

## Geochemistry of ferromanganese nodule-sediment pairs from Central Indian Ocean Basin

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### Abstract

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Fourteen ferromanganese nodule-sediment pairs from different sedimentary environments such as siliceous ooze (eleven), calcareous ooze (two) and red clay (one) from Central Indian Ocean Basin (CIOB) were analysed for major, trace and rare earth elements (REE) to understand the possible elemental relationship between them. Nodules from siliceous and calcareous ooze are diagenetic to early diagenetic whereas, nodule from red clay is of hydrogenetic origin. Si, Al and Ba are enriched in the sediments compared to associated nodules; K and Na are almost in the similar range in nodule-sediment pairs and Mn, Fe, Ti, Mg, P, Ni, Cu, Mo, Zn, Co, Pb, Sr, V, Y, Li and REEs are all enriched in nodules compared to associated sediments (siliceous and calcareous). Major portion of Si, Al and K in both nodules and sediments appear to be of terrigenous nature. The elements which are highly enriched in the nodules compared to associated sediments from both siliceous and calcareous ooze are Mo (307, 273), Ni – (71, 125), Mn – (64, 87), Cu – (43, 80), Co – (23, 75), Pb – (15, 24), Zn – (9, 11) and V- (8, 19) respectively. These high enrichment ratios of elements could be due to effective diagenetic supply of metals from the underlying sediment to the nodule. Enrichment ratios of transition metals and REEs in the nodule to sediment are higher in CIOB compared to Pacific and Atlantic Ocean. Nodule from red clay, exhibit very small enrichment ratio of 4 with Mn and Ce while, Al, Fe, Ti, Ca, Na, K, Mg, P, Zn, Co, V, Y and REE are all enriched in red clay compared to associated nodule. This is probably due to presence of abundant smectite, fish teeth, micronodules and phillipsite in the red clay. The strong positive correlation ( $r = >0.8$ ) of Mn with Ni, Cu, Zn and Mo and a convex pattern of shale-normalized REE pattern with positive Ce-anomaly of siliceous ooze could be due to presence of abundant manganese micronodules. None of the major trace and REE exhibits any type of inter-elemental relationship between nodule-sediment pairs. Therefore, it may not be appropriate to correlate elemental behaviour between these pairs.

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**Keywords:** nodule-sediment pairs, Central Indian Ocean Basin, chemical composition, elemental ratios, inter-element relation, micronodules.

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## 1. Introduction

Manganese nodules occur in both marine and fresh water sedimentary environments in the worldwide. These ferromanganese nodules are of particular interest due to their large area coverage with high abundance of the deposits, contain high concentration of Ni, Cu and Co and are considered as a potential economic resource. Generally, ferromanganese nodules have been classified as hydrogenetic, diagenetic and hydrothermal origin based on the source of metals supplied to the nodules and their distribution varies with topographic features. During the last two and half decades, India has done considerable amount of research on ferromanganese nodules and sediments from Central Indian Ocean Basin (CIOB). Ferromanganese nodules from CIOB were studied for chemical composition, size, morphology, mineralogy, oxidation state of Fe and Mn and growth rates (Jauhari and Pattan, 2000; Mukhopadhyay et al., 2008 & reference therein). Similarly, surface sediments from CIOB were also studied for elemental abundance, their distribution and process of incorporation of metals (Nath et al., 1989; Banakar et al., 1998). Accumulation of Fe-Mn oxide of 1 mm thick in the nodules takes ~ 1-2 mm/My (Banakar, 1990) while, associated sediment accumulate at much faster rate of ~ 1-2 mm/ka (Banakar et al., 1991). This suggests that older nodules are lying on the younger sediments. However, the phenomena of keeping older nodules on the younger sediment remains still an enigma.

Major and trace element concentrations of co-existing manganese nodules, micronodules and sediments from Central and Southwest Pacific Ocean was studied by Stoffers et al (1981). They observed remarkable compositional differences between equatorial high productivity zone and low productivity region and related to *in-situ* dissolution of siliceous tests. The equatorial and SW Pacific deep sea manganese nodules and their associated sediments showed enrichment of Mn, Fe, Co, Ni Cu and Zn in nodules whereas, Na, Sc, Cr and Ba in the sediments (Glasby et al., 1987). Results of few major, trace and rare earth elements in the co-existing manganese nodules, micronodules and sediments from Guatemala Basin, Peru Basin and northern equatorial Pacific Ocean, Dubinin and Sval'nov (2000) recorded enrichment of Mn, Cu, Ni and Co in the nodules whereas, Al, Fe, P and REE in sediments. Based on chemical composition of associated nodules and sediments from East-West transect along 22°N in North Atlantic Ocean, Dubinin and Rozanov (2001) observed that Mn, Th, REE, P and Fe are concentrated in nodules and only Al is enriched in the associated sediment. A detailed major and trace element composition and REE of associated ferromanganese nodules and sediments from Pacific Ocean were made by Calvert and Price (1977) and Elderfield et al (1981) respectively. In CIOB, no detailed effort has been made to understand the associated nodule-sediment pair geochemistry as was done for

the Pacific and Atlantic Oceans. Therefore, in the present study, ferromanganese nodule-sediment pairs from different sedimentary environments such as siliceous, calcareous ooze and red clay from CIOB were analysed for major, trace and rare earth elements to understand the possible elemental relationship between them and compare with Pacific and Atlantic Oceans.

## **2. Materials and Methods**

Fourteen nodule-sediment pairs from different sedimentary environments such siliceous ooze (eleven), calcareous ooze (two) and red clay (one) in the CIOB were used in the present study (Fig.1). These nodule-sediment pairs were collected by either Petterson or Van Veen grab during different cruises under Polymetallic Nodules program. Sediment adhered to nodule was washed with distilled water and dried in an oven. Outer oxide layer of few mm thick was scrapped from the nodule, then dried and powdered in an agate mortar. Associated sediments were made salt free initially, dried and later powdered. Known quantity of moisture free Fe-Mn oxide sample of nodules and bulk sediments were treated with 10 ml of 7:3 acid mixtures of HF and HClO<sub>4</sub> in open PTFE beakers and evaporated to dryness. Dissolution is repeated with additional 5 ml of HF and HClO<sub>4</sub> acid mixture and evaporated until a cake was formed, and to that 10 ml of 6 N HCl was added, warmed and made to 100 ml final solutions with distilled water. Part of the solution was used for major and few trace element analyses and remaining part of the solution was used for rare earth element separation using Dowex AG 50W-X8 (200-400 mesh) ion exchange resin following the procedure of Jarvis and Jarvis (1985). Major, few trace and rare earth elements were analysed on a Phillips simultaneous Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES). To check the accuracy of the data, standard reference materials (MESS, BCSS, P-1 and A-1) were used. The accuracy based on standard reference materials and precision based on duplicate sample analysis were  $\pm 4\%$ . For total silica measurements, both nodules and sediments were fused with lithium metaborate in a furnace and clear solutions obtained were analysed with ICP-AES. Accuracy was better than  $\pm 4\%$  based on standard reference material.

## **3. Results**

The chemical compositional data of all fourteen nodule-sediment pairs is presented in Table 1 along with values of Mid Oceanic Ridge Basalts (MORB, Anderson, 1989) and upper continental crust (UCC, Taylor and McLennan, 1985). Correlation matrix of all the elements analysed in both nodules and sediments is shown in Table 2 and 3 respectively. The mean Si and Al, content of sediments (25.29 %, 5.24 %) is higher than associated nodules (10.3 %, 3.02 %), K and Na in both sediments (1.32%; 1.66

%) and nodules (1.27%; 1.82%) are almost in the similar range respectively. Fe, Mn, Ti, Na, Mg and P of sediment (3.14%, 0.66%, 0.22%, 1.66%, 1.41% and 0.1%) are lower than associated nodules (7.9%, 25.49%, 0.30%, 1.82% 2.12% and 0.18%). Highly enrichment of Mn, Cu and Ni is recorded in the nodules (25.49%, 1.12% and 0.89%) compared to sediments (0.66%, 249 ppm and 288 ppm). We have not analysed all the fourteen rare earth elements (REE) in both nodules and sediments. Therefore, instead of total REE ( $\Sigma$ REE) we are using La as its representative because all the REE behaves cohesively in a system. La in the nodules (119 ppm) is quite higher than the associated sediment (36 ppm). Principal component analysis of both the nodules and associated sediments is made to group the elements based on their mutual association and is presented in Tables 4 and 5 respectively. Elemental enrichment ratio of nodules to sediments varies considerably between themselves and with different sediment types and is represented in the form of bar diagrams (Fig.6). Most of the trace and REE are enriched in nodules and sediments compared to UCC and MORB whereas Si, Al, Fe, Ca, Na, K are enriched in UCC compared to sediments (Table 1). Fe and Mn are highly enriched in nodules compared to associated sediment, MORB and UCC.

