for sediment amended with Cs-phlogopite to bring it to 3.1% by weight Cs. Cesium in Cs-phlogopite is not exchanged for Na^+. The tracer should be applicable to estuarine and marine sediments, as well as to soils.

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