

Trace elements in ferromanganese nodules from the Central Indian Ocean Basin

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ABSTRACT

Thirty-three bulk ferromanganese nodules from the sediment-water interface of siliceous sediment domain from the Central Indian Ocean Basin were analysed for fifty elements including six new (Be, As, Se, Sn, Sb and Bi) using Inductively Coupled Plasma– Mass Spectrometer. The Mn/Fe ratio and triangular plot (Fe-Mn- {Cu+Ni+Co x10}) suggest that ferromanganese nodules are of hydrogenetic, early diagenetic and diagenetic origin. In the ferromanganese nodules, Mo, Sb, Bi and As are highly enriched ~ 320, 160, 90 and 50 times compared to upper continental crust respectively. Majority of the elements such as Be, Sc, Ti, V, Co, As, Se, Sr, Y, Zr, Nb, Sn, REEs, Pb, Bi, P, Th, U, Hf and Ta are associated with Fe, whereas, Cu, Ni, Zn, Mo, Li, Ga, Sb, Mg and Cs are associated with Mn in the ferromanganese nodules. Redox proxies such as U/Th(0.14) and Mo/Mn (0.0019) ratio in the ferromanganese nodules suggest their formation under oxic conditions.

Keywords: Trace elements, Ferromanganese nodules, Central Indian Ocean Basin, hydrogenetic, early diagenetic, diagenetic, U/Th, Mo/Mn ratio.

1. Introduction

Ferromanganese nodules are concretions of manganese, iron and other transition metal oxides that form in marine and freshwater sedimentary environments worldwide. Ferromanganese nodules and crusts are of economic interest mainly due to the enrichment of number of metals such as Cu, Ni, Co, Mo and high field strength elements such as rare earth elements (REE), Ti, and Nb (Hein et al., 2013). During the last three decades, extensive research has been carried out by the National Institute of Oceanography, Goa, India on different scientific aspects of surface (sediment-water interface) and subsurface (buried) ferromanganese nodules from the Central Indian Ocean Basin (CIOB)(also named as Indian Ocean Nodule Field by Mukhopadhyay et al., 2008) to unravel their processes of formation. Most of the previous work on these ferromanganese nodules was focused on analysis of few common metals such as Mn, Fe, Cu, Ni, Zn, Co and Pb mainly to understand their economic potential and genesis (Jauhari and Pattan, 2000; Mukhopadhyay et al., 2008). With the availability of instruments like Inductively Coupled Plasma- Mass Spectrometer (ICP-MS), it is easier to analyse number of trace and ultra-trace elements with 3-4 ml of solution in 4-5 minutes with a better precision compared to Inductively Coupled Plasma-Optical Emission Spectrometer. Li (1982), Baturin (1988), and Hein et al., (2013) have analysed more than 50 elements in the ferromanganese nodules from Clarion Clipperton Zone (CCZ) and Peru Basin of Pacific Ocean and other ocean basins but no such analysis has been carried out for the CIOB nodules. However, Baturin and Dubinchuk (2010) analysed number of trace elements in five ferromanganese nodule`s (oxide layer and core) from the Indian Ocean, of which four nodules were from the southern part of Wharton Basin in the red clay sediment domain and one sample from siliceous sediment of CIOB. This report is intended to through light on number of trace and ultra-trace elements concentration in the surface ferromanganese nodules. In the present study a suite of thirty-three surface

ferromanganese nodules from CIOB (Figure 1) were analysed for fifty elements including major, minor, trace and ultra-trace elements using ICP-MS to understand their concentration, mechanism of formation, their sequestration from seawater and sediment pore fluids and their composition is compared with the nodules from CCZ and Peru Basin of Pacific Ocean. Six of the trace elements (Be, As, Se, Sn, Sb and Bi) concentration in the ferromanganese nodules have not been reported earlier.

2. Material and Methods

Thirty-three ferromanganese nodules from the siliceous sediment domain in the Central Indian Ocean Basin (Latitude: 13° S to 14° S and Longitude : 74°30' E to 75°30' E) were collected with the help of grab sampler during different cruises of a project “Polymetallic Nodules from CIOB” funded by the Ministry of Earth Sciences, Government of India. Water depth in the study area varies from 4450 m to 5250 m (Fig. 1). Most of the area lies in the water depth of ~ 5250 m and appears to be plain with the occurrence of isolated north-south oriented small seamounts and comparatively bigger seamount in the eastern part of study area. Most of the seamounts are of ~ 100 m height and circular to elliptical in shape. Representative bulk ferromanganese nodules from the above collection, were crushed, powdered in an agate mortar and oven dried at 110°C for twenty-four hours. 20 mg of finely powdered sample was weighed in a Teflon beaker, made wet with few drops of ultra pure water, then added 10 ml of acid mixture of HF+HClO₄+HNO₃ (7:3:1) heated on a hot plate till it became a paste. To this paste 2 ml of 1:1 HCl was added, heated on a hot plate till it dries. Then add 4 ml of 1:1 HNO₃, warm for 5-10 minutes. Subsequently, 1 ml of Rhodium was added as an internal standard and made to final volume of 100 ml with ultra pure water. Blanks, duplicate samples, international standard reference materials (P-1, A-1) and Indian Ocean standard (IO-1) were also digested and made solutions. All the acids used were of supra-pure and ultra-pure water was of 18.2 mega ohms. Chemical analysis has been carried out on Inductively Coupled Plasma- Mass Spectrometer (Thermo – X Series 2). Accuracy and precision of the chemical data is shown in Figure 2.

3. Results and discussion

Mn/Fe ratio is one of the important criteria in identifying the source of elements in the ferromanganese nodules. Mn/Fe ratio in the nodules varies from 1.4 to 7.6 suggesting hydrogenous, early diagenetic and diagenetic origin (Halbach et al., 1981; Jauhari 1987, 1989; Jauhari and Pattan, 2000). Of the thirty-three ferromanganese nodules, thirteen are of hydrogenetic, twelve early diagenetic and eight diagenetic origin. Ferromanganese nodules from the northern part of study area

(13°50'S) are diagenetic whereas, they are of early diagenetic and hydrogenetic origin in the southern part. At few locations, there is large variation in Mn/Fe ratio of 2.3 to 6.7 (eg: sample no. F6/308B and F6/308A) suggesting hydrogenetic and diagenetic processes occurring in a very closely spaced samples. This suggests there is large variability in the chemical composition of nodules. The origin of these ferromanganese nodules is also confirmed by the triangular diagram (Figure 3; Halbach et al., 1981). The combined Cu+Ni+Zn content which are of economic interest in these nodules varies from 1.26 % to 2.73% with an average of 2% (Table 1). Total rare earth elements (Σ REE) content varies from 400 to 1674 ppm with an average of 842 ppm and are within the range of 348 to 2098 ppm reported (Pattan and Banakar, 1993; Nath et al., 1992; Jauhari and Pattan, 2000; Mukhopadhyay et al., 2008). The highest REE content (1674 ppm) is associated with highest Fe (14.4%) but lowest Mn (20%). On the contrary, lowest REE content is (400 ppm) is associated with highest Mn (29%) but with lowest Fe (3.8 %). REE's are associated with combined phase of Fe+Ti+P ($r=0.96$, $n=33$) and is similar to the earlier observation (Pattan and Banakar, 1993, Pattan and Parthiban, 2006, 2007) suggesting REE's are sorbed onto a titanium-ferri-phosphate phase. Shale-normalized REE pattern shows a strong positive Ce-anomaly suggesting oxic depositional conditions with middle REE enrichment (hat type) which is the characteristic feature of Fe-Mn nodules (Fig. 4).

Despite, the relatively low and constant U content (3.3 $\mu\text{g/l}$) in the seawater (Ku et al., 1977), deep sea sediments and ferromanganese nodules have enriched in U nearly three order of magnitude than in the seawater (Kunzendorf et al., 1982; 1983). U content in the CIOB ferromanganese nodules varies from 3 to 5 ppm with an average of 3.6 ppm (Table 1). The mean U content is higher than buried nodules (2 ppm mean, $n=5$) from the siliceous ooze domain (Pattan and Parthiban, 2006) but lower than the buried nodules within the red clay sediments (5.8 ppm; mean, $n=7$) of CIOB (Pattan and Parthiban, 2007). The mean U content of CIOB nodules is nearly similar to that of nodules from MANOP sites of Pacific Ocean (3-5 ppm: Dymond et al., 1984), Peru Basin (3-5 ppm; Kunzendorf et al., 1983), Gulf of Cadiz (4 ppm; Gonzalez et al., 2012), and global mean of nodules (5 ppm; Table-2, Baturin, 1988). The nodules exposed to seawater have higher U and Fe content compared to that exposed to lower part of nodule surrounded with the sediment (Kunzendorf and Friedrich, 1976) and further showed decrease of U content from out layer to inner layers of nodule. The sediments from CIOB have an U content ranging from 0.93 ppm to 1.4 ppm with an average of 1.2 ppm (Pattan et al., 2005). This suggests that ferromanganese nodules are enriched nearly three times compared to sediments. There exist a strong positive correlation between U and Fe in both nodules and sediments from CIOB suggesting sorption of U onto Fe-oxyhydroxides during hydrogenetic process (Table 3)