#### **4. Discussion**

##### **4.1 Geochemistry of nodules**

Silica content in the nodules could be due to presence of aluminosilicates and siliceous shells such as radiolarians. Seven nodules from siliceous ooze area have  $Si_{exc}$  ( $SiO_2 - 3.38 \times Al_2O_3$ , Turekian and Wedepohl, 1961) which is structurally unsupported and is present as biogenic opal. However, four nodules from siliceous ooze and one from calcareous ooze have no  $Si_{exc}$ . Out of eleven nodules from siliceous ooze only three of them have  $Si_{exc}$  varying from 3.5 % to 6.9 %; where as remaining four nodules have < 1 %. This  $Si_{exc}$  in the nodules is due to presence of radiolarian shells within the oxide layers. Detrital silica ( $Si_{tot} - Si_{exc}$ ) in the three nodules from siliceous ooze varies from 30-50 % and for the remaining four nodules is very high (80-95%). Nodule from calcareous ooze (N-84) has highest Si (15.1 %) which is entirely of terrigenous origin. Most of Si, Al and K in the nodules are of terrigenous nature and is evident by the reasonably good positive correlation ( $r=0.49$ ) between them (Table 2). A combined phase of Ti- ferri-phosphate in the nodules derived from sea water column by hydrogenetic process is evident and is similar to the surface and subsurface nodules from the same basin (Pattan and Banakar, 1993; Jauhari and Pattan, 2000; Pattan and Parthiban, 2007). Nodules from siliceous ooze have highest Mn/Fe ratio, followed by calcareous ooze and are of diagenetic to early diagenetic nature

(Jauhari, 1987) while, lone nodule from red clay is of hydrogenetic origin. Elements such as Ni, Cu, Zn, Mo, and Ba, show strong positive correlation with Mn ( $r = > 0.8$ ) suggest their supply from the underlying sediment by diagenetic process and they mostly stabilize the todorokite structure (Burns and Burns, 1977). Nodules have very high Mo up to 871 ppm and are highly enriched compared to associated sediment as well as continental crust (1 ppm, Taylor and McLennan, 1985). La in the nodules varies between 60 and 137 ppm with an average of 119 ppm and is in the similar range as reported earlier (Nath et al., 1992; Pattan and Banakar, 1993; Jauhari and Pattan, 2000) as well as equatorial Pacific Ocean nodules (Elderfield et al., 1991).

#### **4.2 Geochemistry of sediments**

Highest bulk Si is associated with siliceous ooze (33%) as expected, followed by with red clay (22%) and lowest in calcareous ooze (12 %).  $Si_{exc}$  in the siliceous ooze is maximum (up to 20 %), reduces in calcareous ooze (~ 4 %) and red clay do not have it. Al in the sediment is comparatively higher than in the associated nodule (Table.1).  $Al_{exc}$  in the sediment varies between 0.5 to 2.7 % of the total Al and could be due to scavenging of dissolved Al from the water column by the biogenic components (Murray et al., 1993; Banakar et al., 1998)). The positive correlation between  $Al_{exc}$  and biogenic opal suggests that  $Al_{exc}$  can be used as a productivity proxy (Banakar et al., 1998). Some part of  $Al_{exc}$  can also be contributed by the presence of glass shards of Youngest Toba Tuff which occurs in the entire CIOB sediments (Pattan and Shane, 1999). Generally calcareous ooze have the highest Ca (22%) whereas, siliceous ooze and red clay have ~ 1% of Ca which is related to location of sediment with reference of carbonate compensation depth. Mn is highest in red clay (1.9%), decreases to siliceous ooze (0.11 % - 0.95%) and lowest in calcareous ooze (0.26 %) and shows a strong positive correlation ( $r = > 0.8$ ) with Cu, Ni, Zn and Mo (Fig.2). This could be due to presence of Fe-Mn oxide phase probably in the form of Mn-micronodules (Pattan, 1993).

#### **4.3 Nodule-sediment elemental relationship**

Though bulk Si and Al are enriched nearly 2-3 order of magnitude in sediments compared to their associated nodules but detrital silica is higher in the nodules than in the associated sediments. This may be due fact that associated sediments receive large proportion of biogenic opal whereas fine detrital clay particles may deposit within the Fe-Mn layers of nodules. The very low or absence of biogenic opal in the nodules could be due to difficulty in retaining the radiolarian shells within Fe-Mn layers. The bulk of Al within the nodules is entirely contributed by aluminosilicates derived from the continent. A

significant amount of Al is present as structurally unsupported as Al<sub>exc</sub> within the associated sediments. In spite of considerable variations with Si and Al concentrations and their source, a single regression line is drawn through all the points suggesting dominance of similar nature of aluminosilicate incorporated in both nodules and sediments (Fig. 3). It is interesting to note that all the nodules data lies below the best fit line whereas, sediments occupy above it. Potassium in both nodules and sediments is nearly similar and appears to be of aluminosilicate nature which is evident by the positive correlation with Al (Fig.3). High (~ 55 %) and low (< 1%) carbonate in the calcareous and siliceous ooze is due sediment location above and below calcium compensation depth respectively. Siliceous sediment shows presence of few broken foraminifer shells which is responsible for the low Si content. Surprisingly, Ca in the nodules from siliceous ooze is almost two orders more than its siliceous ooze and exhibits strong positive correlation with Mn which probably stabilizes todorokite structure. The association of Mn with Cu, Ni, Zn and Mo is similar in both nodules and sediments (Fig. 2) indicating presence of similar type of Fe-Mn oxide material in the associated sediment. Barium is slightly high in sediments compared to nodules and may occur as an independent phase (Table 3) probably as barite in the sediment while in the nodules it associates with Mn. La as a representative of  $\Sigma$ REE, is nearly 2-5 order enriched in the nodules from siliceous and calcareous ooze whereas it is slightly more in red clay compared to nodule. The distribution of La in red clay and its associated nodule is contrary to nodule-sediment pair from siliceous and calcareous ooze. Earlier, based on comparatively small data set of REE of nodule-sediment pairs (n=8) from siliceous ooze of CIOB, Pattan et al., (2001) observed a moderate positive correlation between REE of nodules and associated sediments. In the present study, we have added six more nodule-sediment pairs of REE data and found that there exist no such correlation (r=0.07) as observed earlier. In the Pacific Ocean, Elderfield et al., (1981) observed that highest REE of nodules are associated with lowest REE of associated sediments and visa versa indicating competitive scavenging of REE between them. Such a relation is not found with CIOB nodule-sediment pairs, as well as in southeast and southwest Pacific Ocean (Courtois and Clauer,1980; Glasby et al.,1987). REE in the nodules are carried by a single authigenic phase comprising of Fe-Ti-P (Pattan and Banakar, 1993; Jauhari and Pattan, 2000) and is different to that of two independent phases consisting of Fe and P (Elderfield et al 1981; Nath et al., 1992). In the associated sediments, REE are associated with three different phases such as Mn, P and Al (Table 3) in varying proportions. The shale (NASC)-normalized REE pattern of nodule-sediment pairs (Fig.4) show that nodules have positive Ce-anomaly which suggests their formation under oxic conditions. The large Ce-anomaly of nodules (SS-210, SS-657 and

F-155) is due to high Fe content and suggests hydrogenetic source. The low Ce-anomaly is associated with high Mn/Fe ratio where nodules are of diagenetic to early diagenetic nature. This suggests that limited supply of REE's to the nodules from underlying sediment and is evident from the oriented nodules study where nodule top has higher REE associated with high Fe (hydrogenetic) while nodule bottom side have low REE corroborated with high Mn (diagenetic) is observed in both CIOB and Pacific Ocean (Elderfield et al., 1981; Nath et al., 1992). The associated sediments have a weak positive to weak negative Ce-anomaly except red clay (SS-210) which has a strong negative C-anomaly. This could be due to presence of abundant authigenic smectite and fish bone which have inherent negative Ce-anomalies. The strong negative Ce-anomaly reported in the red clay from near by Wharton basin was also attributed to the presence of authigenic smectite, fish bone teeth and philipsite (Pattan et al., 1995). The most characteristic feature of shale-normalized REE pattern in both nodule-sediment pairs is the presence of convex shape (Hat shape) suggests an enrichment of middle REE over both light REE and heavy REE (Fig.4). Generally Fe-Mn oxides have the tendency to develop middle REE enrichment (Grandjea-Lecuyer et al., 1993). The enrichment of MREE in the associated sediment could be due presence of Fe-Mn oxide phase probably micronodules. Correlation coefficient of elements between nodule and sediment (Table 5) shows that, none of the element exhibit any significant correlation ( $r < 0.1$ ) between them. Nodules and sediments receive metals by different processes and are entirely of two different systems. Further, nodules of few million years occur on younger sediment of few ka old. Therefore, it may not proper to correlate any elemental behaviour between nodules and their associated sediments.

