Sorption of lanthanum onto clay minerals: a potential tracer for fine sediment transport in the coastal marine environment?

K. L. SPENCER[1], S. L. JAMES[2], J. A. TAYLOR[1] & T. KEARTON-GEE[3].

[1]*Geography Department, Queen Mary, University of London, Mile End Road, Londen E1 4NS, UK (e-mail: k.spencer@qmul.ac.uk.)*

[2]*Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, UK*

[3]*School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*

Abstract: In order to improve predictions of coastal morphological response to sea-level rise and sustainably manage dredged sediment there is an urgent need to develop a field methodology that can measure accurately transport pathways of the <63 μm sediment fraction in coastal and estuarine environments. Techniques such as sediment trend analysis and sediment tracing using fluorescent sands are well established for the silt and sand fraction but are unsuitable for clay sediments due to their cohesive nature. Geochemically labelled clays have been used as fine sediment tracers in freshwater environments with some success, although little is known about their chemical or physical behaviour once released in saline environments.

A number of pure clays and natural estuarine sediments were labelled with La following agitation in a 0.01M solution of La Cl_3. In order to examine the retention of La on the clay mineral surface the labelled sediment was washed sequentially four times using both de-ionised water and artificial seawater. A labelled bentonite retained 43000 μg g^{-1} La and this was only reduced to 36000 μg g^{-1} La after washing in seawater. This suggests that retention of La is good even in saline conditions and concentrations of La are high enough to enable detection after considerable signal dilution. Sorption of La is dependent predominantly upon the cation exchange capacity of the sediment.

Understanding dispersion patterns for the fine sediment fraction (<63 μm) and its associated contaminants is of fundamental importance to the sustainable management of coastal and marine resources. Information on sediment transport pathways can be used to improve predictions of coastal morphological response to extreme events such as storm surges and sea level rise, as well as coastal engineering schemes. Recent trends towards the beneficial re-use of dredged sediment for inter-tidal habitat re-creation and the adoption of new dredging techniques such as water injection dredging, mean that understanding fine sediment transport is more pertinent than ever. Consequently, understanding and managing fine sediment transport in estuarine and coastal waters is of increasing importance to local authorities, port and harbour authorities and central government.

The prediction of sediment dispersion in the coastal zone relies on accurate and reliable techniques for the measurement of sediment transport pathways. Historically, this role has been fulfilled by the use of sediment tracing techniques using fluorescent sands (Voulgaris *et al.* 1998) and sediment trend analysis (McLaren & Bowles 1985; Gao & Collins 1992, 1994). These techniques are relatively well established, but due to the cohesive nature of clays are unsuitable and inaccurate for measuring transport pathways of fine grained sediments. The release of short-lived radionuclides into the natural environment has previously been used for tracing the dispersion and transport of the fine sediment fraction (Courtois & Monaco 1969; Heathershaw & Carr 1978). However, there is increasing reticence to use such environmentally sensitive techniques and it is unlikely that a discharge licence would be granted by the Environment Agency of England and Wales. Therefore, there is a need to develop and trial a methodology suitable for studying the dispersion and transport of the <63 μm fraction and in particular the clay component. It is important that the tracer developed should: (1) be easily detectable using routinely available analytical

From: BALSON, P. S. & COLLINS, M. B. 2007. *Coastal and Shelf Sediment Transport*. Geological Society of London, Special Publications, **274**, 17–24. 0305-8719/07/$15.00

techniques; (2) be environmentally benign; and (3) have physical properties similar to the sediment it is intended to mimic.

