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Distribution and modelling of rare earth elements in Chinese river sediments

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Abstract

Fifty-nine sediment samples were collected from the major rivers of China and analysed using Inductively Coupled Plasma–Mass Spectrometry (ICP–MS). The background rare earth element (REE) concentrations ($\mu g/g$) of these samples were: Sc, 11.1 (1.3–23.1); Y, 13.7 (3.3–24.8); La, 30.8 (7.6–57.2); Ce, 64.4 (16.5–122.6); Pr, 7.3 (1.6–14.4); Nd, 27.8 (5.6–58.5); Sm, 5.74 (1.1–11); Eu, 0.98 (0.05–1.7); Gd, 8.9 (1.6–16.8); Tb, 0.62 (0.12–1.2); Dy, 3.0 (0.53–5.0); Ho, 0.55 (0.09–1.00); Er, 1.4 (0.26–2.4); Tm, 0.19 (0.06–0.4); Yb, 1.0 (0.22–2.9); Lu, 0.16 (0.05–0.42). The total REE concentration (Σ REE), light-REE concentration (LREE) and heavy-REE concentration (HREE) were 44.5–315.8, 38.1–264.6 and 6.36–51.2 $\mu g/g$, respectively. The ratio of LREE to HREE ranged from 3.7 to 7.7. The average ratio was approx. 5.1 and did not show much variation with location. Total and individual element concentrations were normally distributed. The variation in the average REE concentration was not greater than 25 $\mu g/g$. A high degree of correlation was found between the REEs. Factor analysis indicated that REE concentrations in sediments were mainly described by two factors and the loading of the first two factors could be described by: $Y = 1 - X^2$. Factor score plots were employed to distinguish between samples of natural and anthropogenic origin. Based on the inter-correlation determined between REEs in sediment samples, a model was developed to predict REE concentrations. © 1997 Elsevier Science B.V.

Keywords: Rare earth elements (REEs); Sediments; Distribution; Modelling; Factor analysis

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1. Introduction

In the past decades, many publications dealing with distribution, accumulation, transportation as well as ecological effects of trace elements in river sediment have emerged (Kersten and Forstner, 1989; Zdened, 1996). A large body of literature is available concerning the distribution and abundance of REEs from the geochemical and mineralogical stand point (Herderson, 1984; Bhatia and Crook, 1986; Taylor and McLeennan, 1988; Wronkiewicz and Condie, 1990, McLennan et al., 1990; Scott, 1990; Liu et al., 1993; Braun and Pagel, 1994). However, in recent years more attention has been paid to rare earth element behaviour in sediments and, in particular, aquatic environmental aspects of REEs (Bhatia, 1985; Goldsttein and Jacobsen, 1988; Markert et al., 1989; Wood, 1990; Cullers, 1994; Denchev et al., 1994; Jarvis et al., 1994; Albarede and Semhi, 1995; Ross et al., 1995; Wang et al., 1995; Kreamer et al., 1996). This is important because under different environmental conditions sediments can act as efficient sinks for metals released into aquatic environments, or as a source thereof.

Rare earth elements (REEs) have great economic value, which is best illustrated by their increased usage in recent years, in particular for industrial and agricultural purposes. Compounds of Sm, Pr and Ce are applied as magnetic materials and La and Yb are applied in the preparation of high temperature super conductors. Some REEs are used as catalysts for chemical reactions or are necessary for the production of laser crystals. Human activities, such as mining, extraction of metal from ores and minerals and metal refining, release trace amounts into the biosphere at increasing rates, augmented by the worldwide use of metal-bearing fossil fuels as a source of energy. Moreover, millions of tons of fertilizers containing REEs are used worldwide for increasing agricultural productivity (Bremmer, 1994; Diatloff et al., 1995; Xu, 1995; Yu and Chen, 1995).