#### **4.4 Elements enrichment ratio**

Elements enrichment ratio in nodules from siliceous and calcareous ooze exhibit almost similar pattern (Fig.5) and shows highest enrichment of Mo (~ 300 times) followed by Ni, Cu, Mn, Co and Pb (20 to 120 times). Generally nodules have very high Mo concentration of up to 871 ppm and are highly enriched (~ 300 times) compared to associated sediment and ~870 times to that of continental crust (1 ppm, Taylor and McLennan, 1985). High Mo is invariably associated with high Mn in both nodules and sediments (up to 30 ppm) which may be related to their occurrence under oxic condition. Significant enrichment of Mo was reported in the nodules from Pacific Ocean (Calvert and Price, 1977), surficial Mn oxyhydroxides in continental margin and near shore sediments (Shimmield and Price, 1986). Mo is generally enriched in both oxic and anoxic sediments where it is associated with high Mn and total organic carbon respectively. The high Mo content in nodules and sediments of CIOB is not due to

anoxic conditions because normally nodules form at oxic condition and is evident by the presence of positive Ce-anomaly. Nodule from red clay have very low concentration of transition metals and REE compared to those from siliceous and calcareous ooze and appears to be starved nodule. However, it showed very small enrichment of Mn and Ce (~ 4 times) and still less with Ni, Cu, Co and Pb (~2 times). The rest of the elements analysed are depleted compared to its associated red clay. Nodule-sediment pairs from Pacific Ocean have highest enrichment ratio with Mn (10), followed by Cu (5.6), Ni (4.8) and Co (4) whereas REE (0.96), Al (0.54) and Fe (0.25) are enriched in the associated sediments (Dubinin and Sval'nov, 2000). Atlantic Ocean nodule-sediment pairs also showed highest enrichment ratio with Mn (30), followed by Th (8), P (4.5), REE (4.7) and Fe (2.8), whereas only Al is enriched in the associated sediments (Dubinin and Rozanov, 2001). It is evident from this study that enrichment ratio of Mo, Ni, Cu, Mn, Co, Pb and REEs higher in CIOB compared to Pacific and Atlantic Oceans. This probably related to the composition of associated sediments in different ocean basins.

#### **4.5 Principal component analysis (PCA)**

PCA of nodules show mainly three components and account for 90.4 % of the total variance (Table 4). The highlighted variables have their absolute values of loadings greater than 0.5 indicating the participation of the variables in each principal component (PC). PC-1 accounts for 56.8 % of the total variance and is characterized by very high positive loadings of Fe, Ti, P, Y and REEs and negative loadings of Na, Ni, Cu, Zn, Li, Ba, and Mn. All the positive loading elements are supplied to the nodules from seawater and is designated as “hydrogenous factor”. PC-2 contributes 26.7 % of the total variance and has positive loadings of Mn, Ca, Mg, Ni, Cu, Mo, Zn, Co, Ba, Pb, V, Sr and Li. Most of these variables are supplied to the nodules from underlying sediments through pore water and mostly stabilizing the todorokite structure. Therefore, PC-2 may be termed as “diagenetic factor”. PC-2 has a negative loading of Al which is acting as a dilutant to diagenetic factor. PC-3 represents only 7 % of the total variance and has negative loadings of Al and K and difficult to assign any source.

PCA of sediments showed mainly three components and account for 85.2 % of the total variance (Table 5). PC-1 accounts for 62.7 % of the total variance and appears to be a complicated factor. It has positive loadings of almost all analysed elements such as Al, Fe, Mn, Ti, K, Mg, P, Ni, Cu, Mo, Co, Pb, V, Y, Li and REEs. This factor appears to be ad-mixture of both lithogenous and diagenetic elements. PC-2 contributes to 16.2 % of the total variance and has positive loadings of Ca and Sr which is known as “carbonate factor”. PC-3 accounts for only 6.2 % of the total variance and there is no element with



positive loadings and has one element (Na) with negative loadings. Plot of PC-1 against PC-2 for both nodules and sediments (Fig.6) suggest that elements which are behaving similarly are placed close to each other and none of the elements occupy the same position in both nodule and sediment suggesting further their independent behaviour. Therefore it is not ideal to correlate elements between nodule-sediment pairs.

## **5. Conclusions**

Based on the behaviour of major, trace and REE concentration of nodule-sediment pairs from different sedimentary environments such as siliceous, calcareous ooze and red clay from CIOB, the following conclusions are drawn:

- 1.** Sediments invariably have higher concentration of Si, Al and Ba compared to associated nodules, K and Na are almost in the same range in nodule-sediment pairs while, Mn, Fe, Ti, Mg, P, Ni, Cu, Mo, Zn, Co, Pb, Sr, V, Y, Li and REEs are all enriched in nodules compared to their associated siliceous and calcareous ooze. Most of the Al, K and Si in both nodule-sediment pairs appear to be of terrigenous origin.
- 2.** Associated sediment has a strong component of Fe-Mn oxide phase probably as manganese micronodules and is responsible for the similar type of association of Mn with Cu, Ni, Zn and Mo as observed in the nodules.
- 3.** Rare earth elements are generally lower in the calcareous and siliceous ooze than the associated nodules. On the contrary, red clay has higher REE abundance compared to its associated nodule and as well as siliceous and calcareous ooze. The high REE content in red clay could be due to presence of large abundance of micronodules, smectite and fish teeth which have generally higher REE content. REE in the nodules are carried by a single phase consisting of Fe-Ti-P and in the sediments by multiple phases comprising of Mn (micronodules), P (fish teeth) and Al (aluminosilicates). Shale-normalized REE pattern of both nodule-sediment pairs exhibit convex pattern suggesting enrichment of middle REE over light and heavy REE. Generally Fe-Mn oxides have the tendency to develop middle REE enrichment. Therefore, enrichment of middle REE over light and heavy REE in the associated sediment is due to presence of manganese micronodules.
- 4.** Element enrichment ratio in the nodule-sediment pairs from calcareous and siliceous ooze have highest ratio with Mo (~ 300), followed by Ni, Cu, Zn, Mn, Co and Pb (20 to 120 times). Nodule from

red clay exhibit very low enrichment ratio with Mn and Ce (~ 4 times) followed by Ni, Cu, Co, Pb and Sr (~ 2 times) compared to its associated sediment. This could be due fact that nodule from red clay receive less metals from both hydrogenous and diagenetic source and appears to be starved nodule. Enrichment ratio of transition metals and REEs are much higher in the nodule-sediment pairs from CIOB compared to Pacific and Atlantic Oceans.

5. None of the major, trace and REE exhibit any inter-elemental relation between nodule-sediment pairs. Co-occurrence of older nodule with younger sediment, both nodule and sediment represents two different systems and receive metals independently. Therefore, it is not proper to correlate elemental behaviour between nodule-sediment pairs.

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### **Caption for the figures**

Fig.1. Map showing location of nodule-sediment pairs from CIOB.

Fig.2. Relationship of Mn with Ni, Cu, Zn, Mo and Ba contents in both nodules and sediments.

Fig.3. Relationship between Al-Si and Al-K contents of nodules and sediments. A single regression line is drawn for both nodules and sediments.

Fig.4. Shale-normalized REE patterns of nodule-sediment pairs (part of the data is from Pattan et al., 2001).

Fig. 5. Bar diagram showing enrichment ratio of elements in nodules compared to sediments from different sedimentary environments such as calcareous (top), siliceous (middle) and red clay (bottom) .

Fig.6. Scatter plot of PC-1 and PC-2 for both sediment and nodules.

### **Caption for the Tables.**

Table. 1. Major, trace and REE concentration in nodule-sediment pairs along with average nodule to sediment elemental ratio, values of MORB and UCC.

Table.2. Correlation matrix of elements analysed in the nodules from CIOB (n=14)

Table.3. Correlation matrix of elements analysed in the sediments from CIOB (n=14)

Table.4. Principal component analysis of nodules from CIOB

Table.5. Principal component analysis of sediments from CIOB

Table.6. Correlation coefficient of elements between nodules and sediment pairs(n=14 pairs) from CIOB