Labelling clay minerals for use as environmental sediment tracers has received some interest in the past. Iridium-labelled sediments have been used to investigate the redistribution of marine sediments (Yin *et al.* 1993) and lanthanide-labelled clay particles have been used successfully to determine sediment transport pathways in karst systems (Mahler *et al.* 1998) and in lake sediments (Krezoski 1989). The lanthanide group of elements (also known as the rare earth elements, REEs) all have similar properties and can be incorporated easily into the clay-mineral lattice as they are trivalent and have similar ionic radii to Ca^{2+}. Previous research has shown that lanthanides are accepted readily into the montmorillonite lattice and up to 100% of the cation exchange capacity (CEC) can be achieved (Bruque *et al.* 1980). Mahler *et al.* (1998) also found that the retention of lanthanides in saline conditions was good and that they may be suitable for use in coastal marine environments. Additionally, lanthanides have been used as geochemical tracers for groundwater mixing (Johanesson *et al.* 1997), to investigate the dynamics of soils (Braun *et al.* 1998; Matisoff *et al.* 2001; Zhang *et al.* 2003; Xue *et al.* 2004) and as chemical analogues to study the uptake of trivalent actinides in the field of storage/disposal of nuclear waste (Chapman & Smellie 1986). Consequently, there has been considerable work looking at sorption mechanisms including the irreversibility of sorption (Miller *et al.* 1983), migration into the clay structure (Miller *et al.* 1982) and the effect of pH (Bruque *et al.* 1980). However, there is still uncertainty concerning whether sorption leads to fractionation of the lanthanide group and little is known about the nature of the chemical bonds between metal cations and the clay structure (Coles & Yong 2002; Coppin *et al.* 2002). There are a limited number of studies reporting partitioning coefficients of REEs between clay minerals and aqueous solutions (Sinitsyn *et al.* 2000) and applications in the saline environment have not been studied in any detail.

Here, we have investigated whether the use of La-labelled clays and natural sediments may be suitable for use as a tracer of fine sediment in the estuarine environment. Dispersion in the estuarine environment means that once the tracer sediment is released, the tracer element signal will be diluted considerably. Hence, one of the key aims of this project is to determine whether sufficiently high concentrations of sorbed La are achievable in labelled sediments to enable their use as sediment tracers. As the tracer element may be exchanged with competing cations in saline environments, a second aim is to ascertain the extent of La desorbtion when exposed to both freshwater and saline conditions.

Methodology

Two samples of natural estuarine sediment were collected from an area of mud flat and vegetated salt marsh the Medway Estuary, Kent, representing sediments with both low and high organic content respectively. These sediments have been previously studied in detail (Spencer 2002) and the $<2\,\mu m$ fraction has the approximate composition: smectite (49%), kaolinite (22%), illite (27%) and chlorite (2%). Samples of bentonite, smectite, kaolinite, phlogopite and illite were also used in order to determine the effect of clay mineral type and cation exchange capacity (CEC) on La sorption. A 1% sediment suspension was prepared by adding 2.5 g of oven-dried, crushed sediment to 250 ml of 0.01M $LaCl_3$ solution. The pH of the suspension was recorded and the sediments were then left to equilibrate before being shaken for 30 minutes using a mechanical wrist shaker. The suspension was then centrifuged at 3000 rpm for 15 minutes. The pH of the supernatant was recorded and retained for analysis by inductively coupled plasma optical emission spectrometry (ICP OES) using a Perkin Elmer Optima 3300RL. In order to determine whether La was desorbed from the labelled sediment when exposed to a freshwater environment, the labelled sediment samples were washed sequentially four times with de-ionised water. After each wash, the suspension was shaken for 30 minutes and then centrifuged at 3000 rpm for 15 minutes. The pH of the supernatant wash was recorded and the wash retained for analysis by ICP-OES. Initially, the labelled sediments were washed eight times, however La concentrations were consistently below 1 mg L^{-1} after four washes and therefore this was considered sufficient. In order to mimic the re-suspension of the labelled sediment in saline waters, the sediments were also washed in artificial seawater made up to the manufacturer's recommendations (Tropic-Marin™). The CEC of both the pure and natural sediments was calculated following the US EPA 9081 method (US Environmental Protection Agency 2005). Total La concentrations were determined in the sediments before labelling and after washing in de-ionized and in saline water using a total HF–$HClO_4$–HCl dissolution technique (Thompson & Walsh 1989). Resultant digestates were analysed by ICP-OES.

Precision was determined by carrying out all labelling experiments in triplicate and was generally < 5% relative standard deviation (RSD) for La concentrations in sediment analyses, < 2% RSD in the supernatant, but very variable in the sample washes. Accuracy was assessed by analysing in-house reference materials and was between 12 and 16% bias. The in-house reference materials used were prepared from four igneous rock samples representing a range of major and trace metal concentrations.