Thorium content in the nodules varies from 16 to 52 ppm with an average of 30 ppm (Table 1 & 2) and is similar to the buried nodules from CIOB (35 ppm; Pattan and Parthiban, 2006, 2007) and mean global oceanic nodules of 30 ppm (Baturin, 1988). However, it is highly enriched compared to nodules of MANOP sites of Pacific Ocean (1-3 ppm: Dymond et al., 1984), Gulf of Cadiz (4 ppm: Gonzalez et al., 2012). Fe-Mn crusts from Northeast Pacific, Atlantic and Indian Ocean are relatively enriched in Th (50-52 ppm) compared to nodules (Hein et al., 2013). The enrichment of Th may be related to deep-water source and Asian dust plume (Hein et al., 2012). Th content of sediments from CIOB varies from 9.8 to 12.7 ppm with an average content of 11 ppm (Pattan et al., 2005) and is similar to that of upper continental crust (10.7 ppm; McLennan, 2001). This suggests that Th content in the nodules is enriched nearly three times more compared to the sediments and is comparable to U enrichment. Th in dissolved form is highly particle reactive with residence time of <100 years (Okubo et al., 2012). It shows strong positive correlation with Fe ($r = 0.90$) in both nodules and sediments suggesting removal by the hydrogenetic process (Table 3). On the contrary, Dymond et al., (1984) noticed in the MANOP sites of Pacific Ocean that ferromanganese nodule's bottom side were enriched with U and exhibit a strong positive correlation with Mn ($r=0.89$) suggesting suboxic conditions in the sediments. U enrichment at the bottom side of nodule could be linked to reduction of U^{+6} to more soluble U^{+4} . The absence of such a correlation in CIOB could be due to oxic nature of sediments. U/Th ratio in the marine sediments have been used to understand the depositional environments (Algeo et al., 2012). Jones and Manning (1994) suggested that a low U/Th ratio of < 0.75 is indicative of an oxic depositional environment. U/Th ratio of nodules varies from 0.09 to 0.22 with an average of 0.14 and is nearly similar to the sediments from the same basin (0.12) (Pattan et al., 2005) suggesting nodules and sediments are accumulating under oxic depositional conditions.

Molybdenum (Mo) concentration in the Earth's crust is very low (1.5 ppm; McLennan, 2001) and is conservative in oxic environments (Collier, 1985). The removal of Mo from the seawater to the bottom sediments is controlled largely by the redox conditions. Mo content in the ferromanganese nodules varies from 326 to 640 ppm with an average of 478 ppm (Table.1) and is lower than Clarion-Clipperton Zone (CCZ) Pacific Ocean of 590 ppm and Peru Basin (547 ppm) (Hein et al., 2013). Hydrogenetic nodules (Mn/Fe ratio < 2) have low Mo content whereas diagenetic nodules with high Mn/Fe ratio (> 5) have highest Mo content. This attests Mo association with Mn content in the nodules and is mostly stabilizing the todorokite structure. Mo shows a strong positive correlation with Mn ($r=0.70$) suggesting major portion of it is associated with diagenetic process (Table 3). Mo content in the CIOB sediments ranges from 1 to 22 ppm with an average of 10 ppm.

This high Mo content in the sediments could be due to presence of large abundance of manganese micronodules which are highly enriched in Mn content (Pattan, 1993) and shows positive correlation with Mn ($r = 0.57$). In the marine sediments, Mo is generally associated with Mn oxyhydroxide phase under oxidizing condition with nearly constant Mo/Mn ratio of 0.002 (Shimmiel and Price, 1986; Crusius et al., 1996; Tribovillard et al., 2006). Mo/Mn ratio in the ferromanganese nodules varies from 0.0016 to 0.002 with an average of 0.0019 suggesting their formation under oxic depositional conditions. Mo is enriched nearly 320 times compared to upper continental crust and its extraction from the nodules can be considered in future. In addition to Ce-anomalies, U/Th and Mo/Mn ratios in the ferromanganese nodules can also be used to understand their depositional conditions.

Tantalum (Ta) and Neobium (Nb) have their average upper continental crustal abundance of 1.5 ppm and 1.0 ppm respectively (McLennan, 2001). In the seawater both Nb and Ta exist as Nb(OH)_6^- , Nb(OH)_5 , and Ta(OH)_6^- , Ta(OH)_5 respectively (Cotton and Wilkinson, 1980; Turner et al., 1981) having residence time of ~5000-6000 y (Sohrin et al., 1998). Ta content in the CIOB nodules varies from 0.1 to 0.37 ppm with an average of 0.23 ppm (Table.1) and is nearly similar to the Pacific and Peru Basin nodules (Hein et al., 2013) but lower than upper continental crustal abundance (McLennan, 2001). Compared to Ta content, Nb concentration is enriched ranging from 9 to 30 ppm with an average of 19 ppm and is also enriched compared to upper continental crustal abundance (McLennan, 2001). Nb shows strong positive correlation with Fe ($r=0.90$) while, Ta shows a weak positive correlation with Fe ($r= 0.20$) suggesting their removal by sorption in the hydrogenetic process (Table 3).

Hafnium (Hf) content in the seawater is mainly controlled by weathering of continental crust and to some extent by hydrothermal contribution (Rickli et al., 2009). Hf is particle reactive and generally affected by scavenging process and its removal in the surface ocean leading its depletion relative to the deep oceans (Rickli et al., 2009). Hf content in the nodules varies from 2.5 to 7.8 ppm with an average of 4.6 ppm (Table 1) and compare well with nodules from CCZ of Pacific and Peru Basin (4.7 ppm) (Hein et al., 2013). Hf concentration in the buried nodules is nearly two times more than the surface nodules (8.5 ppm; Pattan and Parthiban, 2006; 2007). Hf in the nodules is associated with Fe ($r=0.94$) suggesting its sorption from the seawater during hydrogenetic process (Table 3 & Fig.5). Gallium (Ga) is present as Ga (III) in the seawater as Ga(OH)_3^0 and Ga(OH)_4^- (Savenko and Savenko, 2010) and its concentration varies from 0.00014 to 0.0042 ppm (Orion and Boyle, 1993). Ga content in the CIOB ferromanganese nodule varies from 18.3 to 29.2 ppm with a mean content of 22 ppm and is low compared to that Pacific Ocean-CCZ (36 ppm) and Peru Basin (32 ppm) (Hein et al., 2013) and even Fe-Mn crusts from Ninetyeast Ridge (14 ppm) of Northern Indian

Ocean (Hein et al., 2016). Ga in CIOB ferromanganese nodules is positively correlated with Mn ($r=0.53$) suggesting its removal by diagenetic process (Table 3).

Scandium (Sc) concentration in the water column shows nutrient like profile, it increases gradually from surface (0.00009 ppm) to the ocean floor (0.0009 ppm) in the Pacific Ocean (Hiroshi et al., 2007). Sc content in the CIOB ferromanganese nodules have an average content of 12.5 ppm and is similar to that of upper continental crustal value of 13 ppm (McLennan, 2001) and CCZ Pacific Ocean nodules (11 ppm) but slightly enriched compared to Peru Basin nodules (7 ppm) (Hein et al., 2013). Sc shows strong positive correlation with Fe ($r=0.78$) suggesting its removal by hydrogenetic process (Table. 3). In contrast, Sc in the Pacific Ocean nodules is associated with aluminosilicate phase (Li, 1982). Sc content in the CIOB sediments varies from 16 to 27 ppm with an average content of 23 ppm (Pattan unpublished data) indicating its enrichment compared to nodules and shows positive correlation with Ti ($r=0.54$) which is terrigenous representing element suggesting its source as detrital (Pattan and Jauhari, 2001). This indicates that source of Sc is different in both nodules and sediments of CIOB. As expected, most of the trace and ultra-trace elements except Sc are enriched in the nodules compared to the bottom sediments.

New trace elements

Arsenic (As) is ubiquitous element, toxic in nature, found in the atmosphere, soils, rocks, natural waters and organisms and toxic in nature. As content in the nodules varies from 37 to 118 ppm with an average of 73 ppm (Table 1) and is enriched ~ 50 times compared to upper continental crust (McLennan, 2001). Similar to As, Antimony (Sb) is also an element of environmental concern due to its toxicity. The dominant form of Sb (V) is $Sb(OH)_6$ and Sb (III) is $Sb(OH)_3$. Its concentration (0.2 ppm) in the upper continental crust is low (McLennan, 2001). Sb content in the CIOB nodules varies from 22 to 47 ppm with an average of 32 ppm (Table 1) and is enriched ~ 160 times compared to upper continental crustal value. As shows strong positive correlation with Fe ($r=0.94$) while, Sb shows good positive correlation with Mn ($r=0.59$) suggesting their sorption by hydrogenetic and diagenetic processes respectively (Fig.5).

Bismuth (Bi) concentration in the CIOB nodules varies from 4 to 22 ppm with an average of 12 ppm and is higher compared to global oceanic nodule 7 ppm (Baturin, 1988; Mckelvey et al., 1983) but lower than Atlantic (15 ppm) and North Pacific (18 ppm: Hein et al., 2016). CIOB nodules are enriched ~ 90 times as compared to upper continental crustal value of 127 ppb (McLennan, 2001). Bi shows a very strong positive correlation with Fe ($r =0.94$) suggesting its sorption by hydrogenetic process (Fig.5). Beryllium (Be) is highly particle reactive, its concentration in the

pelagic sediments is 2.6 ppm (Li and Schoonmaker, 2003). Be content in the seawater varies from 0.0002 to 0.0006 ppm (Winter, 2011) and its concentration increases from surface to deep water in North Pacific Ocean suggesting nutrient type behavior (Tazoe et al., 2014). Be content in the CIOB nodules varies from 1 to 6 ppm with an average of 2.9 ppm and is similar to that of upper continental crustal value of 3 ppm (McLennan, 2001). Be is enriched in CIOB ferromanganese nodules compared to CCZ Pacific (2 ppm) and Peru Basin (1.4 ppm) ferromanganese nodules (Hein et al., 2013). Be shows a strong positive correlation with Fe ($r=0.91$, Fig.5) reflecting its sorption from seawater through hydrogenetic process.