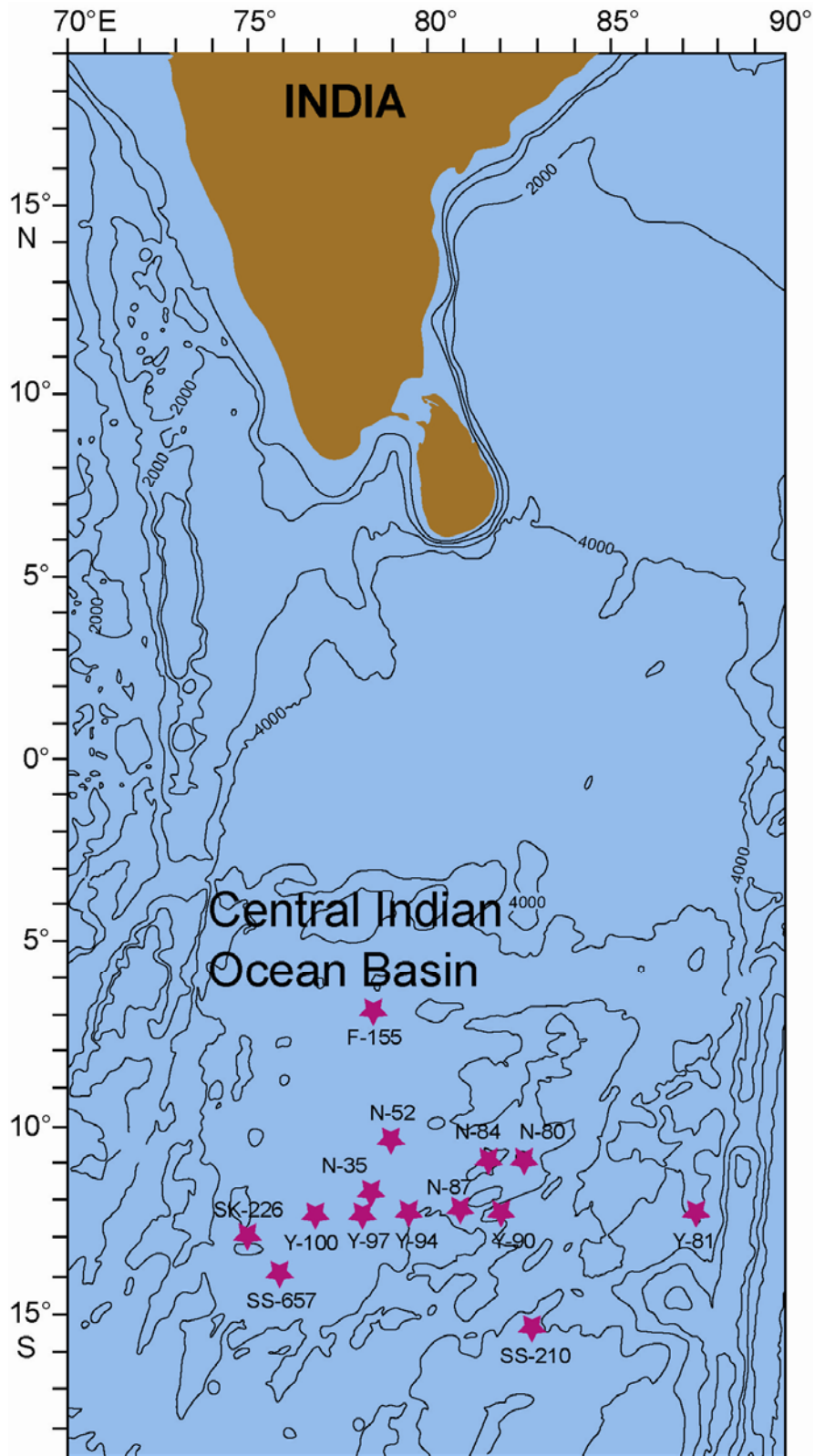


Fig.1

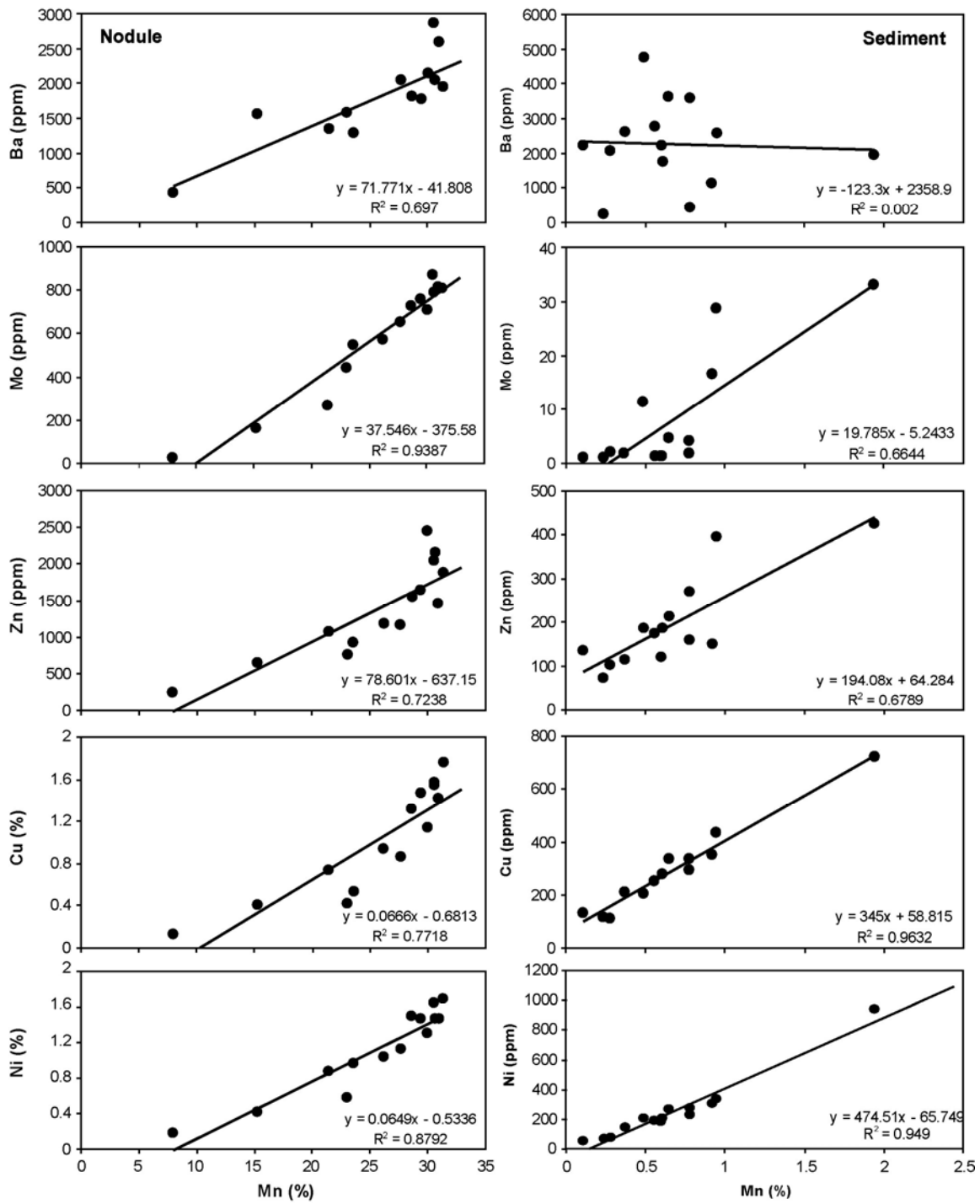


Fig.2



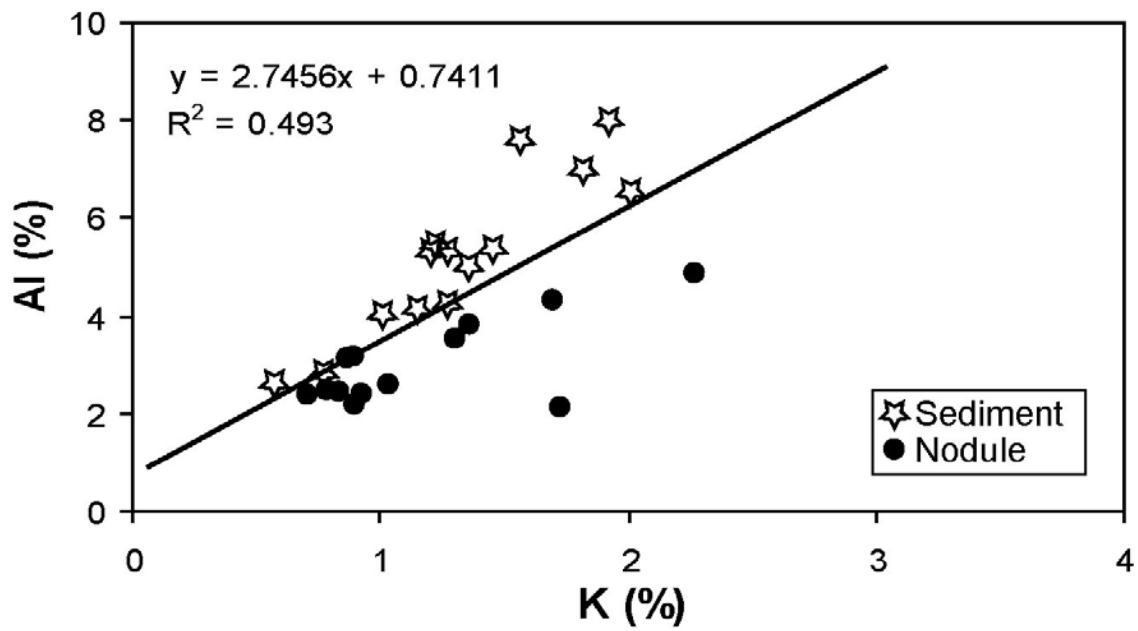
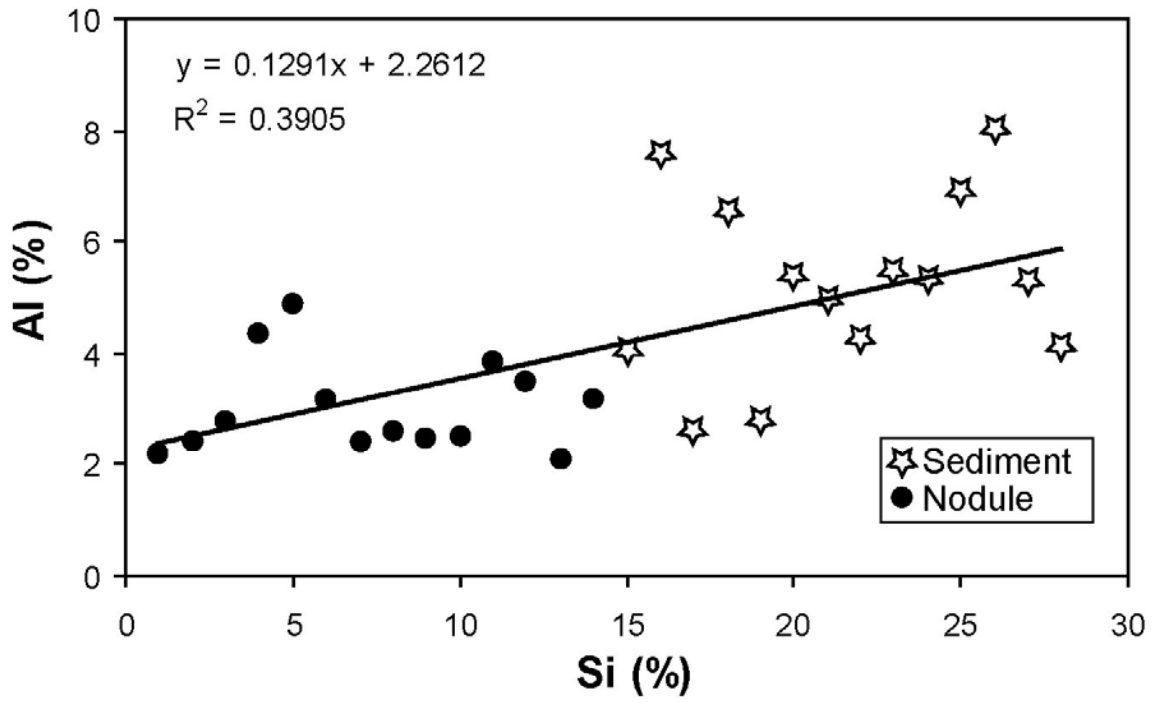