China has the largest REE reserves in the world (80%) and is a major producer of REEs for the world market. Since 1990, REE fertilizer has been widely used in more than 20 Chinese

provinces (Wu and Guo, 1995; Xu, 1995; Yu and Chen, 1995). REE fertilizers intended for agriculture production was predicted to cover over $16-20\times10^6$ ha of Chinese agricultural land in 1995 (Tu et al., 1994; Zhong and Min, 1995). A study of background levels of REEs in the water and sediment of the Yangtze River was carried out by Zhong and Min (1995). This study focused on the characteristics of REEs in suspended matter, sediment and the aqueous phase. A report of the geochemical characteristics of REEs in Wuhan section of the Yangtze River was published by Wang et al. (1995), indicating the REE content of the suspended fraction of the river. Results indicated that speciation characteristics of REEs in both sediment and suspended matter were quite similar. However, in general, information on background REE levels in sediments throughout China is very sparse.

Factor analysis is a technique suitable for simplifying large and complex data sets in such a way that it may create a limited number of factors, each representing a cluster of interrelated variables within a data set. In recent years, the technique has been frequently applied in environmental pollution studies with the aim of identifying possible sources of pollution and to determination the elemental composition of these sources as well as the contribution of each source to the total pollution level (Alpert and Hopke, 1980; Hopke, 1988; Kuik et al., 1993; Sloof, 1993). This technique has also been applied widely in the field of chemistry (e.g. spectral chemistry and analytical chemistry) (Malinowski, 1980; Geladi and Kowalski, 1986; Brereton, 1990; Helland, 1990; Vaughan and Horlick, 1990; Meloun et al., 1992; De Jong, 1993; Diatloff et al., 1993; Wang et al., 1995).

The aims of the present work are: (i) to determine the distribution of REEs in Chinese river sediment and to establish the correlation between individual REEs; (ii) to develop a model based on these internal correlations to predict total and individual REE concentrations in river sediments; and (iii) using the results of factor analysis to extract the major variables and to identify polluted/contaminated samples.

2. Fate of REEs in soil and aquatic environments in China

There are seven major rivers in China, i.e Yangtze river, Yellow river, Sunhuaiing river, Pearl river, Haihe river, Huaihe river and Liaohe river. Their river basins cover an area of approx. 4300000 km². No systemic data are available with respect to REE background levels in the earth's crust around China. However, in the past 20 years, some progress has been achieved with respect to background levels of REEs in Chinese soil (Zhong and Min, 1995). The concentration of REEs reported in Chinese soil is similar to that reported worldwide (Wang et al., 1995; Bowen, 1979). The average Σ REE concentration in Chinese soil is 177 μ g/g (Wang et al., 1995), which is a little higher (13%) than the average world concentration (156 μ g/g). Large variations in Σ REE concentrations were reported for different areas of China. The highest concentrations were recorded in the areas of Guangzhou, Hanan (Pearl river basin) and Hunan (Yangtze basin) and the lowest concentrations were recorded in the areas of Xingiiang. The ratio of LREE to HREE in Southern China (Pearl river basin and part of Yangtze river basin) were reported to be higher than that of other areas in China, Light REE enrichment in the soil, relative to the earth's crust, was reported in most areas of China (Zhong and Min, 1995).

Data on REE background levels in aquatic environments is limited for China. Reported REE concentrations in freshwater (rivers and lakes) were in the range $10^{-3}-10^{-2}$ µg/l. The range of concentrations of REEs in Chinese sediments were 9-200, 5-651, 7-246, 1.4-42, 0.1-3.6, 0.12-6.2, 0.5-13.6 and 0.1-1.95 for La, Ce, Nd, Sm, Eu, Tb, Yb and Lu, respectively (Zhong and Min, 1995).