Selenium (Se) is a redox-sensitive element and its chemical behavior depends strongly on redox reactions. There exist three species of dissolved Selenium such as Selenite, Selenate and organic Selenide in the seawater (Cutter and Bruland, 1984). Se content in the CIOB ferromanganese nodules varies from 2.8 to 4.8 ppm with an average of 3.7 ppm (Table 1) and is enriched compared to that of nodules from CCZ of Pacific Ocean (0.72 ppm), Peru Basin (0.5 ppm) and even global nodule average (0.6 ppm) (Hein et al., 2013; Baturin, 1988) and 0.6 ppm for marine ferromanganese concretions from other basin (Takematsu et al., 1990). As ferromanganese nodules form under oxic conditions, therefore Se could be present as Se-VI in the nodules (Wen et al., 2014). Se shows strong positive correlation with Fe ($r=0.76$) suggesting its sorption during hydrogenetic process (Fig. 5). Tin (Sn) content in the seawater ranges from 0.1 to 2.21 $\mu\text{g/l}$ and occurs as Sn (IV) (Safaa A Abdel Ghani, 2015). The mean Sn content of CIOB ferromanganese nodules is 1.33 ppm and is lower than CCZ Pacific Ocean nodules (Hein et al., 2013) and shows strong positive correlation with Fe ($r=0.81$) suggesting its sorption from the seawater during hydrogenetic process (Fig.5).

In general, the chemical composition of ferromanganese nodules from CIOB are comparable to that from Clarion- Clipperton Zone of Pacific Ocean.

Enrichment factor (EF) has been calculated by dividing the mean concentration of each element with the upper crustal value of respective element (McLennan, 2001). There is a large variation of EF ranging from 0.07 to 430 (Fig.76) wherein Cu, Mn and Mo having maximum enrichment (~ 430) and minimum is with Se (0.07). Based on the values EF, nodules have been classified into four groups. Group-1, consists of elements such as Cu, Mn, Mo, Ni, Sb, Bi, Co, As, Pb, Zn and Li where EF varies from 10 to 430. Group-2 includes all the fourteen REE's, Y and P which have EF ranging from 4 to 10. Group-3 includes elements like Th, Ba, Fe, Sr, Mg, Zr, Nb,

Ga, U and Ca with EF varies from 1- 4. Group-4 includes Sc, Be, Ti, K, Al, Ta, Sn, V, Rb, Cr and Se which are depleted compared to upper crust and their EF varies from 0.1 to 1.

4. Conclusions

The present study reports fifty elements including six new trace elements in thirty-three ferromanganese nodules from CIOB. Elements such as Mo, Sb, Bi and As in the nodules are highly enriched compared to upper continental crust. Most of the trace elements such as Be, Sc, Ti, V, Co, As, Se, Sr, Y, Zr, Nb, Sn, REEs, Pb, Bi, P, Th, U, Hf and Ta are sorbed from the seawater during hydrogenetic process whereas, Cu, Ni, Zn, Mo, Li, Ga, Sb, and Mg are sourced from the sediment pore-fluids through diagenetic process into ferromanganese nodules. The chemical composition of CIOB ferromanganese nodules is comparable to that of CCZ of Pacific Ocean.

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Captions for the tables

Table 1. Major, minor and trace element concentration of ferromanganese nodules analysed on ICP-MS.

(Major elements concentration is expressed in %, and rest of the elements are in ppm)

Table 2. Comparison of mean chemical composition of ferromanganese nodules from CIOB, CCZ- Pacific Ocean, Peru Basin, global nodule and Earth's upper continental crustal values.

Table 3. Correlation coefficient (r) value of Mn and Fe with number of elements (n=33).

Table 1. Major, minor and trace element concentration of ferromanganese nodules analysed on ICP-MS. (Concentration of elements from Mn to Cu are in %, and rest of the elements are in ppm).

Element	AAS-12/ 15A	AAS-12/ 15B	AAS-12/ 16B	AAS-12/ 16C	AAS-15/ GR-118	F-6/ 291-B	F6/ 293-A	F-6/ 293-B	F-6/ 294-A	F-6/ 294-B	F-6/ 295-A	F-6/ 295-B
Mn (%)	<u>25.77</u>	<u>26.64</u>	<u>26.93</u>	<u>25.20</u>	<u>27.05</u>	<u>27.79</u>	<u>25.63</u>	<u>22.96</u>	<u>28.67</u>	<u>29.06</u>	<u>28.52</u>	<u>31.82</u>
Fe	<u>8.38</u>	<u>7.31</u>	<u>4.12</u>	<u>5.33</u>	<u>3.87</u>	<u>3.66</u>	<u>7.98</u>	<u>11.17</u>	<u>6.10</u>	<u>6.85</u>	<u>8.70</u>	<u>5.15</u>
Al	<u>2.87</u>	<u>2.38</u>	<u>1.98</u>	<u>1.87</u>	<u>1.79</u>	<u>1.99</u>	<u>1.69</u>	<u>3.40</u>	<u>2.61</u>	<u>2.15</u>	<u>3.11</u>	<u>2.24</u>
Mg	<u>2.39</u>	<u>2.54</u>	<u>1.93</u>	<u>1.90</u>	<u>1.82</u>	<u>1.78</u>	<u>1.87</u>	<u>2.10</u>	<u>2.61</u>	<u>2.50</u>	<u>2.79</u>	<u>2.64</u>
P	<u>0.42</u>	<u>0.44</u>	<u>0.30</u>	<u>0.22</u>	<u>0.23</u>	<u>0.33</u>	<u>0.50</u>	<u>0.40</u>	<u>0.37</u>	<u>0.41</u>	<u>0.51</u>	<u>0.40</u>
Ca	<u>3.68</u>	<u>3.63</u>	<u>2.29</u>	<u>1.92</u>	<u>2.01</u>	<u>2.27</u>	<u>2.37</u>	<u>4.14</u>	<u>3.54</u>	<u>3.34</u>	<u>4.13</u>	<u>3.37</u>
K	<u>0.91</u>	<u>0.85</u>	<u>1.36</u>	<u>1.15</u>	<u>1.24</u>	<u>1.32</u>	<u>1.19</u>	<u>0.89</u>	<u>0.96</u>	<u>0.85</u>	<u>0.92</u>	<u>0.96</u>
Ti	<u>0.23</u>	<u>0.19</u>	<u>0.17</u>	<u>0.17</u>	<u>0.17</u>	<u>0.17</u>	<u>0.25</u>	<u>0.32</u>	<u>0.16</u>	<u>0.20</u>	<u>0.22</u>	<u>0.16</u>
Co	<u>0.13</u>	<u>0.12</u>	<u>0.11</u>	<u>0.12</u>	<u>0.09</u>	<u>0.09</u>	<u>0.15</u>	<u>0.13</u>	<u>0.09</u>	<u>0.12</u>	<u>0.13</u>	<u>0.09</u>
Ni	<u>1.01</u>	<u>1.05</u>	<u>1.22</u>	<u>1.17</u>	<u>1.18</u>	<u>1.23</u>	<u>1.07</u>	<u>0.83</u>	<u>1.14</u>	<u>1.11</u>	<u>1.12</u>	<u>1.24</u>
Cu	<u>0.95</u>	<u>1.09</u>	<u>1.37</u>	<u>1.21</u>	<u>1.28</u>	<u>1.26</u>	<u>0.95</u>	<u>0.75</u>	<u>1.22</u>	<u>1.09</u>	<u>1.12</u>	<u>1.38</u>
Li (ppm)	<u>113</u>	<u>131</u>	<u>175</u>	<u>139</u>	<u>226</u>	<u>264</u>	<u>95</u>	<u>74</u>	<u>188</u>	<u>161</u>	<u>124</u>	<u>234</u>
Be	<u>2.60</u>	<u>2.19</u>	<u>1.83</u>	<u>2.21</u>	<u>1.72</u>	<u>1.18</u>	<u>3.26</u>	<u>3.64</u>	<u>1.83</u>	<u>2.34</u>	<u>2.44</u>	<u>1.47</u>
Sc	<u>12.22</u>	<u>9.92</u>	<u>11.11</u>	<u>10.89</u>	<u>10.82</u>	<u>8.08</u>	<u>11.06</u>	<u>14.87</u>	<u>12.31</u>	<u>10.63</u>	<u>12.92</u>	<u>8.37</u>
V	<u>75.7</u>	<u>130.4</u>	<u>180.5</u>	<u>205.4</u>	<u>155.3</u>	<u>217.7</u>	<u>302.3</u>	<u>355.2</u>	<u>94.1</u>	<u>184.6</u>	<u>249.7</u>	<u>209.1</u>
Cr	<u>6.43</u>	<u>5.01</u>	<u>7.99</u>	<u>7.84</u>	<u>6.85</u>	<u>8.28</u>	<u>5.33</u>	<u>13.13</u>	<u>8.19</u>	<u>6.78</u>	<u>8.82</u>	<u>21.67</u>
Zn	<u>864</u>	<u>1008</u>	<u>1474</u>	<u>1198</u>	<u>1576</u>	<u>1838</u>	<u>1567</u>	<u>1078</u>	<u>1351</u>	<u>1384</u>	<u>1184</u>	<u>1728</u>
Ga	<u>21.71</u>	<u>22.97</u>	<u>29.17</u>	<u>25.85</u>	<u>27.44</u>	<u>26.67</u>	<u>25.34</u>	<u>18.63</u>	<u>24.85</u>	<u>24.16</u>	<u>23.54</u>	<u>27.08</u>
As	<u>76.48</u>	<u>65.43</u>	<u>40.21</u>	<u>57.44</u>	<u>40.07</u>	<u>48.20</u>	<u>84.24</u>	<u>89.66</u>	<u>53.93</u>	<u>58.48</u>	<u>69.75</u>	<u>51.87</u>
Se	<u>3.27</u>	<u>3.25</u>	<u>3.23</u>	<u>3.46</u>	<u>2.80</u>	<u>3.50</u>	<u>3.72</u>	<u>4.38</u>	<u>3.50</u>	<u>3.67</u>	<u>4.23</u>	<u>3.63</u>
Rb	<u>15.32</u>	<u>13.81</u>	<u>17.01</u>	<u>14.30</u>	<u>17.91</u>	<u>21.03</u>	<u>11.12</u>	<u>17.02</u>	<u>18.20</u>	<u>14.46</u>	<u>15.93</u>	<u>17.61</u>
Sr	<u>633</u>	<u>581</u>	<u>610</u>	<u>547</u>	<u>578</u>	<u>511</u>	<u>728</u>	<u>790</u>	<u>556</u>	<u>638</u>	<u>635</u>	<u>554</u>
Y	<u>79.50</u>	<u>72.50</u>	<u>54.50</u>	<u>65.70</u>	<u>51.20</u>	<u>47.40</u>	<u>95.70</u>	<u>108.10</u>	<u>57.80</u>	<u>76.50</u>	<u>79.30</u>	<u>61.50</u>
Zr	<u>384</u>	<u>287</u>	<u>204</u>	<u>241</u>	<u>173</u>	<u>171</u>	<u>395</u>	<u>482</u>	<u>241</u>	<u>303</u>	<u>353</u>	<u>158</u>