Results and discussion

Equilibration times for the sorption of REEs onto clay minerals used in the literature vary considerably from 10 minutes (Bonnot-Courtois & Jaffrezic-Renaut 1982) to 72 hours (Coppin *et al.* 2002). In this study a preliminary experiment was completed where bentonite was equilibrated with 0.01 M $LaCl_3$ for 30 minutes, 1 hour, 24 hours and 1 week. The amount of La sorbed onto the clay mineral surface was calculated from the decrease in aqueous La concentration at the end of the experiment. This calculation assumes that any La removed from solution is removed due to sorption on the clay mineral surface and/or migration to the mineral lattice and not due to loss from precipitation or sorption onto the container walls. It is possible that La hydroxide may be precipitated during sorption experiments and this is discussed in detail later in this paper. The sorption coefficient, K_d, values (in ml g^{-1}) have been normalised to the solution volume/solid mass ratio as used by Coppin *et al.* (2002) and shown in Equation 1.

$$K_d = \frac{(C_{initial} - C_{final})}{C_{final}} \frac{V}{M} \quad (1)$$

where,

K_d = solid/solution partitioning coefficient (ml g^{-1})
$C_{initial}$ = aqueous concentration of La at the beginning of the experiment (mg L^{-1})
C_{final} = aqueous concentration of La in the supernatant (mg L^{-1})
V = solution volume (ml)
M = mass of the solid (g)

Figure 1 shows the K_d values for La for the timed equilibration experiments. The results indicate that equilibrium between the La aqueous solution and the clay fraction was not achieved after 168 hours, although the K_d values increase rapidly after 1 hour. This would suggest that equilibration times in excess of 1 week are required. If we consider the La sediment concentrations rather than K_d values, a final La sediment concentration of 44 000 μg gDW^{-1} (dry weight) was achieved after the sediment had been equilibrated for 30 minutes and this only increased to 46 000 μg gDW^{-1} after 1 week. This demonstrates that La uptake may increase with equilibration times in excess of 168 hours and this is in disagreement with other workers who have shown the REE uptake by clay minerals is complete after as little as 5 minutes (Aja 1998). However, the increase in the final La sediment concentration is minimal after 24 hours. Consequently, we equilibrated the La solution and all the sample clays for 24 hours before shaking and centrifuging the samples the following day. It should be noted that it may be inappropriate to apply K_d values calculated for bentonite to the other clay minerals used in this experiment, however this does give an approximate guideline as to equilibration times needed.

Coppin *et al.* (2002) have also suggested that some clays may undergo dissolution during

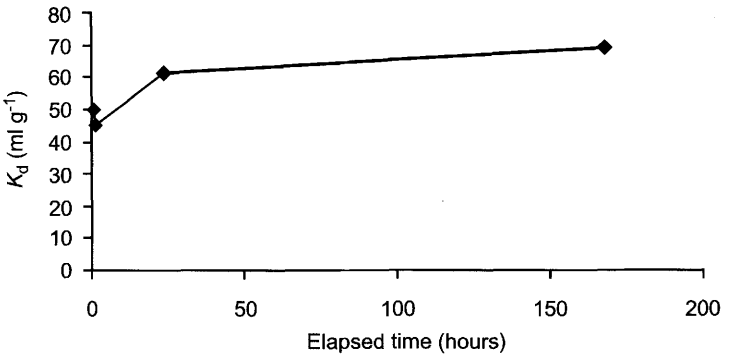

Fig. 1. Calculated K_d values for La and bentonite as a function of elapsed time.

sorption experiments. This would release elements present in the aluminosilicate clay mineral lattice to aqueous solution including Al and any La naturally present in the clay minerals. Therefore K_d values may be decreased due to this additional input of La to aqueous solution. Here, Al is present in both the supernatant and consequent washes at low concentrations (<1 mg l^{-1}) for the freshwater washes and below detection limits for the majority of the saline washes. Dissolution of clays is largely pH dependent and loss of Al due to the dissolution of montmorillonites occurs only at pH values <2 (Bruque *et al.* 1980). In the present study pH values of the initial sediment suspension were >4. This suggests that dissolution of the clay minerals is likely to be minimal and has not been considered further.