3. Experiment

3.1. Sampling

Fifty-nine sampling sites, covering the major rivers of China were selected. The sites were far away from industrial areas and municipal wastewater outlets. Samples were collected in the basins of the Yangtze river (n = 30), Pearl river (n = 12) and the Yellow, Sunhuajing, Haihe, Huaihe and Liao river basins (n = 17). Approx. 2 kg of sediment per sample was collected at a depth approx. 10-20 cm below the surface sediment layer. At least five subsite samples were taken for each site and homogenized. The samples were stored in polyethylene bags. The wet samples were air-dried at room temperature and sieved to remove large particles. Subsequently, the debris was passed through a 2-mm sieve.

3.2. Analytical procedure

The samples were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, a VG Plasmaquad Plus, Fisons Instruments, UK) fitted with a Fassel-type torch, a Gilson 222 automatic sample changer, a Meinhard glass nebuliser (type Tr-30-A3) and a double pass Scott type spray chamber with surrounding liquid jacket (the temperature of which was controlled with a recirculating water refrigeration-heating system). The operating conditions are shown in Table 1. The ICP-MS was optimized with a solution of ¹¹⁵In at 100 ng/ml in 3% HNO₃. The internal standards used during the analysis of samples containing REE was 115 In at 50 ng/ml concentration in 3% HNO3. The following masses were used for REE measurement: ⁴⁵Sc, ⁸⁹Y, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶²Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷⁴Yb and ¹⁷⁵Lu.

Table 1
Typical ICP-MS operating parameters for aqueous REE analysis

| Forward power (W) | 1350 | | | |
|---|---------------|--|--|--|
| Reflected power (W) | 0 | | | |
| Nebulizer gas flow (1 min ⁻¹) | 0.95 | | | |
| Auxiliary gas flow (1 min ⁻¹) | 1.1 | | | |
| Cool gas flow (1 min ⁻¹) | 13.5 | | | |
| Nebulizer solution uptake (ml min ⁻¹) | 0.8 | | | |
| Mass range (m/z) | 40-180 | | | |
| Dwell time (μ s) | 10.2 | | | |
| Scanning mode | Peak-jump | | | |
| Measurement mode | Multi channel | | | |

Prior to analysis, the samples were dried for 24 h at 105°C. Then 0.5 g of the sample was weighed and transferred into a vessel liner and 5 ml of H₂O and 10 ml HNO₃ were added. The mixture was digested by Microwave (MDS-2000, CEM, USA) for 90 min at 100 psi and full power (650 W).

4. Results and discussions

In order to control the quality of sample digestion and analysis, a marine sediment reference material (GBW-07313, from the National Research Centre for Certified Reference Materials, Beijing, China) was used. Results of analysis of marine reference material was compared to the certified values. The average REE recovery was 93.6% of the certified value. Approx. 95% recovery was achieved for the light REEs (94.8%, 97.9%, 94.5%, 96.5%, 95.4%, 95.1% and 96.1% for Sc, La, Ce, Pr, Nd, Sm and Gd, respectively); while the recoveries of the heavy REEs ranged from 83% to 97% (88.4%, 89.3%, 96.1%, 87%, 91.1%, 90.2%, 95.5%, 90.6% and 95.3% for Dy, Er, Eu, Tb, Ho, Tm, Yb, Lu and Y, respectively). The detection limits of ICP-MS were 0.54, 0.066, 0.071, 0.11, 0.053, 0.059, 0.073, 0.012, 0.073, 0.009, 0.007, 0.008, 0.017, 0.008, 0.019 and 0.008 ng/ml for Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy,

Ho, Er, Tm, Yb and Lu, respectively (based on three times the standard deviation of the blank).

4.1. Distribution of REEs in sediments

Table 2 shows the average REE content of the sediment samples (n = 59). The concentration of REEs in Chinese river sediments was as follows: Ce > La > Nd > Y > Sc > Gd > Pr > Sm > Dy > Er > Yb > Eu > Tb, Ho, Tm and Lu, which is similar to the order found in literature (Wang et al., 1995; Zhong and Min, 1995).