Nb	<u>20.00</u>	<u>15.20</u>	<u>10.70</u>	<u>12.90</u>	<u>9.00</u>	<u>10.90</u>	<u>22.90</u>	<u>25.80</u>	<u>11.50</u>	<u>16.10</u>	<u>17.60</u>	<u>9.90</u>
Mo	<u>464</u>	<u>492</u>	<u>511</u>	<u>485</u>	<u>531</u>	<u>526</u>	<u>475</u>	<u>401</u>	<u>531</u>	<u>509</u>	<u>495</u>	<u>640</u>
Sn	<u>1.22</u>	<u>0.86</u>	<u>0.78</u>	<u>0.83</u>	<u>0.72</u>	<u>0.69</u>	<u>1.23</u>	<u>1.81</u>	<u>0.73</u>	<u>0.95</u>	<u>1.15</u>	<u>0.64</u>
Sb	<u>28.58</u>	<u>30.51</u>	<u>41.57</u>	<u>35.60</u>	<u>42.88</u>	<u>43.94</u>	<u>29.50</u>	<u>26.40</u>	<u>38.43</u>	<u>34.81</u>	<u>32.19</u>	<u>47.37</u>
Cs	<u>0.63</u>	<u>0.59</u>	<u>0.77</u>	<u>0.64</u>	<u>0.80</u>	<u>0.96</u>	<u>0.51</u>	<u>0.63</u>	<u>0.82</u>	<u>0.69</u>	<u>0.70</u>	<u>0.77</u>
Ba	<u>1229</u>	<u>1353</u>	<u>1365</u>	<u>1267</u>	<u>1204</u>	<u>1267</u>	<u>1367</u>	<u>1188</u>	<u>1321</u>	<u>1376</u>	<u>1426</u>	<u>1462</u>
Hf	<u>4.42</u>	<u>4.00</u>	<u>3.13</u>	<u>3.73</u>	<u>2.97</u>	<u>2.77</u>	<u>5.50</u>	<u>5.94</u>	<u>3.15</u>	<u>4.13</u>	<u>4.30</u>	<u>3.18</u>
Ta	<u>0.37</u>	<u>0.21</u>	<u>0.24</u>	<u>0.08</u>	<u>0.27</u>	<u>0.27</u>	<u>0.33</u>	<u>0.50</u>	<u>0.17</u>	<u>0.27</u>	<u>0.28</u>	<u>0.13</u>
Pb	<u>638</u>	<u>569</u>	<u>402</u>	<u>526</u>	<u>393</u>	<u>414</u>	<u>803</u>	<u>811</u>	<u>463</u>	<u>573</u>	<u>633</u>	<u>416</u>
Bj	<u>11.25</u>	<u>9.54</u>	<u>6.15</u>	<u>8.41</u>	<u>6.08</u>	<u>5.47</u>	<u>14.27</u>	<u>16.50</u>	<u>7.47</u>	<u>9.47</u>	<u>11.23</u>	<u>6.14</u>
Th	<u>27.93</u>	<u>22.84</u>	<u>15.97</u>	<u>22.13</u>	<u>16.21</u>	<u>16.36</u>	<u>33.45</u>	<u>34.38</u>	<u>17.51</u>	<u>23.08</u>	<u>25.81</u>	<u>14.14</u>
U	<u>3.53</u>	<u>3.18</u>	<u>2.84</u>	<u>3.13</u>	<u>2.97</u>	<u>2.80</u>	<u>4.00</u>	<u>4.07</u>	<u>2.91</u>	<u>3.23</u>	<u>3.42</u>	<u>3.13</u>
La	<u>107</u>	<u>95</u>	<u>78</u>	<u>90</u>	<u>75</u>	<u>63</u>	<u>137</u>	<u>152</u>	<u>85</u>	<u>103</u>	<u>108</u>	<u>76</u>
Ce	<u>420</u>	<u>352</u>	<u>232</u>	<u>295</u>	<u>209</u>	<u>199</u>	<u>495</u>	<u>568</u>	<u>260</u>	<u>336</u>	<u>370</u>	<u>236</u>
Pr	<u>31.10</u>	<u>28.00</u>	<u>23.00</u>	<u>26.80</u>	<u>22.40</u>	<u>19.30</u>	<u>38.80</u>	<u>40.90</u>	<u>24.40</u>	<u>30.10</u>	<u>31.10</u>	<u>22.40</u>
Nd	<u>121.40</u>	<u>108.80</u>	<u>89.60</u>	<u>104.80</u>	<u>87.20</u>	<u>76.70</u>	<u>148.70</u>	<u>158.30</u>	<u>94.00</u>	<u>116.00</u>	<u>120.70</u>	<u>89.30</u>
Sm	<u>28.51</u>	<u>25.65</u>	<u>21.17</u>	<u>25.06</u>	<u>20.78</u>	<u>18.53</u>	<u>34.89</u>	<u>36.56</u>	<u>21.86</u>	<u>27.26</u>	<u>28.54</u>	<u>21.09</u>
Eu	<u>7.11</u>	<u>6.40</u>	<u>5.23</u>	<u>6.11</u>	<u>5.02</u>	<u>4.63</u>	<u>8.60</u>	<u>8.84</u>	<u>5.34</u>	<u>6.68</u>	<u>6.92</u>	<u>5.20</u>
Gd	<u>29.23</u>	<u>26.32</u>	<u>19.94</u>	<u>24.14</u>	<u>19.18</u>	<u>17.64</u>	<u>35.90</u>	<u>38.53</u>	<u>20.74</u>	<u>27.37</u>	<u>28.25</u>	<u>19.52</u>
Tb	<u>4.55</u>	<u>4.10</u>	<u>3.25</u>	<u>3.92</u>	<u>3.09</u>	<u>2.88</u>	<u>5.61</u>	<u>6.01</u>	<u>3.28</u>	<u>4.26</u>	<u>4.46</u>	<u>3.20</u>
Dy	<u>24.46</u>	<u>22.22</u>	<u>17.39</u>	<u>20.93</u>	<u>16.32</u>	<u>15.42</u>	<u>30.40</u>	<u>32.68</u>	<u>17.61</u>	<u>23.30</u>	<u>24.01</u>	<u>17.40</u>
Ho	<u>4.42</u>	<u>4.00</u>	<u>3.13</u>	<u>3.73</u>	<u>2.97</u>	<u>2.77</u>	<u>5.50</u>	<u>5.94</u>	<u>3.15</u>	<u>4.13</u>	<u>4.30</u>	<u>3.18</u>
Er	<u>11.82</u>	<u>10.79</u>	<u>8.42</u>	<u>10.06</u>	<u>7.91</u>	<u>7.32</u>	<u>14.66</u>	<u>16.13</u>	<u>8.54</u>	<u>11.13</u>	<u>11.78</u>	<u>8.65</u>
Tm	<u>1.62</u>	<u>1.47</u>	<u>1.16</u>	<u>1.37</u>	<u>1.08</u>	<u>1.03</u>	<u>2.02</u>	<u>2.24</u>	<u>1.16</u>	<u>1.53</u>	<u>1.61</u>	<u>1.21</u>
Yb	<u>11.12</u>	<u>9.86</u>	<u>7.69</u>	<u>9.18</u>	<u>7.29</u>	<u>6.95</u>	<u>13.55</u>	<u>14.84</u>	<u>7.90</u>	<u>10.30</u>	<u>10.84</u>	<u>8.00</u>
Lu	<u>1.52</u>	<u>1.37</u>	<u>1.07</u>	<u>1.27</u>	<u>0.98</u>	<u>0.96</u>	<u>1.88</u>	<u>2.10</u>	<u>1.08</u>	<u>1.41</u>	<u>1.46</u>	<u>1.12</u>