Fig.3

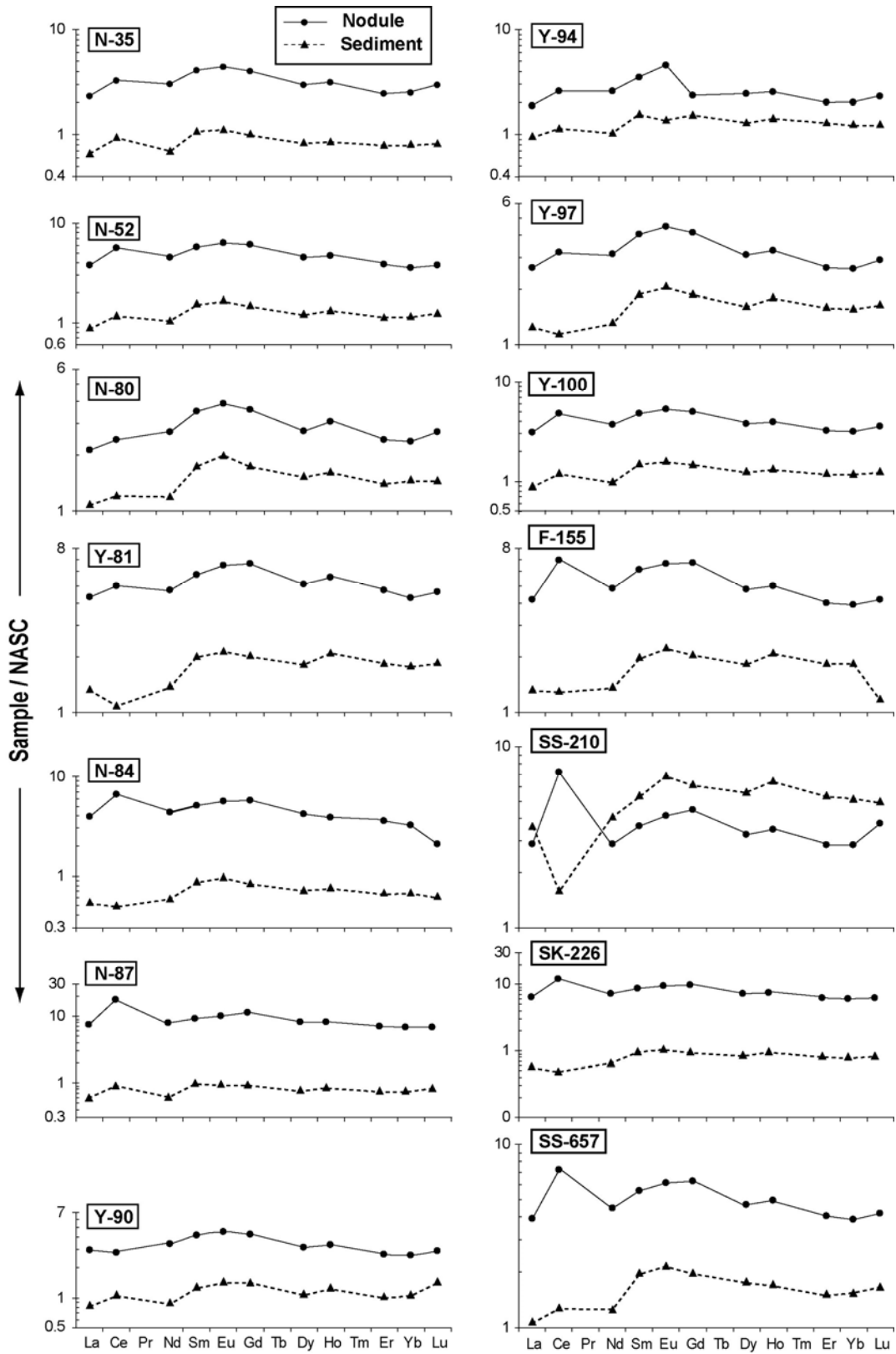


Fig.4

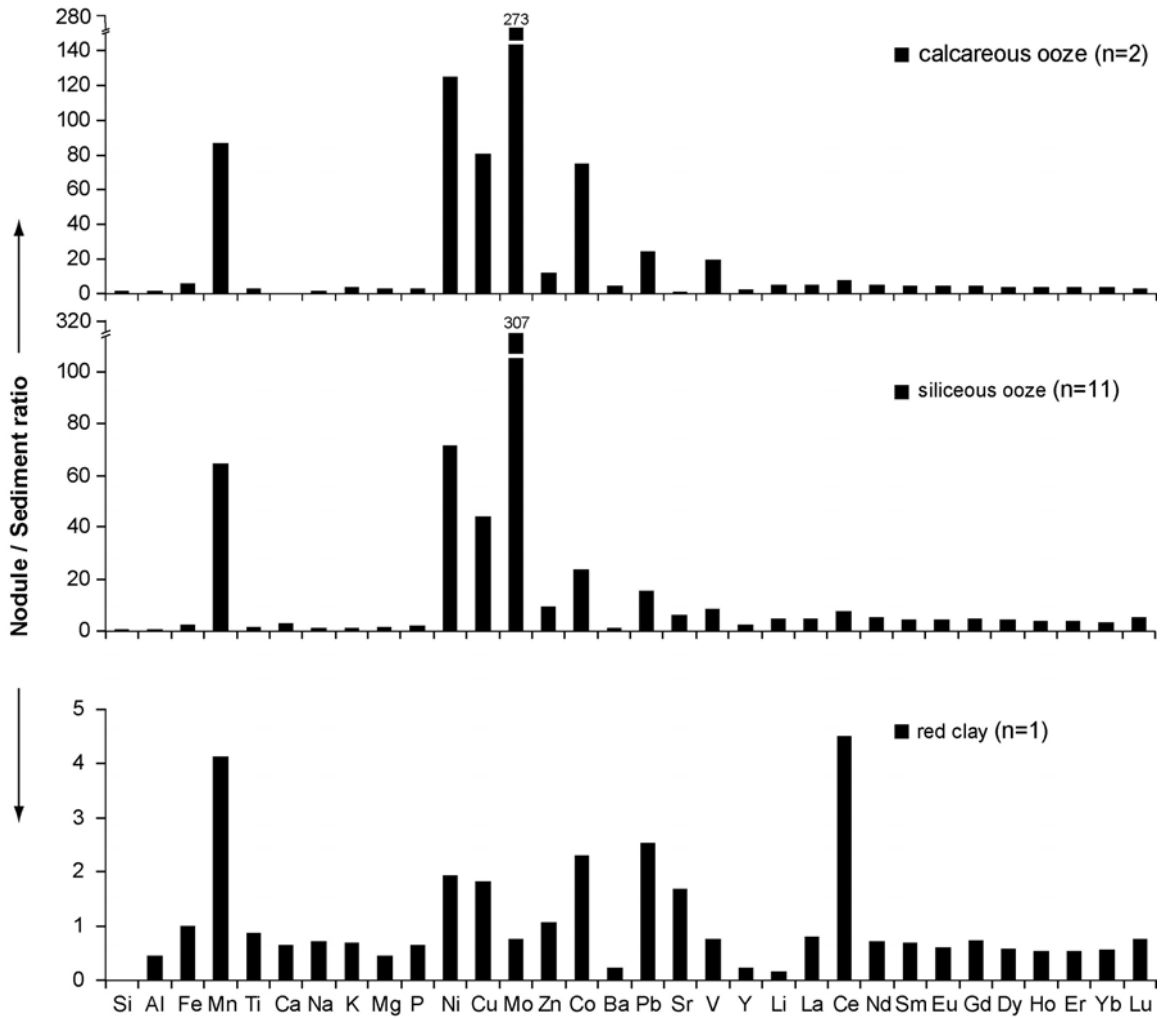


Fig. 5

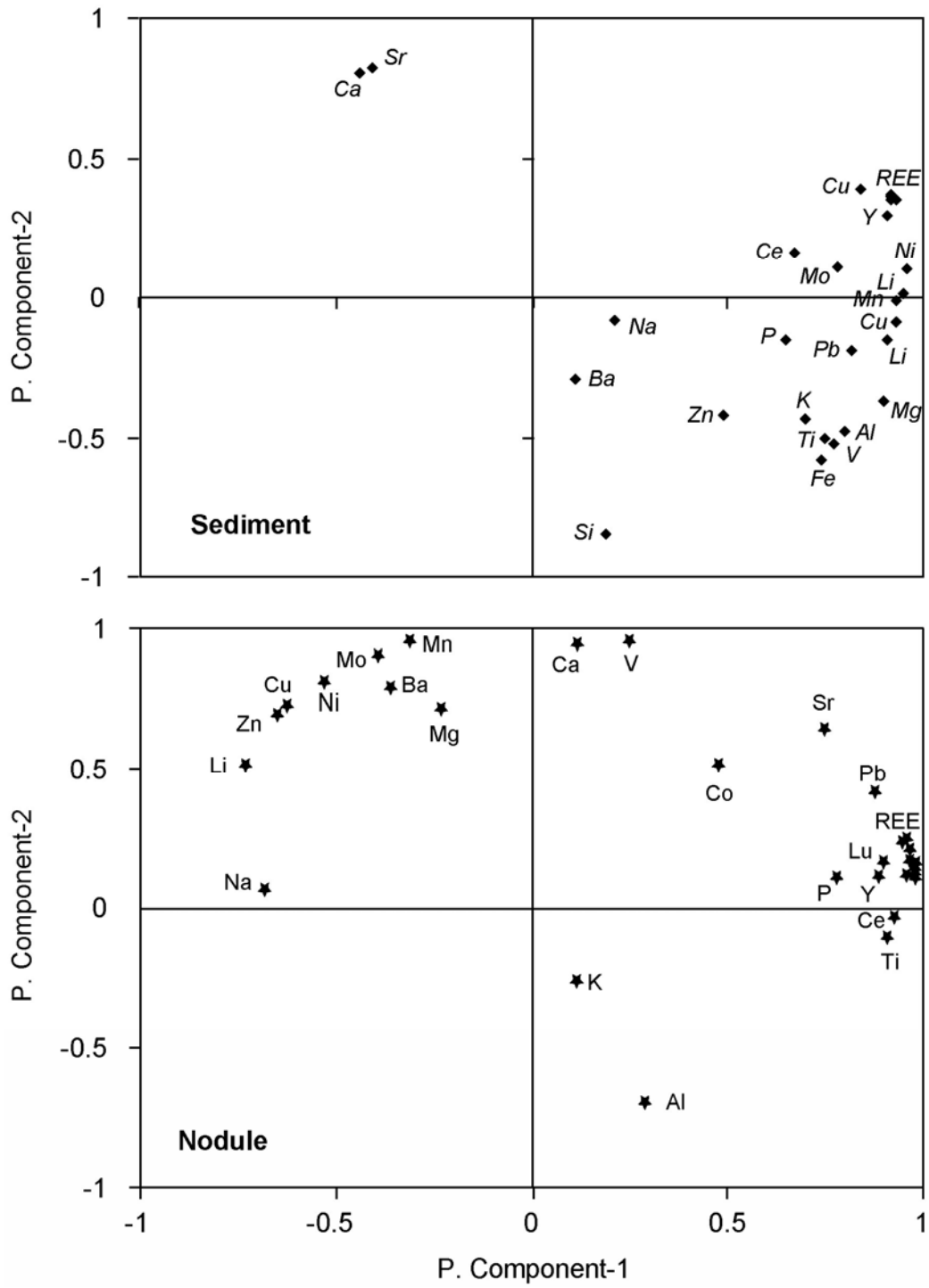


Fig.6



Table.2

	Al	Fe	Mn	Ti	Ca	Na	K	Mg	P	Ni	Cu	Mo	Zn	Co	Ba	Pb	Sr	V	Y	Li	La	Ce	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Lu
Al	1.00																														
Fe	0.30	1.00																													
Mn	-0.73	-0.19	1.00																												
Ti	0.42	<b>0.90</b>	-0.37	1.00																											
Ca	-0.49	0.23	<b>0.86</b>	0.04	1.00																										
Na	0.09	-0.57	0.27	-0.63	0.14	1.00																									
K	<b>0.50</b>	0.13	-0.29	0.28	-0.17	-0.15	1.00																								
Mg	-0.28	-0.07	<b>0.78</b>	-0.25	<b>0.67</b>	0.24	0.04	1.00																							
P	<b>0.60</b>	<b>0.81</b>	-0.21	<b>0.77</b>	0.20	-0.30	0.39	0.15	1.00																						
Ni	-0.75	-0.43	<b>0.94</b>	-0.58	<b>0.66</b>	0.35	-0.33	<b>0.76</b>	-0.38	1.00																					
Cu	-0.72	-0.52	<b>0.88</b>	-0.70	<b>0.54</b>	0.43	-0.32	<b>0.73</b>	-0.47	<b>0.97</b>	1.00																				
Mo	-0.82	-0.28	<b>0.97</b>	-0.42	<b>0.76</b>	0.23	-0.33	<b>0.70</b>	-0.37	<b>0.95</b>	<b>0.90</b>	1.00																			
Zn	-0.67	-0.57	<b>0.85</b>	-0.72	<b>0.62</b>	<b>0.57</b>	-0.39	<b>0.56</b>	-0.51	<b>0.87</b>	<b>0.87</b>	0.84	1.00																		
Co	-0.14	<b>0.54</b>	0.34	<b>0.55</b>	<b>0.55</b>	-0.40	0.44	0.35	0.43	0.11	0.02	0.28	-0.12	1.00																	
Ba	-0.60	-0.23	<b>0.83</b>	-0.39	<b>0.70</b>	0.34	0.03	<b>0.62</b>	-0.22	<b>0.79</b>	<b>0.77</b>	<b>0.84</b>	<b>0.75</b>	0.37	1.00																
Pb	-0.03	<b>0.91</b>	0.12	<b>0.78</b>	0.49	-0.59	-0.11	0.11	<b>0.70</b>	-0.11	-0.26	0.04	-0.28	<b>0.55</b>	-0.05	1.00															
Sr	-0.20	<b>0.81</b>	0.37	<b>0.63</b>	<b>0.72</b>	-0.43	-0.03	0.27	<b>0.60</b>	0.09	-0.03	0.27	-0.04	<b>0.73</b>	0.27	<b>0.92</b>	1.00														
V	-0.57	0.36	<b>0.82</b>	0.20	<b>0.92</b>	-0.12	-0.14	<b>0.64</b>	0.21	<b>0.64</b>	<b>0.51</b>	<b>0.77</b>	0.46	<b>0.70</b>	<b>0.68</b>	<b>0.61</b>	<b>0.80</b>	1.00													
Y	0.40	<b>0.89</b>	-0.16	<b>0.76</b>	0.27	-0.41	0.25	0.05	<b>0.92</b>	-0.38	-0.45	-0.33	-0.47	0.47	-0.19	<b>0.81</b>	<b>0.75</b>	0.30	1.00												
Li	-0.61	-0.68	<b>0.70</b>	-0.79	0.46	<b>0.63</b>	-0.37	0.34	-0.65	0.72	<b>0.74</b>	<b>0.69</b>	<b>0.95</b>	-0.22	<b>0.65</b>	-0.45	-0.20	0.25	-0.60	1.00											
La	0.18	<b>0.95</b>	-0.22	<b>0.84</b>	0.19	-0.63	0.01	-0.21	<b>0.72</b>	-0.44	-0.52	-0.30	-0.53	0.45	-0.28	<b>0.90</b>	<b>0.80</b>	0.31	<b>0.88</b>	-0.63	1.00										