Fig. 1a,b present the distribution of Ce and the total REE concentration for the 59 samples analyzed. The concentration of Ce and Σ REE in the sediment samples was 22–107 μ g/g and 65–289 μ g/g, respectively, at the 95% confidence level. In both cases the data were normally distributed.

The log-normal distribution was also examined for individual REEs and was linear in all cases. In Fig. 1c,d two typical examples (Nd and Yb) of log-normal plots are presented. Chester (1985) reported that the distribution of most elements in sediments approximated the log-normal distribution and such distributions have been used to establish various characteristic (population) parameters, e.g. background and threshold levels. From the REE log-normal distribution plots, it can be seen that almost all sediment samples are

Table 2 The maximum, median, minimum and average REE content ($\mu g/g$) of 59 Chinese sediment samples

| | Max. | Median | Min. | Average | | Max. | Median | Min. | Average |
|----|--------|--------|-------|---------|----------------|--------|--------|--------|---------|
| Sc | 23.09 | 11.63 | 1.32 | 11.11 | Er | 2.44 | 1.40 | 0.26 | 1.41 |
| La | 57.25 | 31.14 | 7.56 | 30.83 | Tm | 0.38 | 0.18 | 0.06 | 0.19 |
| Ce | 122.59 | 65.25 | 16.54 | 64.42 | Yb | 2.89 | 0.96 | 0.22 | 1.01 |
| Pr | 14.35 | 7.57 | 1.59 | 7.25 | Lu | 0.42 | 0.15 | < 0.02 | 0.16 |
| Nd | 58.54 | 29.31 | 5.59 | 27.81 | Y | 24.83 | 14.62 | 3.31 | 13.68 |
| Sm | 10.98 | 5.33 | 1.09 | 5.12 | | | | | |
| Eu | 1.72 | 0.87 | 0.05 | 0.85 | Σ REEs | 315.78 | 185.10 | 44.46 | 176.90 |
| Gd | 16.81 | 8.86 | 1.64 | 8.89 | Σ LREEs | 264.56 | 151.74 | 38.10 | 147.40 |
| Tb | 1.16 | 0.65 | 0.12 | 0.62 | ΣHREEs | 51.22 | 30.24 | 6.36 | 29.51 |
| Dy | 4.96 | 3.20 | 0.53 | 2.99 | L/H | 7.67 | 5.02 | 3.66 | 5.11 |
| Ho | 0.99 | 0.57 | 0.09 | 0.55 | L/H* | 14.4 | 8.8 | 5.2 | 9.0 |

L/H: the ratio of light REE (Sc, La, Ce, Pr, Nd, Sm, Eu) to heavy REE (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y).

L/H*: the ratio of light REE (La, Ce, Pr, Nd, Sm, Eu) to heavy REE (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) without Sc and Y.

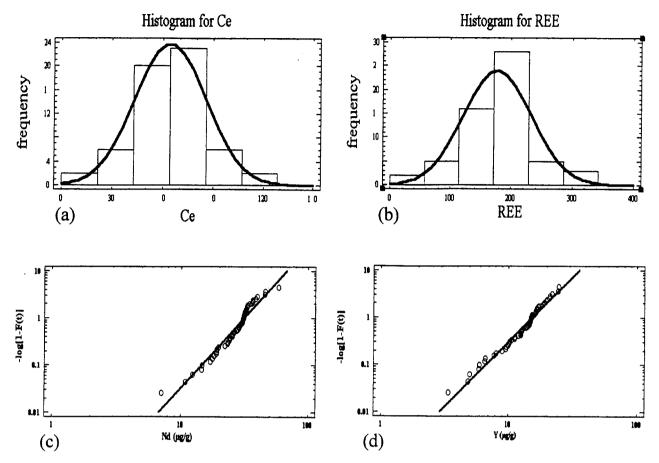


Fig. 1. (a-b) Histograms of Ce and ΣREE concentration. (c-d) Plots of log-normal distribution for Nd and Yb.

of natural origin and the few samples which depart slightly from linearity may result from pollution and/or random sample preparation errors.