Table 1 continued-----

Element	F-6/ 296-A	F6/ 296-B	F-6/ 298-B	F6/ 300-A	F6/ 300-B	F6/ 302-A	F6/ 302-B	F6/ 303-A	F6/ 303-B	F-6/ 304-A	F6/ 304-B	F6/ 305-A	F6/ 305-B
Mn (%)	<u>27.69</u>	<u>19.24</u>	<u>19.88</u>	<u>27.41</u>	<u>28.31</u>	<u>28.00</u>	<u>20.09</u>	<u>23.59</u>	<u>24.66</u>	<u>19.65</u>	<u>24.42</u>	<u>27.69</u>	<u>19.24</u>
Fe	<u>6.21</u>	<u>12.60</u>	<u>12.37</u>	<u>5.80</u>	<u>5.62</u>	<u>5.84</u>	<u>14.38</u>	<u>7.84</u>	<u>12.25</u>	<u>9.52</u>	<u>10.07</u>	<u>6.21</u>	<u>12.60</u>
Al	<u>3.11</u>	<u>3.08</u>	<u>2.54</u>	<u>2.16</u>	<u>2.25</u>	<u>1.90</u>	<u>2.13</u>	<u>3.35</u>	<u>2.00</u>	<u>3.23</u>	<u>2.03</u>	<u>3.11</u>	<u>3.08</u>
Mg	<u>2.87</u>	<u>1.74</u>	<u>1.61</u>	<u>2.22</u>	<u>2.45</u>	<u>2.19</u>	<u>1.64</u>	<u>2.51</u>	<u>1.91</u>	<u>1.70</u>	<u>1.96</u>	<u>2.87</u>	<u>1.74</u>
P	<u>0.68</u>	<u>0.45</u>	<u>0.34</u>	<u>0.25</u>	<u>0.29</u>	<u>0.44</u>	<u>0.43</u>	<u>0.27</u>	<u>0.60</u>	<u>0.50</u>	<u>0.32</u>	<u>0.68</u>	<u>0.45</u>
Ca	<u>3.65</u>	<u>3.76</u>	<u>3.31</u>	<u>2.72</u>	<u>3.52</u>	<u>2.61</u>	<u>3.65</u>	<u>3.81</u>	<u>3.74</u>	<u>3.06</u>	<u>3.37</u>	<u>3.65</u>	<u>3.76</u>
K	<u>1.35</u>	<u>1.42</u>	<u>1.28</u>	<u>1.17</u>	<u>1.36</u>	<u>1.31</u>	<u>1.72</u>	<u>1.13</u>	<u>1.23</u>	<u>1.71</u>	<u>1.26</u>	<u>1.35</u>	<u>1.42</u>
Ti	<u>0.20</u>	<u>0.36</u>	<u>0.35</u>	<u>0.18</u>	<u>0.17</u>	<u>0.18</u>	<u>0.42</u>	<u>0.23</u>	<u>0.37</u>	<u>0.32</u>	<u>0.31</u>	<u>0.20</u>	<u>0.36</u>
Co	<u>0.08</u>	<u>0.16</u>	<u>0.16</u>	<u>0.11</u>	<u>0.10</u>	<u>0.11</u>	<u>0.17</u>	<u>0.11</u>	<u>0.18</u>	<u>0.14</u>	<u>0.17</u>	<u>0.08</u>	<u>0.16</u>
Ni	<u>1.14</u>	<u>0.67</u>	<u>0.69</u>	<u>1.10</u>	<u>1.13</u>	<u>1.15</u>	<u>0.63</u>	<u>1.01</u>	<u>0.89</u>	<u>0.78</u>	<u>0.97</u>	<u>1.14</u>	<u>0.67</u>
Cu	<u>1.26</u>	<u>0.53</u>	<u>0.66</u>	<u>1.17</u>	<u>1.26</u>	<u>1.19</u>	<u>0.47</u>	<u>0.89</u>	<u>0.65</u>	<u>0.58</u>	<u>0.79</u>	<u>1.26</u>	<u>0.53</u>
Li (ppm)	<u>172</u>	<u>47</u>	<u>46</u>	<u>161</u>	<u>173</u>	<u>189</u>	<u>37</u>	<u>121</u>	<u>64</u>	<u>64</u>	<u>nd</u>	<u>172</u>	<u>47</u>
Be	<u>1.78</u>	<u>4.74</u>	<u>5.40</u>	<u>2.02</u>	<u>2.03</u>	<u>2.41</u>	<u>5.94</u>	<u>2.44</u>	<u>4.41</u>	<u>3.54</u>	<u>4.18</u>	<u>1.78</u>	<u>4.74</u>
Sc	<u>12.61</u>	<u>15.77</u>	<u>16.29</u>	<u>12.56</u>	<u>11.02</u>	<u>12.00</u>	<u>16.80</u>	<u>14.58</u>	<u>14.00</u>	<u>15.67</u>	<u>13.21</u>	<u>12.61</u>	<u>15.77</u>
V	<u>176.2</u>	<u>356.3</u>	<u>302.2</u>	<u>177.6</u>	<u>131.4</u>	<u>229.6</u>	<u>356.9</u>	<u>170.3</u>	<u>410.6</u>	<u>246.5</u>	<u>339.9</u>	<u>176.2</u>	<u>356.3</u>
Cr	<u>8.16</u>	<u>10.52</u>	<u>11.97</u>	<u>9.40</u>	<u>8.09</u>	<u>9.37</u>	<u>7.22</u>	<u>6.74</u>	<u>6.16</u>	<u>7.89</u>	<u>6.99</u>	<u>8.16</u>	<u>10.52</u>
Zn	<u>1415</u>	<u>683</u>	<u>706</u>	<u>1252</u>	<u>1238</u>	<u>1410</u>	<u>694</u>	<u>971</u>	<u>822</u>	<u>921</u>	<u>821</u>	<u>1415</u>	<u>683</u>
Ga	<u>24.69</u>	<u>19.14</u>	<u>19.96</u>	<u>26.88</u>	<u>27.74</u>	<u>28.23</u>	<u>18.72</u>	<u>21.21</u>	<u>21.57</u>	<u>19.15</u>	<u>23.20</u>	<u>24.69</u>	<u>19.14</u>
As	<u>45.10</u>	<u>116.20</u>	<u>88.83</u>	<u>58.89</u>	<u>46.67</u>	<u>66.89</u>	<u>118.60</u>	<u>66.93</u>	<u>105.80</u>	<u>94.68</u>	<u>94.03</u>	<u>45.10</u>	<u>116.20</u>
Se	<u>4.19</u>	<u>4.06</u>	<u>3.87</u>	<u>3.06</u>	<u>3.24</u>	<u>2.98</u>	<u>3.87</u>	<u>3.67</u>	<u>4.33</u>	<u>3.72</u>	<u>3.84</u>	<u>4.19</u>	<u>4.06</u>

Rb	17.84	17.68	13.88	16.20	16.99	15.03	10.57	18.94	10.04	21.17	10.90	17.84	17.68
Sr	599	824	837	564	565	595	933	632	908	685	818	599	824
Y	59.60	110.90	122.00	66.70	67.60	70.00	137.20	72.40	128.10	100.50	111.00	59.60	110.90
Zr	224	410	515	188	236	145	441	336	247	322	417	224	410
Nb	10.80	27.70	29.30	11.40	12.40	10.10	37.20	17.30	30.30	25.50	23.20	10.80	27.70
Mo	515	351	326	512	503	537	350	498	474	379	478	515	351
Sn	0.98	2.11	2.31	0.93	0.75	0.74	2.52	1.12	2.09	1.89	1.52	0.98	2.11
Sb	37.02	25.63	26.54	34.54	34.84	35.52	27.22	28.65	26.82	22.33	26.52	37.02	25.63
Cs	0.82	0.61	0.52	0.74	0.76	0.65	0.43	0.67	0.44	0.60	0.46	0.82	0.61
Ba	1436	1347	1513	1316	1386	1313	1287	1342	1446	1115	1495	1436	1347
Hf	3.30	6.07	6.89	3.68	3.77	3.68	7.79	4.03	7.23	5.66	6.28	3.30	6.07
Ta	0.17	0.18	0.17	0.04	0.10	0.02	0.17	0.37	0.15	0.08	0.11	0.17	0.18
Pb	439	922	912	512	490	513	1090	616	1051	789	913	439	922
Bi	7.18	15.29	15.58	8.59	8.51	8.68	22.49	11.11	21.14	16.80	18.13	7.18	15.29
Th	17.20	41.83	37.49	20.69	19.04	21.39	54.04	24.62	52.23	38.36	38.84	17.20	41.83
U	2.85	4.50	4.16	3.14	2.93	3.37	5.06	3.24	5.14	3.87	4.45	2.85	4.50
La	83	170	189	92	90	93	217	104	195	147	162	83	170
Ce	237	777	774	291	284	312	974	356	800	586	647	237	777
Pr	24.10	44.00	48.50	26.00	26.30	26.70	55.70	28.80	52.80	41.20	43.10	24.10	44.00
Nd	93.80	168.70	184.50	102.00	101.90	102.60	211.40	111.10	201.50	157.10	164.90	93.80	168.70
Sm	21.82	38.67	41.82	23.93	24.25	24.08	48.40	25.80	46.53	36.72	38.28	21.82	38.67
Eu	5.42	9.23	10.35	5.90	6.03	5.91	11.67	6.36	11.17	8.89	9.38	5.42	9.23
Gd	21.03	41.68	45.92	23.33	24.12	23.86	52.81	26.00	49.39	38.83	40.46	21.03	41.68
Tb	3.35	6.20	7.03	3.74	3.80	3.79	7.77	4.05	7.48	5.88	6.23	3.35	6.20
Dy	18.05	33.36	37.67	19.95	20.57	20.28	41.97	21.88	39.79	31.44	33.66	18.05	33.36
Ho	3.30	6.07	6.89	3.68	3.77	3.68	7.79	4.03	7.23	5.66	6.30	3.30	6.07
Er	8.84	16.29	18.73	9.89	9.96	9.92	20.47	10.65	19.31	15.28	16.87	8.84	16.29
Tm	1.23	2.24	2.61	1.34	1.36	1.37	2.85	1.46	2.67	2.08	2.34	1.23	2.24
Yb	8.26	15.35	17.74	8.97	9.02	9.21	19.39	9.83	17.99	14.13	15.77	8.26	15.35
Lu	1.11	2.19	2.50	1.19	1.26	1.25	2.78	1.33	2.51	1.96	2.22	1.11	2.19