Total La concentrations for each of the sediments studied are given in Table 1 and demonstrate considerable variation in the natural concentrations of La in the sample materials. Concentrations of La in the sediments collected from the Medway Estuary are similar to those analysed in other estuarine sediments (e.g. Weltje *et al.* 2002). In order to determine whether La would be desorbed from the sediments when exposed to either freshwater or saline environments the total La concentration in sediments before and after labelling have also been compared (Table 1). All sediments show significant increases in the amount of La present after labelling and this is retained to varying extents after subsequent washing in both fresh and saline waters. The highest La concentrations are present in bentonite, with a concentration of 43 200 μg gDW^{-1} after washing in de-ionized water only decreasing to 36 000 μg gDW^{-1} after repeated washing in saline water. The lowest concentrations of La are present in kaolinite with concentrations of 1900 μg gDW^{-1} after washing in de-ionized water. Concentrations of La in all the samples, with the exception of kaolinite, decrease in the sediments that have been washed in saline water with respect to washing in de-ionized water. This suggests that for most of the sediments La is desorbed to some extent under saline conditions and in the presence of a high concentration of competing cations. The loss of La due to desorption varies from 17% for bentonite to 49% for phlogopite. This again suggests that bentonite may be the most effective clay for retaining La in both fresh and saline conditions. The different behaviour of kaolinite may be due to the nature of the mineral lattice. The CEC of kaolinite is controlled primarily by pH dependent charges arising from broken bonds along mineral edges (Coles & Yong 2002). Consequently the concentration of metal cations sorbed to the mineral surface is strongly dependent upon changes in ambient pH. In the present study the differences in the amount of La sorbed after washing in saline and fresh water environments may have been due to variations in the pH. Most authors who have studied partitioning coefficients between clay minerals and REEs in aqueous solutions have also noted a dependency on the ionic strength of the REE solution. Beall *et al.* (1979) studied the uptake of La in NaCl solutions buffered to pH 5 and they found that metal uptake decreased with increasing ionic strength. However, they did not consider the effects of competing metal complexation in the saline environment.

If chemical parameters during sorption are optimised, it is possible that 100% of the CEC can be achieved. Table 1 shows the percentage of CEC occupied by La after desorption in both fresh and saline environments assuming that all

Table 1. *Total sediment La concentration after shaking in de-ionized water (FW) and saline water (SW) and % of CEC (in milliequivalents) occupied by La after desorption in de-ionized water (FW) and saline water (SW)*

	La in mg $kgDW^{-1}$*	La in mg $kgDW^{-1}$ (FW)	La in mg $kgDW^{-1}$ (SW)	CEC in meq $100g^{-1}$	La as % of total CEC (FW)	La as % of total CEC (SW)
Bentonite	57	43200	36000	121	75	64
Illite	49	NA	9600	30	NA†	70
Kaolinite	7	1900	5100	22	19	51
Smectite	28	20600	16000	58	76	59
Phlogopite	4	8500	4300	27	68	34
Natural sediment 1 (low organic content)	36	16900	13200	44	77	60
Natural sediment 2 (high organic content)	39	19200	13600	65	64	46

*Natural La concentration in sediments, NA, data not available.

the La present is sorbed to cation exchange sites. This indicates that higher La concentrations in the final labelled sediments could be achieved if the chemical parameters for partitioning and equilibrium are examined for each of the clay sediments in detail. Metal uptake onto clay mineral surfaces may be a function of pH, ionic strength of the solution and the initial concentration of the sorbant in aqueous solution (Sinitsyn *et al.* 2000). Additionally, these factors are influenced by both the type of clay and the lanthanide element used. However, there are a limited number of studies reporting optimum chemical parameters for the partitioning of REEs between clays and aqueous solution. Bruque *et al.* (1980) examined the sorption of La onto montmorillonite and found that maximum sorption was achieved between pH values of 4–5, while at values >5, precipitation of La hydroxide may occur. Whilst Sinitsyn *et al.* (2000) found that maximum uptake of Eu and Nd onto illite occurred at pH values >5. In the present study, pH values of the initial sediment suspension were between 4 and 5 and pH values of the washes increased as the solutions were not buffered. Thus, a decrease in La concentrations in sediment washes (Fig. 2) may be an indication of La hydroxide precipitation and increases in total La concentrations in the final labelled sediments may be due to the presence of precipitated La hydroxide. Lanthanum concentrations in wash solutions show a strong relationship with pH and the sorption edges as a function of wash pH (fresh water washes) are given in Figure 3. This shows that La concentrations in the wash solution decrease significantly at a pH value of between 5.5 and 6. This is in agreement with the sorption edge data for saline washes, although the data are incomplete and are therefore not presented.