The range of concentration of total REEs, light REEs and heavy REEs were 44.5-315.8, 38.1-264.6 and $6.36-51.1~\mu g/g$, respectively. Distribution tests indicated that these data were also normally distributed. The ratio of LREEs to HREEs ranges from 3.7 to 7.7 (without Sc and Y, the ratio ranges from 5.2 to 14.2). Approx. 85% of samples have a ratio of 4.1-6.1. The average ratio was 5.1. Correlation between three light and heavy elements is presented in Fig. 2a and Fig. 2b, respectively. Good correlation was found in both cases.

4.2. Variation of REE concentrations in the major Chinese rivers

The average total REE concentration in the Chinese rivers investigated was: Pearl river (196.3

 μ g/g) > Haihe river (185 μ g/g) > Song Liao River (179.5 μ g/g) > Yangtze river (175.6 μ g/g) > Yellow river (173.3 μ g/g). The differences between average concentrations were not greater than 25 μ g/g. The results are consistent with the average concentration of REEs in the earth's crust (Herderson, 1984).

5. Factor analysis

5.1. Number of factors required to describe the river sediment data set

In order to extract the most important parameters influencing REE sediment concentrations, factor analysis was employed in this study. A sharp increase in the explained variance was observed when two factors were used (Fig. 3). However, increasing the number of factors above two had little effect on the explained variance. Approx. 87% of the variance could be explained

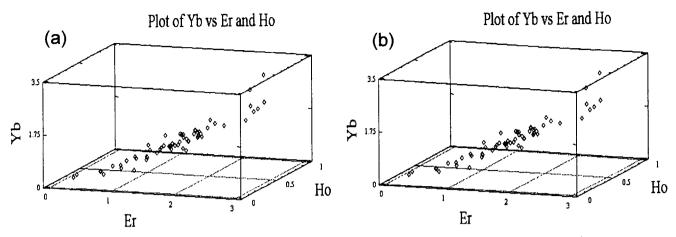


Fig. 2. Correlation between three light REEs (La,Ce,Nd) and three heavy REEs (Lu,Yb,Ho).

by factors 1 and 2. Factors 3-5 explained approx. 10% of the variance, while factors 6-16 only explained approx. 3% of the variance. It can be concluded that REE concentrations (16 elements) in sediments are mainly described by factors 1-2.

5.2. Which factors describe heavy and light REEs in the river sediment data set?

5.2.1. Factor loadings

Loading expresses the relationship between variables and factors in a model. It can be seen which rare earth elements (variables) are important for each factor. In Fig. 4a the loadings of factor 1 are presented as a function of the loadings of factor 2, for all elements. Factor 1 describes all REE elements with a loading range of 0.59–0.97. Loadings in excess of 0.9 were recorded for Ce, Dy, Er, Ho, La, Nd, Pr, Sm, Gb and Tm.

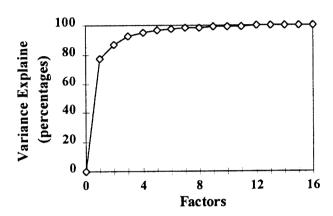
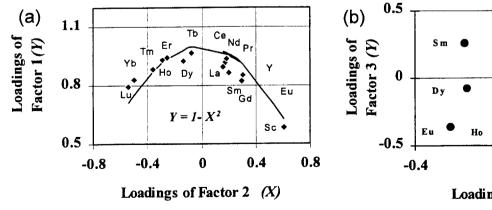


Fig. 3. The relation between the variance explained and the number of factors.

Loadings between 0.8 to 0.9 were recorded for Eu, Gd, Lu, Y and Yb. Only Sc, with a loading of 0.59 did not fall within this loading range.