Table 1 continued-----

Element	F-6/ 306-A	F6/ 306-B	F6/ 308-A	F6/ 308-B	F6/ 310-A	F-6/ 310-B	F6/ 311-A	F6/ 311-B	Mini -mum	Maxi -mum	Mean	STDEV
Mn (%)	21.00	21.86	30.75	24.06	25.40	24.60	27.44	22.64	19.24	31.82	25.40	3.29
Fe	10.27	9.48	4.59	10.42	11.57	7.70	7.95	11.57	3.66	14.38	7.97	3.00
Al	3.24	2.51	2.05	2.32	2.58	3.03	2.07	2.86	1.69	3.66	2.53	0.56
Mg	1.97	1.90	2.30	2.17	2.19	2.61	2.24	2.19	1.61	2.87	2.15	0.35
P	0.27	0.32	0.39	0.36	0.41	0.34	0.32	0.63	0.22	0.68	0.39	0.11
Ca	3.32	3.15	3.80	3.85	3.82	3.75	3.01	3.81	1.92	4.14	3.34	0.61
K	0.98	0.97	1.73	1.02	0.95	0.94	1.15	1.30	0.85	1.73	1.19	0.24
Ti	0.30	0.27	0.17	0.29	0.30	0.26	0.25	0.31	0.14	0.42	0.24	0.07
Co	0.14	0.14	0.09	0.16	0.16	0.12	0.13	0.15	0.08	0.18	0.12	0.03
Ni	0.88	0.91	1.21	0.93	0.91	1.04	1.12	0.89	0.63	1.24	1.01	0.17
Cu	0.66	0.76	1.43	0.74	0.73	1.03	1.04	0.75	0.47	1.43	0.98	0.27
Li (ppm)		76	220	76	75	127	118	75	37.00	264.00	134.87	64.58
Be	3.38	3.68	1.51	3.75	3.83	2.55	3.19	4.15	1.18	5.94	2.87	1.22
Sc	14.76	13.50	8.63	12.53	12.45	16.48	12.23	14.25	7.64	16.80	12.48	2.43
V	240.1	242.6	140.7	255.4	285.4	197.7	269.2	369.3	75.7	410.6	225.9	89.2
Cr	5.75	8.35	5.43	6.41	7.25	9.64	8.89	6.77	5.01	21.67	8.33	3.05

<u>Zn</u>	<u>746</u>	<u>805</u>	<u>1523</u>	<u>887</u>	<u>793</u>	<u>1081</u>	<u>1029</u>	<u>844</u>	<u>683</u>	<u>1838</u>	<u>1135</u>	<u>328</u>
<u>Ga</u>	<u>18.30</u>	<u>19.79</u>	<u>26.90</u>	<u>20.13</u>	<u>19.75</u>	<u>23.82</u>	<u>26.91</u>	<u>22.13</u>	<u>18.30</u>	<u>29.17</u>	<u>23.21</u>	<u>3.34</u>
<u>As</u>	<u>96.02</u>	<u>89.12</u>	<u>47.66</u>	<u>89.79</u>	<u>100.80</u>	<u>65.70</u>	<u>74.25</u>	<u>102.20</u>	<u>37.13</u>	<u>118.60</u>	<u>72.10</u>	<u>23.92</u>
<u>Se</u>	<u>4.77</u>	<u>3.94</u>	<u>3.26</u>	<u>4.04</u>	<u>4.28</u>	<u>3.95</u>	<u>3.67</u>	<u>4.25</u>	<u>2.80</u>	<u>4.77</u>	<u>3.70</u>	<u>0.47</u>
<u>Rb</u>	<u>18.79</u>	<u>13.15</u>	<u>15.96</u>	<u>14.41</u>	<u>11.74</u>	<u>20.13</u>	<u>13.32</u>	<u>12.74</u>	<u>10.04</u>	<u>46.64</u>	<u>17.07</u>	<u>6.82</u>
<u>Sr</u>	<u>725</u>	<u>715</u>	<u>532</u>	<u>762</u>	<u>791</u>	<u>572</u>	<u>674</u>	<u>766</u>	<u>473.00</u>	<u>933.00</u>	<u>661.77</u>	<u>121.31</u>
<u>Y</u>	<u>90.40</u>	<u>92.00</u>	<u>54.50</u>	<u>97.00</u>	<u>107.15</u>	<u>70.00</u>	<u>99.50</u>	<u>111.00</u>	<u>43.40</u>	<u>137.20</u>	<u>82.07</u>	<u>25.55</u>
<u>Zr</u>	<u>493</u>	<u>353</u>	<u>194</u>	<u>442</u>	<u>468</u>	<u>338</u>	<u>323</u>	<u>271</u>	<u>136.20</u>	<u>515.40</u>	<u>304.20</u>	<u>113.99</u>
<u>Nb</u>	<u>28.80</u>	<u>22.10</u>	<u>10.60</u>	<u>24.80</u>	<u>24.80</u>	<u>16.90</u>	<u>20.70</u>	<u>24.70</u>	<u>9.00</u>	<u>37.20</u>	<u>18.58</u>	<u>7.62</u>
<u>Mo</u>	<u>430</u>	<u>427</u>	<u>611</u>	<u>458</u>	<u>461</u>	<u>451</u>	<u>518</u>	<u>436</u>	<u>326.00</u>	<u>640.00</u>	<u>477.88</u>	<u>68.59</u>
<u>Sn</u>	<u>1.97</u>	<u>1.47</u>	<u>0.54</u>	<u>3.98</u>	<u>1.59</u>	<u>1.18</u>	<u>1.16</u>	<u>1.78</u>	<u>0.54</u>	<u>3.98</u>	<u>1.33</u>	<u>0.72</u>
<u>Sb</u>	<u>27.16</u>	<u>26.17</u>	<u>46.43</u>	<u>27.53</u>	<u>25.99</u>	<u>28.39</u>	<u>30.59</u>	<u>25.38</u>	<u>22.33</u>	<u>47.37</u>	<u>32.34</u>	<u>6.89</u>
<u>Cs</u>	<u>0.57</u>	<u>0.51</u>	<u>0.87</u>	<u>0.67</u>	<u>0.50</u>	<u>0.48</u>	<u>0.59</u>	<u>0.50</u>	<u>0.43</u>	<u>2.01</u>	<u>0.72</u>	<u>0.33</u>
<u>Ba</u>	<u>1358</u>	<u>1240</u>	<u>1283</u>	<u>1514</u>	<u>1337</u>	<u>1304</u>	<u>1473</u>	<u>1351</u>	<u>1115</u>	<u>1522</u>	<u>1354</u>	<u>101.30</u>
<u>Hf</u>	<u>4.91</u>	<u>5.03</u>	<u>3.86</u>	<u>2.97</u>	<u>5.63</u>	<u>6.01</u>	<u>5.32</u>	<u>6.06</u>	<u>2.46</u>	<u>7.79</u>	<u>4.56</u>	<u>1.44</u>
<u>Ta</u>	<u>0.92</u>	<u>0.36</u>	<u>0.21</u>	<u>0.22</u>	<u>0.31</u>	<u>0.28</u>	<u>0.33</u>	<u>0.14</u>	<u>0.02</u>	<u>0.92</u>	<u>0.23</u>	<u>0.16</u>
<u>Pb</u>	<u>767</u>	<u>766</u>	<u>428</u>	<u>833</u>	<u>868</u>	<u>567</u>	<u>690</u>	<u>854</u>	<u>321</u>	<u>1090</u>	<u>647.57</u>	<u>211.21</u>
<u>Bi</u>	<u>13.79</u>	<u>14.42</u>	<u>6.57</u>	<u>15.20</u>	<u>17.06</u>	<u>9.62</u>	<u>13.09</u>	<u>17.22</u>	<u>4.19</u>	<u>22.49</u>	<u>11.58</u>	<u>4.87</u>
<u>Th</u>	<u>35.28</u>	<u>32.92</u>	<u>13.67</u>	<u>37.08</u>	<u>39.10</u>	<u>22.41</u>	<u>32.37</u>	<u>38.25</u>	<u>13.67</u>	<u>54.04</u>	<u>28.16</u>	<u>10.83</u>
<u>U</u>	<u>3.85</u>	<u>3.81</u>	<u>3.12</u>	<u>4.07</u>	<u>4.43</u>	<u>3.11</u>	<u>3.71</u>	<u>4.26</u>	<u>2.79</u>	<u>5.14</u>	<u>3.60</u>	<u>0.65</u>
<u>La</u>	<u>136</u>	<u>130</u>	<u>74</u>	<u>151</u>	<u>151</u>	<u>104</u>	<u>127</u>	<u>153</u>	<u>58.00</u>	<u>217.00</u>	<u>117.14</u>	<u>41.16</u>
<u>Ce</u>	<u>565</u>	<u>533</u>	<u>232</u>	<u>608</u>	<u>637</u>	<u>324</u>	<u>498</u>	<u>655</u>	<u>180.00</u>	<u>974.00</u>	<u>438.80</u>	<u>210.19</u>
<u>Pr</u>	<u>37.30</u>	<u>35.85</u>	<u>21.80</u>	<u>41.10</u>	<u>41.45</u>	<u>29.30</u>	<u>36.20</u>	<u>41.40</u>	<u>18.20</u>	<u>55.70</u>	<u>32.68</u>	<u>9.98</u>
<u>Nd</u>	<u>144.50</u>	<u>137.35</u>	<u>84.30</u>	<u>158.00</u>	<u>160.45</u>	<u>114.00</u>	<u>140.20</u>	<u>158.40</u>	<u>72.30</u>	<u>211.40</u>	<u>126.12</u>	<u>37.43</u>
<u>Sm</u>	<u>33.56</u>	<u>31.73</u>	<u>20.14</u>	<u>36.74</u>	<u>37.25</u>	<u>26.09</u>	<u>33.51</u>	<u>36.75</u>	<u>17.56</u>	<u>48.40</u>	<u>29.46</u>	<u>8.39</u>
<u>Eu</u>	<u>8.06</u>	<u>7.76</u>	<u>4.98</u>	<u>8.90</u>	<u>9.00</u>	<u>6.38</u>	<u>8.29</u>	<u>8.95</u>	<u>4.35</u>	<u>11.67</u>	<u>7.20</u>	<u>2.00</u>
<u>Gd</u>	<u>34.72</u>	<u>33.28</u>	<u>19.13</u>	<u>37.51</u>	<u>38.90</u>	<u>25.88</u>	<u>34.73</u>	<u>38.91</u>	<u>15.99</u>	<u>52.81</u>	<u>30.02</u>	<u>9.97</u>
<u>Tb</u>	<u>5.18</u>	<u>5.13</u>	<u>3.11</u>	<u>5.83</u>	<u>5.95</u>	<u>4.03</u>	<u>5.43</u>	<u>6.05</u>	<u>2.57</u>	<u>7.77</u>	<u>4.67</u>	<u>1.44</u>
<u>Dy</u>	<u>28.00</u>	<u>27.58</u>	<u>16.53</u>	<u>31.13</u>	<u>32.37</u>	<u>21.60</u>	<u>29.11</u>	<u>32.80</u>	<u>13.77</u>	<u>41.97</u>	<u>25.10</u>	<u>7.78</u>
<u>Ho</u>	<u>5.02</u>	<u>5.03</u>	<u>2.97</u>	<u>5.63</u>	<u>5.94</u>	<u>3.86</u>	<u>5.32</u>	<u>6.06</u>	<u>2.46</u>	<u>7.79</u>	<u>4.56</u>	<u>1.44</u>
<u>Er</u>	<u>13.41</u>	<u>13.56</u>	<u>7.99</u>	<u>15.12</u>	<u>15.92</u>	<u>10.36</u>	<u>14.47</u>	<u>16.42</u>	<u>6.51</u>	<u>20.47</u>	<u>12.25</u>	<u>3.87</u>
<u>Tm</u>	<u>1.85</u>	<u>1.88</u>	<u>1.11</u>	<u>2.06</u>	<u>2.19</u>	<u>1.41</u>	<u>1.98</u>	<u>2.27</u>	<u>0.91</u>	<u>2.85</u>	<u>1.69</u>	<u>0.54</u>
<u>Yb</u>	<u>12.55</u>	<u>12.75</u>	<u>7.45</u>	<u>14.19</u>	<u>14.74</u>	<u>9.52</u>	<u>13.06</u>	<u>15.38</u>	<u>6.13</u>	<u>19.39</u>	<u>11.39</u>	<u>3.65</u>
<u>Lu</u>	<u>1.76</u>	<u>1.78</u>	<u>1.02</u>	<u>1.96</u>	<u>2.08</u>	<u>1.31</u>	<u>1.83</u>	<u>2.14</u>	<u>0.84</u>	<u>2.78</u>	<u>1.58</u>	<u>0.53</u>