In order to determine whether La hydroxide was being precipitated out during washing, labelled sediments were investigated using semi-quantitative scanning electron microscopy (SEM) with Link Isis energy dispersive x-ray analysis (Hitachi S-3000-N SEM). Discreet particles with a micro-crystalline structure were observed adhered to the surfaces of clay particles in both fresh and saline washed sediments. Figure 4 shows a SEM image for bentonite and the accompanying element distribution map clearly shows that the crystalline structures are La rich. The sediments were also analysed using x-ray diffraction (XRD), however diffraction traces were not observed for La hydroxide or any other commonly occurring La salts. This suggests that although some of the total La concentrations in labelled sediments may be attributed to the presence of La hydroxide, concentrations are low and can not be detected by XRD analysis. One of the primary mechanisms for the sorption of metal cations to clay mineral surfaces is due to cation exchange. Scatterplots of CEC against total La concentration in labelled sediments from both fresh water and salt water washes are shown in Figure 5. These indicate that

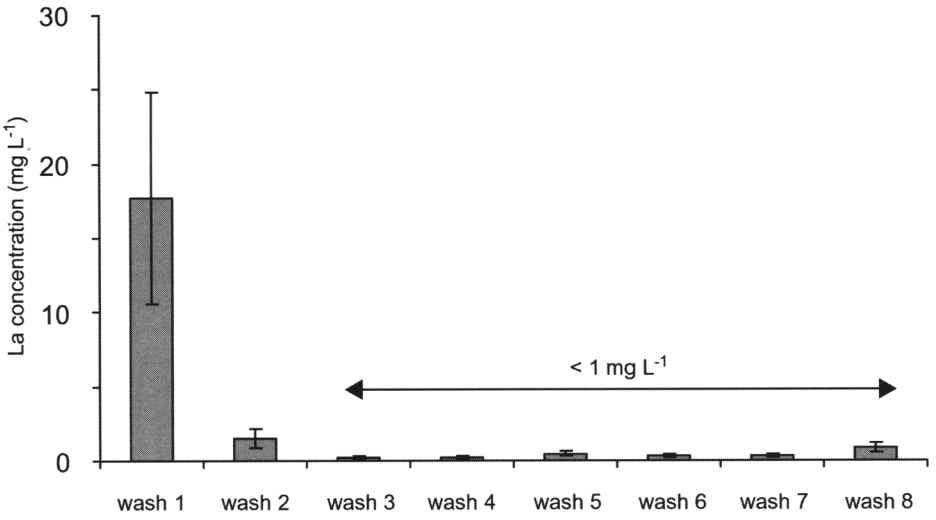

Fig. 2. Lanthanum concentrations in sequential fresh water sediment washes.