Factor 2 also describes the REEs and loadings of 0.31 to -0.54 were recorded. However, as can



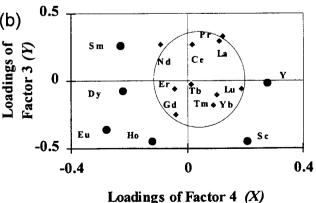


Fig. 4. (a) Plot of loadings on factor 1 to 2. (b) Plot of loadings on factor 3 to 4.

be seen from Fig. 4a, factor 2 exhibited negative loading for heavy REEs (e.g. Lu, Yb, Tm, Ho, Dy, Er and Tb) while positive loadings were found for light REEs (Eu, Y, Gd, Sm, La, Pr, Ce, Nd: 0.13–0.30; except Sc: 0.62). Increasing the atomic weight of the REEs (from Sc to Lu) decreased the factor 2 loadings (Fig. 4a), however, no clear relationship could be found between atomic weight and the loadings of factor 1.

The loadings of factors 1 and 2 can be described mathematically by the equation $Y = 1 - X^2$ (Fig. 4a). This model was used to test if the same relationship between factors 1 and 2 existed in other samples.

From Fig. 4b, it can be seen that the element loadings of factors 3 and 4 are approximately the same (i.e. -0.26 to 0.29 and -0.04 to 0.3 for factors 3 and 4, respectively) illustrated by the circle on Fig. 4b. However, as mentioned previously, factors 3 and 4 only explain approx. 8% of the variance. From Fig. 4b, Y and Sc are far removed from the main bulk of element loadings. This may be due to the fact that their atomic weights are considerably lower than the other REE. The deviation of Sm, Dy, Eu and Ho may be explained by analytical and/or sampling errors.

5.2.2. Identification of contamination sources using factor score plots

The relationship between samples (objects) and factors is expressed as score. A score plot can be used to identify outliers. The total REE concen-

tration of the samples was well described by the scores of factors 1 and 2. From Fig. 5a, it can be seen that sample scores of factors 1 and 2 are mostly located in the circle (i.e. -20 to 20 and -3 to 3 for factor 1 and 2, respectively), which divides the score data. Approx. eight of the 59 samples are located outside the circle (i.e. sample number S7, S25, S38, S45, S49, S50 and S55). Factor scores which clearly lie outside the constructed circle in Fig. 5a have either very high or low total REE concentrations. High REE concentrations may result from high natural background levels or anthropogenic pollution. For example, in Fig. 5a S7, S49 and S50 lay outside the circle because the total REE concentration is very low (68 μ g/g) in the samples compared to the concentration of most samples in the circle is approx. 3 times higher. Furthermore, sample S38 and S55 have total REE concentrations approx. twice as high as the average.

Score plots of factors 1 and 2 do not give any information on the nature of specific element(s) causing contamination. For this detailed information, scores of factors 3 and 4 are needed. These are presented in Fig. 5b. Most of the sample scores are inside the constructed circle (i.e. -1.2 to 1.2 and -0.5 to 0.7 for factors 3 and 4, respectively). Sample numbers S4, S25, S38, S52 and S56 are clearly outside the circle. Samples which lie outside the circle, for example in sample 4 (S4), the concentration of La, Ce, Pr and Nd is twice the average LREE concentration. The concentrations of Sc and Dy in sample S52 are ap-

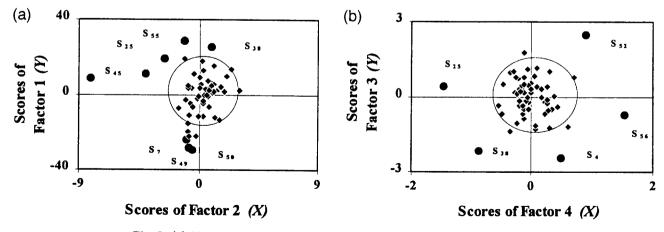


Fig. 5. (a) Plot of scores on factor 1 to 2. (b) Plot of scores on factor 3 to 4.

prox. 1.5 and 2 times the average, respectively. Other samples e.g. S25 and S38 have high levels of HREEs while S56 has a high level of LREEs. Score plots of factor 3 and 4 are useful for identifying the exact element(s) involved in contamination. The nature of the contamination can also be confirmed (i.e. natural or anthropogenic) because internal correlation coefficients (see Table 3) between all the elements exist and if the contamination is of natural origin then the ratio between all elements is increased or decreased; while if the contamination is of anthropogenic origin, only one or two of the ratios will be altered and these can easily be identified as contamination.