Ce	0.15	<b>0.87</b>	-0.34	<b>0.83</b>	0.04	-0.64	-0.05	-0.45	<b>0.53</b>	-0.56	-0.62	-0.38	-0.60	0.40	-0.35	<b>0.78</b>	<b>0.69</b>	0.18	<b>0.72</b>	-0.62	<b>0.94</b>	1.00									
Nd	0.11	<b>0.95</b>	-0.12	<b>0.83</b>	0.29	-0.62	-0.01	-0.12	<b>0.72</b>	-0.35	-0.45	-0.21	-0.45	0.49	-0.19	<b>0.94</b>	<b>0.86</b>	0.41	<b>0.89</b>	-0.57	<b>0.99</b>	<b>0.91</b>	1.00								
Sm	0.07	<b>0.94</b>	-0.08	<b>0.82</b>	0.33	-0.62	-0.04	-0.11	<b>0.71</b>	-0.31	-0.42	-0.17	-0.42	0.50	-0.17	<b>0.96</b>	<b>0.88</b>	0.45	<b>0.87</b>	-0.54	<b>0.98</b>	<b>0.90</b>	<b>1.00</b>	1.00							
Eu	0.08	<b>0.93</b>	-0.08	<b>0.81</b>	0.34	-0.60	-0.04	-0.13	<b>0.70</b>	-0.32	-0.44	-0.18	-0.40	0.49	-0.17	<b>0.95</b>	<b>0.87</b>	0.43	<b>0.87</b>	-0.50	<b>0.98</b>	<b>0.90</b>	<b>0.99</b>	<b>1.00</b>	1.00						
Gd	0.16	<b>0.95</b>	-0.20	<b>0.85</b>	0.19	-0.66	0.01	-0.17	<b>0.72</b>	-0.41	-0.50	-0.28	-0.55	0.47	-0.27	<b>0.92</b>	<b>0.81</b>	0.34	<b>0.88</b>	-0.66	<b>0.99</b>	<b>0.93</b>	<b>0.99</b>	<b>0.98</b>	<b>0.97</b>	1.00					
Dy	0.14	<b>0.94</b>	-0.17	<b>0.83</b>	0.24	-0.64	0.00	-0.17	<b>0.73</b>	-0.39	-0.49	-0.26	-0.50	0.48	-0.25	<b>0.92</b>	<b>0.83</b>	0.36	<b>0.89</b>	-0.61	<b>0.99</b>	<b>0.92</b>	<b>0.99</b>	<b>0.99</b>	<b>0.99</b>	<b>0.99</b>	<b>0.99</b>	<b>0.99</b>	1.00		
Ho	0.11	<b>0.92</b>	-0.14	<b>0.82</b>	0.25	-0.66	-0.01	-0.13	<b>0.73</b>	-0.36	-0.46	-0.24	-0.49	0.49	-0.25	<b>0.92</b>	<b>0.83</b>	0.37	<b>0.89</b>	-0.60	<b>0.98</b>	<b>0.90</b>	<b>0.98</b>	<b>0.98</b>	<b>0.98</b>	<b>0.98</b>	<b>0.98</b>	<b>0.98</b>	<b>0.98</b>	1.00	
Er	0.17	<b>0.93</b>	-0.19	<b>0.83</b>	0.22	-0.63	0.02	-0.17	<b>0.74</b>	-0.41	-0.50	-0.29	-0.52	0.48	-0.27	<b>0.90</b>	<b>0.81</b>	0.33	<b>0.91</b>	-0.62	<b>0.99</b>	<b>0.92</b>	<b>0.99</b>	<b>0.98</b>	<b>0.98</b>	<b>0.99</b>	<b>1.00</b>	<b>1.00</b>	1.00		
Yb	0.12	<b>0.93</b>	-0.17	<b>0.83</b>	0.23	-0.65	-0.01	-0.18	<b>0.71</b>	-0.40	-0.49	-0.26	-0.51	0.49	-0.25	<b>0.91</b>	<b>0.82</b>	0.35	<b>0.88</b>	-0.61	<b>0.99</b>	<b>0.93</b>	<b>0.99</b>	<b>0.98</b>	<b>0.98</b>	<b>0.99</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	1.00	
Lu	-0.05	<b>0.79</b>	-0.13	<b>0.75</b>	0.20	-0.72	-0.14	-0.22	<b>0.55</b>	-0.32	-0.42	-0.19	-0.45	0.44	-0.27	<b>0.85</b>	<b>0.74</b>	0.34	<b>0.74</b>	-0.54	<b>0.91</b>	<b>0.88</b>	<b>0.90</b>	<b>0.91</b>	<b>0.90</b>	<b>0.92</b>	<b>0.93</b>	<b>0.95</b>	<b>0.93</b>	<b>0.95</b>	1.00