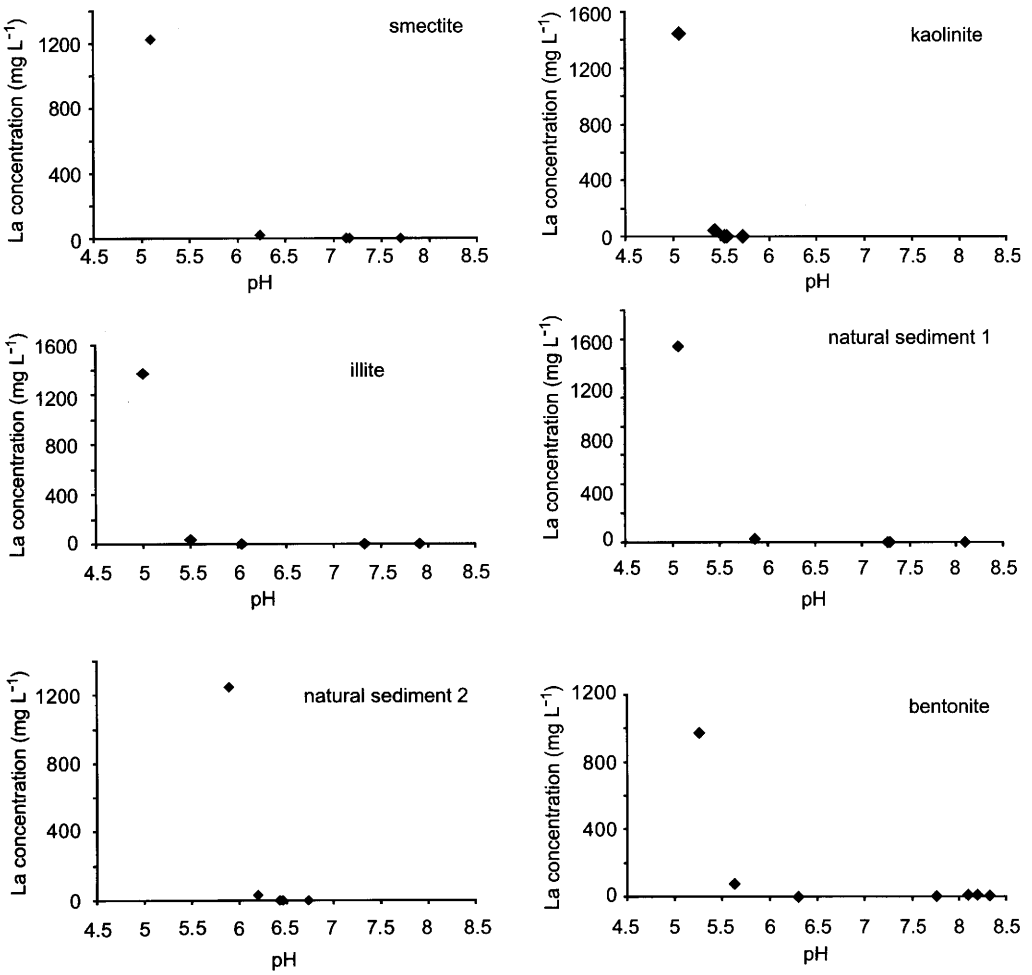

Fig. 3. Relationship between La concentrations in sequential saline sediment washes and pH.

total sediment La concentration is controlled strongly by the CEC of the sediment with correlation coefficients of $r=0.99$ for freshwater washes and $r=0.98$ for salt water washes. This indicates that although La hydroxide is present in the labelled sediments, it probably does not contribute significantly to the final total La concentrations. Consequently, the K_d values calculated earlier in this paper are also valid. These scatterplots also demonstrate that CEC and hence sediment type is probably the most important controlling factor for La sorption. Hence, the clay mineral used as a potential sediment tracer must be selected carefully.

Summary and conclusions

The concentration of La in labelled sediments indicates that metal uptake is strongly dependent upon CEC and hence sediment type. In these experiments the highest concentrations of La were sorbed to bentonite. Concentrations in excess of 40 000 μg gDW^{-1} can be achieved easily and may be improved by carefully controlling the chemical parameters of the sorption process. The precipitation of La hydroxide may occur during the labelling process but is unlikely to contribute significantly to the total La concentrations recorded in the labelled sediments. Under saline conditions La is desorbed to a small extent

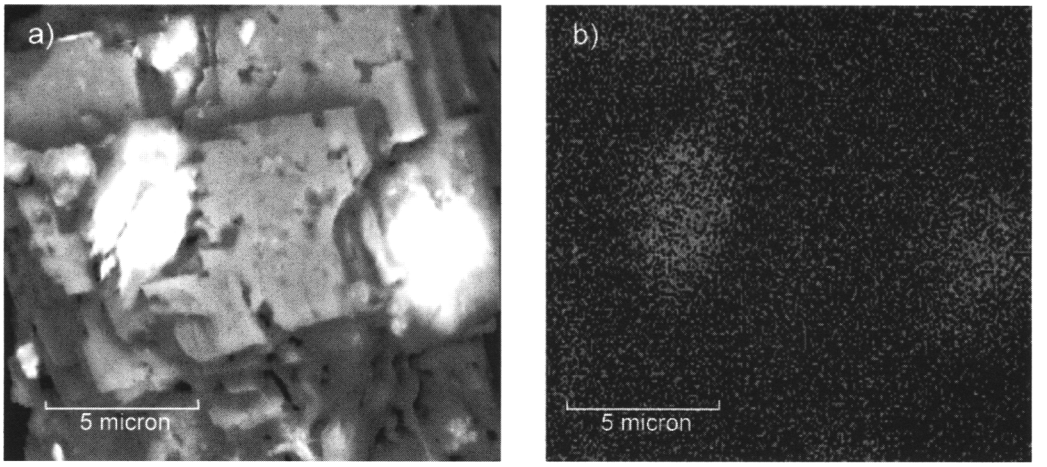

Fig. 4. (**a**) SEM image of bentonite and (**b**) element distribution map for La.