6. Prediction of REE concentrations in river sediment

In most cases fewer samples may be available and/or the required analytical techniques (e.g. ICP-MS, ICP-AES) may not be available. In addition, the use of NAA only allows the analysis of eight of the REEs, thus it is not possible to estimate the total REE loading. To overcome these problems a model is needed which can predict total and individual REE concentrations when only a few REE concentrations are actually known.

Table 3
Inter-correlation coefficients between all the REEs

Based on the inter-correlation coefficients established earlier, the following model was obtained:

$$Y_n = a_n X_n + C_n \tag{1}$$

where Y_n is the unknown parameter to be calculated, X_n is a known input parameter $(X_n \text{ or } Y_n \text{ can be any individual REE concentration, the total REE, the total HREE or the total LREE concentration). Slope <math>(a_n)$ and Intercept (c_n) are calibration coefficients established from the calibration data set.

In total there are 19 REE parameters which can be calculated using this model, i.e. 16 individual REE concentrations, the total HREE, the total LREE and the total REE concentration. Using the above model, 18 parameters can be calculated (predicted) when only one parameter is known. However, in order to ensure accurate prediction, two or more input parameters are recommended, preferably an equal distribution of HREE and LREE data.

6.1. Accuracy of the model

The accuracy of the model was tested using the measured concentration of La and Yb (from the sediment samples) as input data. Thereafter, the

| | Sc | Y | La | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Но | Er | Tm | Yb |
|----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Y | 0.75 | | | | | | | | | | | | | • | |
| La | 0.51 | 0.82 | | | | | | | | | | | | | |
| Ce | 0.54 | 0.83 | 0.99 | | | | | | | | | | | | |
| Pr | 0.55 | 0.84 | 0.98 | 0.98 | | | | | | | | | | | |
| Nd | 0.52 | 0.82 | 0.95 | 0.95 | 0.99 | | | | | | | | | | |
| Sm | 0.47 | 0.77 | 0.87 | 0.88 | 0.92 | 0.96 | | | | | | | | | |
| Eu | 0.76 | 0.71 | 0.65 | 0.68 | 0.73 | 0.75 | 0.74 | | | | | | | | |
| Gd | 0.70 | 0.73 | 0.76 | 0.77 | 0.80 | 0.79 | 0.72 | 0.89 | | | | | | | |
| Tb | 0.56 | 0.80 | 0.84 | 0.86 | 0.88 | 0.88 | 0.84 | 0.77 | 0.81 | | | | | | |
| Dy | 0.47 | 0.73 | 0.75 | 0.76 | 0.80 | 0.83 | 0.84 | 0.80 | 0.73 | 0.91 | | | | | |
| Ho | 0.38 | 0.69 | 0.75 | 0.77 | 0.79 | 0.81 | 0.81 | 0.73 | 0.74 | 0.93 | 0.94 | | | | |
| Er | 0.41 | 0.73 | 0.79 | 0.79 | 0.82 | 0.82 | 0.79 | 0.73 | 0.78 | 0.93 | 0.93 | 0.96 | | | |
| Tm | 0.39 | 0.67 | 0.70 | 0.71 | 0.72 | 0.71 | 0.65 | 0.67 | 0.74 | 0.88 | 0.86 | 0.91 | 0.93 | | |
| Yb | 0.25 | 0.57 | 0.65 | 0.65 | 0.66 | 0.66 | 0.61 | 0.55 | 0.67 | 0.84 | 0.81 | 0.88 | 0.91 | 0.93 | |
| Lu | 0.21 | 0.55 | 0.63 | 0.64 | 0.62 | 0.61 | 0.58 | 0.47 | 0.58 | 0.81 | 0.76 | 0.88 | 0.87 | 0.90 | 0.94 |

average total REE concentration was predicted for all the sediment samples using Eq. 1. The accuracy of prediction was between 6 and 10% when outliers were excluded.