Table.3.

	Si	Al	Fe	Mn	Ti	Ca	Na	K	Mg	P	Ni	Cu	Mo	Zn	Co	Ba	Pb	Sr	V	Y	Li	La	Ce	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Lu			
Si	1.00																																		
Al	0.47	1.00																																	
Fe	<b>0.60</b>	<b>0.86</b>	1.00																																
Mn	0.13	<b>0.71</b>	<b>0.74</b>	1.00																															
Ti	0.48	<b>0.94</b>	<b>0.91</b>	<b>0.68</b>	1.00																														
Ca	-0.88	<b>-0.65</b>	-0.74	-0.37	-0.60	1.00																													
Na	0.01	0.27	0.07	0.09	0.24	-0.32	1.00																												
K	0.44	<b>0.91</b>	<b>0.67</b>	<b>0.53</b>	<b>0.74</b>	-0.67	0.40	1.00																											
Mg	0.43	<b>0.88</b>	<b>0.92</b>	<b>0.87</b>	<b>0.87</b>	-0.68	0.23	<b>0.74</b>	1.00																										
P	0.04	<b>0.71</b>	<b>0.58</b>	<b>0.61</b>	<b>0.69</b>	-0.24	0.18	<b>0.61</b>	<b>0.59</b>	1.00																									
Ni	0.09	<b>0.69</b>	<b>0.68</b>	<b>0.97</b>	<b>0.62</b>	-0.33	0.08	<b>0.57</b>	<b>0.85</b>	<b>0.56</b>	1.00																								
Cu	0.24	<b>0.73</b>	<b>0.77</b>	<b>0.98</b>	<b>0.69</b>	-0.46	0.05	<b>0.56</b>	<b>0.90</b>	<b>0.58</b>	<b>0.96</b>	1.00																							
Mo	0.13	<b>0.52</b>	0.47	<b>0.82</b>	0.48	-0.24	0.02	0.41	<b>0.67</b>	0.36	<b>0.81</b>	<b>0.82</b>	1.00																						
Zn	0.50	<b>0.52</b>	<b>0.53</b>	<b>0.55</b>	0.45	-0.48	-0.32	0.40	<b>0.59</b>	0.29	0.49	<b>0.64</b>	<b>0.65</b>	1.00																					
Co	0.14	<b>0.74</b>	<b>0.75</b>	<b>0.97</b>	<b>0.71</b>	-0.36	0.10	<b>0.56</b>	<b>0.85</b>	<b>0.62</b>	<b>0.97</b>	<b>0.94</b>	<b>0.72</b>	0.44	1.00																				
Ba	0.37	0.21	0.16	-0.04	0.02	-0.40	-0.20	0.42	<b>0.16</b>	<b>-0.02</b>	0.02	0.03	0.03	0.39	-0.07	1.00																			
Pb	0.24	<b>0.69</b>	<b>0.79</b>	<b>0.87</b>	<b>0.63</b>	-0.46	-0.09	<b>0.55</b>	<b>0.83</b>	<b>0.56</b>	<b>0.85</b>	<b>0.87</b>	<b>0.60</b>	<b>0.63</b>	<b>0.88</b>	0.21	1.00																		
Sr	-0.87	-0.65	-0.72	-0.35	-0.60	<b>0.98</b>	-0.33	-0.66	-0.65	-0.25	-0.31	-0.44	-0.22	-0.45	-0.36	-0.29	-0.44	1.00																	
V	<b>0.50</b>	<b>0.90</b>	<b>0.93</b>	<b>0.75</b>	<b>0.96</b>	-0.67	0.28	<b>0.69</b>	<b>0.91</b>	<b>0.73</b>	<b>0.67</b>	<b>0.77</b>	<b>0.51</b>	<b>0.50</b>	<b>0.74</b>	-0.01	<b>0.69</b>	-0.67	1.00																
Y	-0.11	<b>0.64</b>	<b>0.54</b>	<b>0.86</b>	<b>0.54</b>	-0.13	0.10	<b>0.57</b>	<b>0.70</b>	<b>0.59</b>	<b>0.93</b>	<b>0.82</b>	<b>0.67</b>	0.28	<b>0.92</b>	0.01	<b>0.78</b>	-0.12	<b>0.53</b>	1.00															
Li	0.26	<b>0.91</b>	<b>0.80</b>	<b>0.82</b>	<b>0.89</b>	-0.43	0.24	<b>0.75</b>	<b>0.86</b>	<b>0.72</b>	<b>0.83</b>	<b>0.80</b>	<b>0.60</b>	0.36	<b>0.89</b>	-0.04	<b>0.72</b>	-0.44	<b>0.85</b>	<b>0.84</b>	1.00														
La	-0.07	<b>0.57</b>	0.46	<b>0.81</b>	<b>0.49</b>	-0.16	0.17	<b>0.53</b>	<b>0.69</b>	<b>0.50</b>	<b>0.90</b>	<b>0.79</b>	<b>0.76</b>	0.31	<b>0.83</b>	0.10	<b>0.65</b>	-0.11	0.49	<b>0.93</b>	<b>0.77</b>	1.00													
Ce	0.12	0.48	0.37	<b>0.50</b>	<b>0.51</b>	-0.32	<b>0.54</b>	0.45	<b>0.57</b>	0.41	<b>0.53</b>	<b>0.50</b>	<b>0.52</b>	0.13	0.48	0.05	<b>0.23</b>	-0.23	<b>0.54</b>	0.47	<b>0.58</b>	<b>0.71</b>	1.00												
Nd	-0.07	<b>0.56</b>	0.47	<b>0.81</b>	<b>0.50</b>	-0.15	0.18	<b>0.52</b>	<b>0.69</b>	<b>0.51</b>	<b>0.90</b>	<b>0.79</b>	<b>0.75</b>	0.29	<b>0.85</b>	0.06	<b>0.66</b>	-0.11	<b>0.50</b>	<b>0.93</b>	<b>0.78</b>	<b>1.00</b>	<b>0.71</b>	1.00											
Sm	-0.07	<b>0.56</b>	0.47	<b>0.81</b>	<b>0.50</b>	-0.17	0.20	<b>0.52</b>	<b>0.69</b>	<b>0.53</b>	<b>0.89</b>	<b>0.79</b>	<b>0.74</b>	0.28	<b>0.84</b>	0.07	<b>0.65</b>	-0.12	<b>0.51</b>	<b>0.92</b>	<b>0.78</b>	<b>1.00</b>	<b>0.73</b>	<b>1.00</b>	1.00										
Eu	-0.10	<b>0.55</b>	0.47	<b>0.83</b>	0.49	-0.13	0.17	<b>0.49</b>	<b>0.68</b>	<b>0.54</b>	<b>0.91</b>	<b>0.80</b>	<b>0.74</b>	0.28	<b>0.86</b>	0.04	<b>0.67</b>	-0.09	<b>0.50</b>	<b>0.94</b>	<b>0.78</b>	<b>0.99</b>	<b>0.70</b>	<b>1.00</b>	<b>1.00</b>	1.00									
Gd	-0.08	<b>0.56</b>	0.46	<b>0.82</b>	0.49	-0.16	0.19	<b>0.51</b>	<b>0.69</b>	<b>0.51</b>	<b>0.90</b>	<b>0.79</b>	<b>0.74</b>	0.28	<b>0.85</b>	0.06	<b>0.66</b>	-0.12	<b>0.50</b>	<b>0.93</b>	<b>0.77</b>	<b>1.00</b>	<b>0.71</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>				
Dy	-0.09	<b>0.55</b>	0.46	<b>0.81</b>	0.48	-0.15	0.18	<b>0.51</b>	<b>0.68</b>	<b>0.52</b>	<b>0.90</b>	<b>0.79</b>	<b>0.73</b>	0.28	<b>0.84</b>	0.07	<b>0.67</b>	-0.11	0.49	<b>0.93</b>	<b>0.77</b>	<b>1.00</b>	<b>0.70</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>			
Ho	-0.08	<b>0.57</b>	0.47	<b>0.82</b>	0.49	-0.16	0.17	<b>0.54</b>	<b>0.69</b>	<b>0.51</b>	<b>0.91</b>	<b>0.80</b>	<b>0.74</b>	0.30	<b>0.85</b>	0.09	<b>0.68</b>	-0.12	0.49	<b>0.94</b>	<b>0.78</b>	<b>1.00</b>	<b>0.68</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>			
Er	-0.08	<b>0.57</b>	0.47	<b>0.81</b>	0.49	-0.16	0.17	<b>0.54</b>	<b>0.70</b>	<b>0.51</b>	<b>0.90</b>	<b>0.80</b>	<b>0.75</b>	0.30	<b>0.84</b>	0.10	<b>0.67</b>	-0.12	0.49	<b>0.94</b>	<b>0.77</b>	<b>1.00</b>	<b>0.69</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>		
Yb	-0.09	<b>0.57</b>	0.46	<b>0.81</b>	0.49	-0.15	0.18	0.53	<b>0.69</b>	<b>0.52</b>	<b>0.90</b>	<b>0.79</b>	<b>0.74</b>	0.29	<b>0.83</b>	0.10	<b>0.66</b>	-0.11	0.49	<b>0.93</b>	<b>0.77</b>	<b>1.00</b>	<b>0.70</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>	<b>1.00</b>		
Lu	-0.06	0.44	0.36	<b>0.78</b>	0.35	-0.14	0.20	0.39	<b>0.56</b>	0.37	<b>0.85</b>	<b>0.72</b>	<b>0.73</b>	0.25	<b>0.82</b>	-0.01	<b>0.63</b>	-0.10	0.37	<b>0.88</b>	<b>0.68</b>	<b>0.91</b>	<b>0.60</b>	<b>0.92</b>	<b>0.92</b>	<b>0.92</b>	<b>0.93</b>	<b>0.92</b>	<b>0.92</b>	<b>0.91</b>	0.91	1.00			