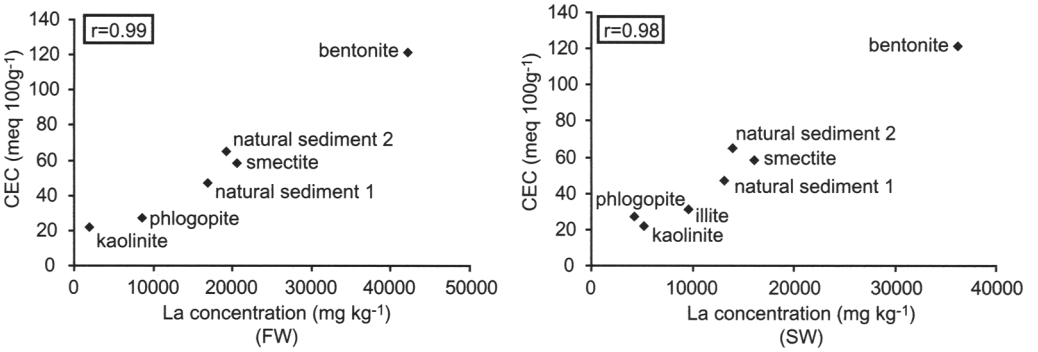

Fig. 5. Scatterplots of CEC against total sediment La concentration for fresh water (FW) and salt water (SW) washed sediments.

in the presence of competing cations, but total La concentrations in the labelled sediment are still in excess of 35 000 μg gDW^{-1}.

In order to use successfully geochemically labelled sediment as a tracer of the fine-grained sediment fraction, concentrations of the geochemical label must be high enough to allow routine detection even after the sediment has dispersed. We have estimated that the tracer signal must be detectable after dilution by a factor of 10^6 to 10^9 in the estuarine system. Using pre-concentration, detection limits of 1 ng g^{-1} are achievable for most lanthanide group elements using inductively coupled plasma mass spectrometry (Jarvis 1988, 1989). Consequently we should be able to detect our tracer after dispersion, although La concentrations will be near the instrumental detection limit. It may, however, be difficult to distinguish the tracer signal from natural background concentrations within estuarine and coastal sediments. Further investigation is required as to the use of alternative lanthanide group elements that have lower natural background concentrations and the use of REE ratios that are more diagnostic than single element signatures alone.

This project was funded by a NERC Connect A grant (NER/E/S/2002/00022).

References

AJA, S. U. 1998. The sorption of the rare earth element, Nd, onto kaolinite at 25 °C. *Clays and Clay Mineralogy*, **46**, 103–109.

BEALL, G. W., KETELLE, B. H., HAIRE, R. G. & O'KELLY, D. G. 1979. Sorption behaviour of trivalent actinides and rare earths on clay minerals. In: FRIED, S. (ed.) *Radioactive Waste in Geological Storage.* ACS Symposium Series, **100**, 201–213.

BONNOT-COUTOIS, C. & JAFFREZIC-RENAUT, N. 1982. Etude des échanges entre terres rares et cations interfoliaires de deux argiles. *Clay Mineralogy*, **17**, 409–420.

BRAUN, J. J., VIERS, J., DUPRE, B., POLVE, M., NDAM, J. & MULLER, J. P. 1998. Solid/liquid REE fractionation in the lateric system of the Goyoum, East Cameroon: the implication for the present dynamics of the soil covers of the humid tropical regions. *Geochimica et Cosmochimica Acta*, **62**, 273–299.

BRUQUE, S., MOZAZ, T. & RODRIGUEZ, A. 1980. Factors influencing retention of lanthanide ions by montmorillonite. *Clay Minerals*, **15**, 413–420.

CHAPMAN, N. A. & SMELLIE, J. A. T. 1986. Introduction and summary of the workshop: natuaral analogues to the conditions around a final repository for high-level radioactive waste. *Chemical Geology*, **55**, 167–173.

COLES, C. A. & YONG, R. N. 2002. Aspects of kaolinite characterisation and retention of Pb and Cd. *Applied Clay Science*, **22**, 39–45.

COPPIN, F., BERGER, G., BAUER, A., CASTET, S. & LOUBET, M. 2002. Sorption of lanthanides on smectite and kaolinite. *Chemical Geology*, **182**, 57–68.

COURTOIS, G. & MONACO, A. 1969. Radioactive methods for the quantitative determination of coastal drift rate. *Marine Geology*, **7**, 183–206.

GAO, S. & COLLINS, M. B. 1992. Net sediment transport patterns inferred from grain-size trends, based upon definition of "transport vectors". *Sedimentary Geology*, **81**, 47–60.

GAO, S. & COLLINS, M. B. 1994. Analysis of grain-size trends, for defining sediment transport pathways in marine environments. *Journal of Coastal Research*, **10**, 70–78.