6.2. Applicability of the model

In order to assess the applicability of the model, literature data (Zhong and Min, 1995) on different part of Yangtze river sediment (Σ HREE and Σ LREE) was used as input data. The prediction error of the model for the Yangtze river was \pm 10–15%.

As well as predicting total REE concentration, individual REE concentrations can also be predicted. The accuracy of the model with respect to the prediction of individual REE concentrations can be seen in Figs. 6a,d. From the slope of the line, the accuracy of the model can be estimated. The accuracy was best for La, Ce, Sm, Nd and total REE, HREE and LREE and poor for Eu,

Tb, Yb and Lu. The discrepancies between the results reported by Zhong and Min and that predicted using the model may be due to (i) different analytical techniques (the concentrations reported were measured using NAA and model established input data were measured by ICP-MS; and (ii) different sample preparation procedures.

The use of the model may be restricted to Chinese river sediments because theinter-correlation coefficients established in this study were based on background REE levels measured in Chinese river sediments. If the model is used to predict REE concentrations in other areas, internal correlation coefficients must be checked.

7. Conclusions

1. The total REE, light REE (LREE), heavy REE (HREE) concentrations and the ratios

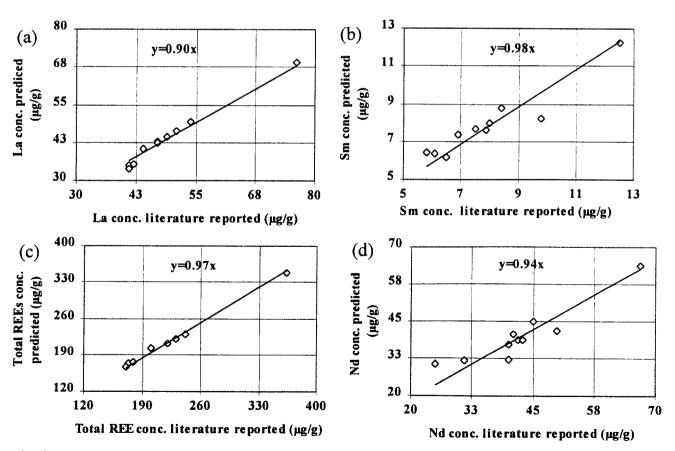


Fig. 6. (a-d) Comparison of REE concentrations in Yangtze river between reported (Zhong and Min, 1995) and predicted values.

- of LREE to HREE ranged from 44.5 to 315.8, 38.1 to 264.6, 6.36 to 51.2 (μ g/g) and 3.7 to 7.7, respectively. REE concentrations in Chinese river sediment samples followed the order: Ce > La > Nd > Y > Sc > Gd > Pr > Sm > Dy > Er > Yb > Eu > Tb, Ho, Tm, Lu.
- 2. The Σ REE and individual element concentrations are normally distributed. The variation in average REE sediment concentration in the Chinese rivers investigated was not greater than 25 g/g.
- 3. Factor analysis indicated that REE concentrations in sediments were mainly described by two factors. The relationship between the loading and the factor loading could be describe by $Y = 1 X^2$. Factor score plots could be employed to identify contaminated samples and contamination sources (natural or anthropogenic).
- 4. Based on the inter-correlation of REEs in the sediment samples, a prediction model was established and accuracy are estimated as 10% and 6%, respectively. The model was also applied for the prediction of REE concentrations in sediment samples which were reported in literature and good agreement between literature and predicted values was found.

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