n d- no data.

Table 2. Comparison of mean chemical composition of ferromanganese nodules from CIOB, CCZ- Pacific Ocean, Peru Basin, global nodule and Earth's upper continental crustal values.

Elements	CIOB nodule **		CCZ Pacific nodule		Peru Basin nodule	Global nodule	Upper cont. crust
	Mean concentration	No. of samples (N)	Mean concentration	No. of samples (N)	Mean concentration	Mean concentration	Mean concentration
Si (%)	9.58	35	6.55	12	4.82	7.69	30.8
Mn	24.41	1188	28.4	66	34.2	18.69	0.6
Fe	7.16	1188	6.16	66	6.12	12.47	3.5
Al	2.75	89	2.36	65	1.5	2.7	8.04
Mg	2.03	93	1.89	66	1.71	1.57	1.33
P	0.23	102	0.21	66	0.15	0.37	0.7
Ca	2.21	93	1.7	66	1.82	2.23	3.
Na	1.79	45	1.99	66	2.65	1.97	2.89
K	1.16	89	0.99	66	0.81	0.73	2.8
Ti	0.33	106	0.32	66	0.16	0.69	0.41
Co	0.11	1177	0.21	66	0.05	0.27	0.0017
Ni	1.09	1177	1.3	66	1.31	0.66	0.0044
Cu	1.03	1177	1.07	66	0.6	0.45	0.0025
Li (ppm)	91.96	86	131	66	311	80	20
Be	2.87	33	1.9	12	1.4	2.5	3
Sc	11.72	41	11	66	7.6	50	13.6
V	361.05	60	445	66	431	520	107
Cr	64.48	46	17	12	16	70	83
Zn	1190.45	745	1366	66	1845	1200	71
Ga	21.54	46	36	12	32	10	17
As	72.10	33	67	12	65	140	1.5
Se	3.70	33	0.72	12	0.5	0.6	50
Rb	24.52	46	23	66	12	17	112
Sr	662.14	89	645	66	687	830	350
Y	90.74	91	96	66	69	150	22
Zr	337.63	46	307	66	325	560	190
Nb	22.87	46	22	66	13	70	12
Mo	535.22	91	590	66	547	380	1.5
Su	1.33	33	5.3	12	0.9	2	5.5

Sb	<u>32.34</u>	<u>33</u>	<u>41</u>	<u>12</u>	<u>61</u>	<u>40</u>	<u>0.2</u>
Cs	<u>0.71</u>	<u>46</u>	<u>1.5</u>	<u>61</u>	<u>0.78</u>	<u>1</u>	<u>4.6</u>
Ba	<u>1523.31</u>	<u>90</u>	<u>3500</u>	<u>66</u>	<u>3158</u>	<u>2300</u>	<u>550</u>
Hf	<u>5.67</u>	<u>46</u>	<u>4.7</u>	<u>66</u>	<u>4.7</u>	<u>8</u>	<u>5.8</u>
Ta	<u>0.38</u>	<u>46</u>	<u>0.33</u>	<u>66</u>	<u>0.23</u>	<u>10</u>	<u>1</u>
Pb	<u>705.44</u>	<u>90</u>	<u>338</u>	<u>66</u>	<u>121</u>	<u>930</u>	<u>17</u>
Bi	<u>11.58</u>	<u>33</u>	<u>8.8</u>	<u>12</u>	<u>3.3</u>	<u>7</u>	<u>0.127</u>
Th	<u>29.43</u>	<u>46</u>	<u>15</u>	<u>66</u>	<u>6.9</u>	<u>30</u>	<u>10.7</u>
U	<u>3.74</u>	<u>46</u>	<u>4.2</u>	<u>66</u>	<u>4.4</u>	<u>5</u>	<u>2.8</u>
La	<u>122.94</u>	<u>106</u>	<u>114</u>	<u>66</u>	<u>68</u>	<u>157</u>	<u>30</u>
Ce	<u>482.47</u>	<u>80</u>	<u>284</u>	<u>66</u>	<u>110</u>	<u>530</u>	<u>64</u>
Pr	<u>31.54</u>	<u>83</u>	<u>33.4</u>	<u>66</u>	<u>14.1</u>	<u>36</u>	<u>7.1</u>
Nd	<u>133.11</u>	<u>106</u>	<u>140</u>	<u>66</u>	<u>63</u>	<u>158</u>	<u>26</u>
Sm	<u>30.25</u>	<u>106</u>	<u>34</u>	<u>66</u>	<u>14</u>	<u>35</u>	<u>4.5</u>
Eu	<u>7.27</u>	<u>102</u>	<u>8.03</u>	<u>66</u>	<u>3.87</u>	<u>9</u>	<u>0.88</u>
Gd	<u>30.14</u>	<u>80</u>	<u>31.8</u>	<u>66</u>	<u>15.6</u>	<u>32</u>	<u>3.8</u>
Tb	<u>4.74</u>	<u>83</u>	<u>4.98</u>	<u>66</u>	<u>2.52</u>	<u>5.4</u>	<u>0.64</u>
Dy	<u>25.32</u>	<u>102</u>	<u>28.5</u>	<u>66</u>	<u>15.8</u>	<u>31</u>	<u>3.5</u>
Ho	<u>4.76</u>	<u>102</u>	<u>5.35</u>	<u>66</u>	<u>3.42</u>	<u>7</u>	<u>0.8</u>
Er	<u>11.98</u>	<u>80</u>	<u>14.6</u>	<u>66</u>	<u>9.8</u>	<u>18</u>	<u>2.3</u>
Tm	<u>1.75</u>	<u>57</u>	<u>2.11</u>	<u>66</u>	<u>1.49</u>	<u>2.3</u>	<u>0.33</u>
Yb	<u>11.42</u>	<u>102</u>	<u>13.7</u>	<u>66</u>	<u>10.3</u>	<u>20</u>	<u>2.2</u>
Lu	<u>1.78</u>	<u>97</u>	<u>2.05</u>	<u>66</u>	<u>1.61</u>	<u>1.8</u>	<u>0.32</u>

CCZ- Pacific Ocean, Peru Basin- Hein et al., (2013), global nodule- Baturin, (1988), Earth's upper continental crust- MeLennan, (2001). ** Data sources :Present study, Jauhari and Pattan-2000, Pattan and Parthiban-2006, 2007, 2011, Pattan and Banakar, 1993.