HEATHERSHAW, A. D. & CARR, A. P. 1978. Measurement of sediment transport rates using radioactive tracers. *In: Coastal Sediments '77.* American Society of Civil Engineers, New York, 399–416.

JARVIS, K. E. 1988. Inductively Coupled Plasma Mass Spectrometry: A new technique for the rapid or ultra-trace level determination of the rare-earth elements in geological materials. *Chemical Geology*, **68**, 31–39.

JARVIS K. E. 1989. Determination of rare earth elements in geological samples by Inductively Coupled Plasma Mass Spectrometry. *Journal of Analytical Atomic Spectroscopy*, **4**, 563–570.

JOHANNESSON, K. H., STETZENBACH, K. J. & HODGE, V. F. 1997. Rare earth elements as geochemical tracers of regional groundwater mixing. *Geochimica et Cosmochemica Acta*, **61**, 3605–3618.

KREZOSKI, J. R. 1989. Sediment reworking and transport in eastern Lake Superior – in situ rare earth element tracer studies. *Journal of Great Lakes Research*, **15**, 26–33.

MAHLER, B. J., BENNETT, P. C. & ZIMMERMAN, M. 1998. Lanthanide-labeled clay: A new method for tracing sediment transport in Karst. *Ground Water*, **36**, 835–843.

MATISOFF, G., KETTERER, M. E., WILSON, C. G., LAYMAN, R. & WHITING, P. J. 2001. Transport of Rare Earth element-tagged soil particles in the response to thunderstorm runoff. *Environmental Science and Technology*, **35**, 3356–3362.

MCLAREN, P. & BOWLES, D. 1985. The effects of sediment transport on grain-size distributions. *Journal of Sedimentary Petrology*, **55**, 457–470.

MILLER, S. E., HEATH, G. R. & GONZALEZ, R. D. 1982. Effects of temperature on the sorption of lanthanides by monmorillonite. *Clays and Clay Mineralogy*, **30**, 111–122.

MILLER, S. E., HEATH, G. R. & GONZALEZ, R. D. 1983. Effects of pressure on the sorption of Yb by montmorillonite, *Clays and Clay Mineralogy*, **31**, 17–21.

SINITSYN, V. A., AJA, U., KULIK, D. A. & WOOD, S. A. 2000. Acid-base surface chemistry and sorption of some lanthanides on K^+-saturated Marblehead Illite: I. Results of an experimental investigation. *Geochimica et Cosmochimica Acta*, **64**, 185–194.

SPENCER, K. L. 2002. Spatial variability of metals in the inter-tidal sediments of the Medway Estuary, Kent, UK. *Marine Pollution Bulletin*, **44**, 933–944.

THOMPSON, M. & WALSH, J. N. 1989. *Handbook of Inductively Coupled Plasma Spectrometry, 2nd Edition*, Blackie, Glasgow.

US ENVIRONMENTAL PROTECTION AGENCY 2005. Test Methods. http://www.epa.gov/epaoswer/hazwaste/test/main.htm#table.

VOULGARIS, G., SIMMONDS, D., MICHEL, D., HOWA, H., COLLINS, M. B. & HUNTLEY, D. A. 1998. Measuring and modelling sediment transport on a macrotidal ridge and runnel beach: An intercomparison. *Journal of Coastal Research*, **14**, 315–330.

WELTJE, L., HEIDENREICH, H., ZHU, W., WOLTERBEEK, H., KORHAMMER, S., DE GOEIJ, J. J. M. & MARKERT, B. 2002. Lanthanide concentrations in freshwater plants and molluscs, related to those in surface water, pore water and sediment. A case study in The Netherlands. *Science of the Total Environment*, **286**, 191–214.

XUE, Y. Z., LIU, P. L., YANG, M. Y. & JU, T. J. 2004. Study of spatial and temporal processes of soil erosion on sloping land using rare earth elements as tracers. *Journal of Rare Earths*, **22**, 707–713.

YIN, Y., CHANG, N., ZHONG, W., SUN, S., ZHANG, Y., CUI, H., CHEN, S., FENG, Y. & SUN, L. 1993. A study of neutron activation tracer sediment technique. *Science in China, Series A*, **36**, 243–248.

ZHANG, X. C., NEARING, M. A., POLYAKOV, V. O. & FRIEDRICH, J. M. 2003. Using rare-earth oxide tracers for studying soil erosion dynamics. *Soil Science Society of America*, **67**, 279–288.