Table.4.

Element	PC-1	PC-2	PC-3
Al	0.29	-0.71	<b>-0.52</b>
Fe	<b>0.96</b>	0.11	-0.12
Mn	-0.31	<b>0.95</b>	-0.03
Ti	<b>0.91</b>	-0.11	-0.18
Ca	0.12	<b>0.94</b>	-0.14
Na	-0.68	0.06	-0.20
K	0.12	-0.27	<b>-0.81</b>
Mg	-0.23	<b>0.71</b>	-0.48
P	<b>0.78</b>	0.00	<b>-0.51</b>
Ni	-0.53	<b>0.81</b>	0.02
Cu	-0.62	<b>0.72</b>	0.02
Mo	-0.39	<b>0.90</b>	0.06
Zn	-0.65	<b>0.69</b>	0.12
Co	0.48	<b>0.51</b>	-0.44
Ba	-0.36	<b>0.79</b>	-0.22
Pb	<b>0.88</b>	0.41	0.05
Sr	<b>0.75</b>	<b>0.64</b>	-0.05
V	0.25	<b>0.95</b>	-0.10
Y	<b>0.89</b>	0.11	-0.28
Li	-0.73	<b>0.51</b>	0.19
La	<b>0.98</b>	0.10	0.10
Ce	<b>0.93</b>	-0.04	0.26
Nd	<b>0.97</b>	0.20	0.08
Sm	<b>0.96</b>	0.24	0.11
Eu	<b>0.95</b>	0.23	0.11
Gd	<b>0.98</b>	0.11	0.09
Dy	<b>0.98</b>	0.15	0.10
Ho	<b>0.97</b>	0.17	0.10
Er	<b>0.98</b>	0.12	0.08
Yb	<b>0.98</b>	0.14	0.12
Lu	<b>0.90</b>	0.16	0.29
eigenvalue	17.60	8.26	2.17
variance %	56.76	26.66	7.00
Cum. variance	56.76	83.42	90.42



Table.5.

Element	PC-1	PC-2	PC-3
Si	0.19	-0.85	0.08
Al	<b>0.80</b>	-0.48	-0.13
Fe	<b>0.74</b>	-0.58	0.07
Mn	<b>0.93</b>	-0.01	0.18
Ti	<b>0.75</b>	-0.50	-0.17
Ca	-0.44	<b>0.80</b>	0.10
Na	0.21	-0.08	-0.87
K	<b>0.70</b>	-0.43	-0.24
Mg	<b>0.90</b>	-0.37	0.01
P	<b>0.65</b>	-0.15	-0.17
Ni	<b>0.96</b>	0.10	0.16
Cu	<b>0.93</b>	-0.09	0.23
Mo	<b>0.78</b>	0.11	0.26
Zn	0.49	-0.42	<b>0.61</b>
Co	<b>0.95</b>	0.01	0.11
Ba	0.11	-0.29	0.29
Pb	<b>0.82</b>	-0.19	0.37
Sr	-0.41	<b>0.82</b>	0.12
V	<b>0.77</b>	-0.52	-0.15
Y	<b>0.91</b>	0.29	0.06
Li	<b>0.91</b>	-0.15	-0.15
La	<b>0.92</b>	0.35	-0.01
Ce	<b>0.67</b>	0.16	-0.97
Nd	<b>0.92</b>	0.36	-0.03
Sm	<b>0.92</b>	0.35	-0.06
Eu	<b>0.92</b>	0.37	-0.02
Gd	<b>0.92</b>	0.36	-0.04
Dy	<b>0.92</b>	0.36	-0.03
Ho	<b>0.93</b>	0.35	-0.02
Er	<b>0.93</b>	0.35	-0.02
Yb	<b>0.92</b>	0.35	-0.03
Lu	<b>0.84</b>	0.39	0.01
Eigenvalue	20.07	5.20	2.01
% variance	62.72	16.25	6.27
cum variance	62.72	78.96	85.23

Table.6.

Element	R <sup>2</sup>
Si	-0.020
Al	0.002
Ti	0.005
K	0.049
Na	0.107
Mg	-0.192
Mn	-0.056
P	0.071
Sc	0.001
Ni	-0.197
Cu	0.051
Mo	0.092
Zn	0.073
Co	0.006
Pb	0.022
V	0.146
Y	-0.526
Li	0.119
La	0.072