Table 3. Correlation coefficient (r) value of Mn and Fe with number of elements (n=33).

Element	Mn	Fe
Li	+0.61	-0.93
Be	-0.59	+0.93
Sc	-0.65	+0.75
Ti	-0.58	+0.95
V	-0.41	+0.76
Cr	+0.11	-0.05
Co	-0.50	+0.91

<u>Ni</u>	<u>+0.71</u>	<u>-0.85</u>
<u>Cu</u>	<u>+0.64</u>	<u>-0.89</u>
<u>Zn</u>	<u>+0.29</u>	<u>-0.83</u>
<u>Ga</u>	<u>+0.53</u>	<u>-0.74</u>
<u>As</u>	<u>-0.55</u>	<u>+0.94</u>
<u>Se</u>	<u>-0.23</u>	<u>+0.76</u>
<u>Rb</u>	<u>+0.01</u>	<u>-0.46</u>
<u>Sr</u>	<u>-0.52</u>	<u>+0.90</u>
<u>Y</u>	<u>-0.45</u>	<u>+0.95</u>
<u>Zr</u>	<u>-0.43</u>	<u>+0.81</u>
<u>Nb</u>	<u>-0.57</u>	<u>+0.93</u>
<u>Mo</u>	<u>+0.70</u>	<u>-0.73</u>
<u>Sn</u>	<u>-0.51</u>	<u>+0.79</u>
<u>Sb</u>	<u>+0.59</u>	<u>-0.82</u>
<u>Ba</u>	<u>+0.30</u>	<u>-0.01</u>
<u>REEs</u>	<u>-0.15</u>	<u>+0.95</u>
<u>Ta</u>	<u>-0.24</u>	<u>+0.20</u>
<u>Pb</u>	<u>-0.50</u>	<u>+0.96</u>
<u>Bi</u>	<u>-0.48</u>	<u>+0.94</u>
<u>Th</u>	<u>-0.53</u>	<u>+0.92</u>
<u>U</u>	<u>-0.46</u>	<u>+0.89</u>
<u>Mg</u>	<u>+0.73</u>	<u>-0.05</u>
<u>Al</u>	<u>-0.08</u>	<u>+0.31</u>
<u>K</u>	<u>-0.22</u>	<u>+0.01</u>
<u>P</u>	<u>-0.01</u>	<u>+0.34</u>
<u>Ca</u>	<u>-0.15</u>	<u>+0.44</u>

Captions for the figures.

Figure 1. Bathymetry map along with sample location of ferromanganese nodules (star) in the Central Indian Ocean Basin (CIOB).

Figure 2. Precision of trace elements based on ferromanganese nodules (AAS-15/GR-118, F-6/294 A, F-6/305 A) analysed on ICP-MS (Top). Precision is better than 5 % for most of the elements analysed. Accuracy of trace elements is based on international reference materials (P-1, A-1, Indian Ocean nodule (NIO std) and mean of all three standard reference material. Accuracy is better than $\pm 5\%$ for most of the elements analysed (Bottom).

Figure 3. Triangular diagram of Fe-Mn- (Cu+Ni+Co x10) for the ferromanganese nodules.

Figure 4. Shale-normalized REE pattern of ferromanganese nodules.

Figure 5. Bivariable plots of trace elements such as As, Se, Be, Bi and Sn with Fe and Sb Vs Mn in the ferromanganese nodules.

Figure 6. Enrichment factor of the elements analysed in the ferromanganese nodules compared to upper continental crustal values.

Figure 1

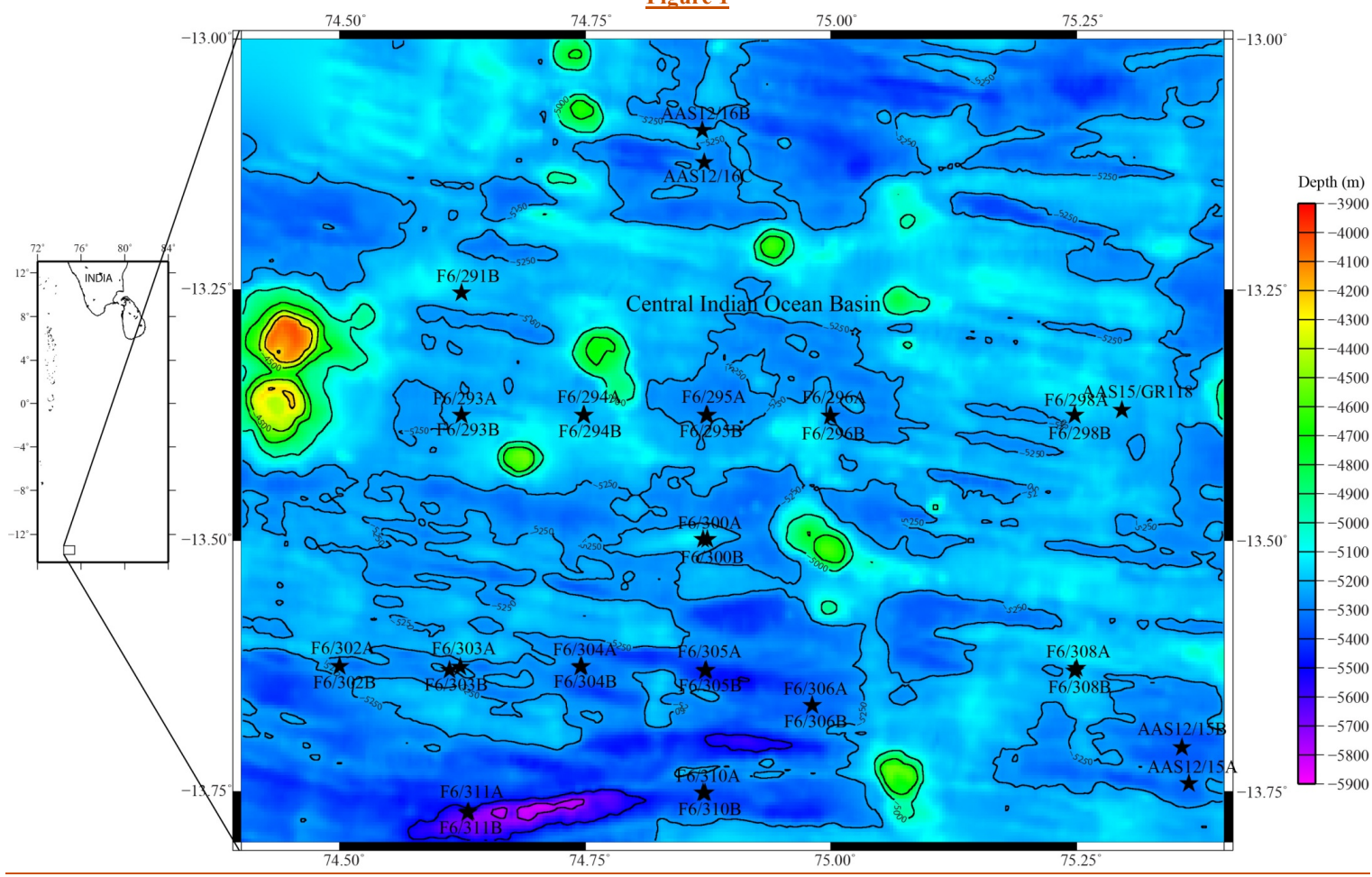
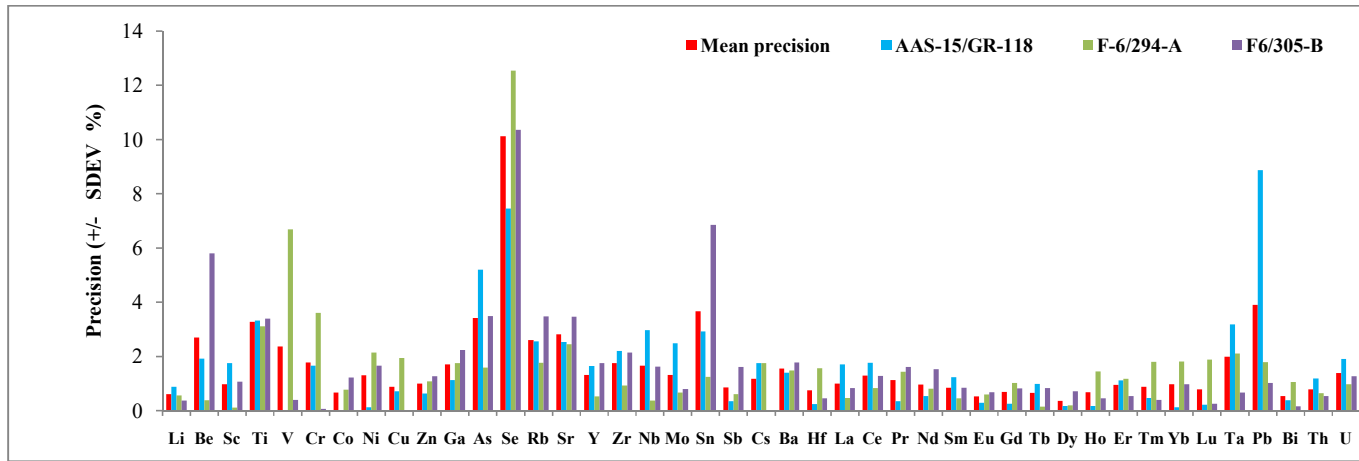


Figure 2



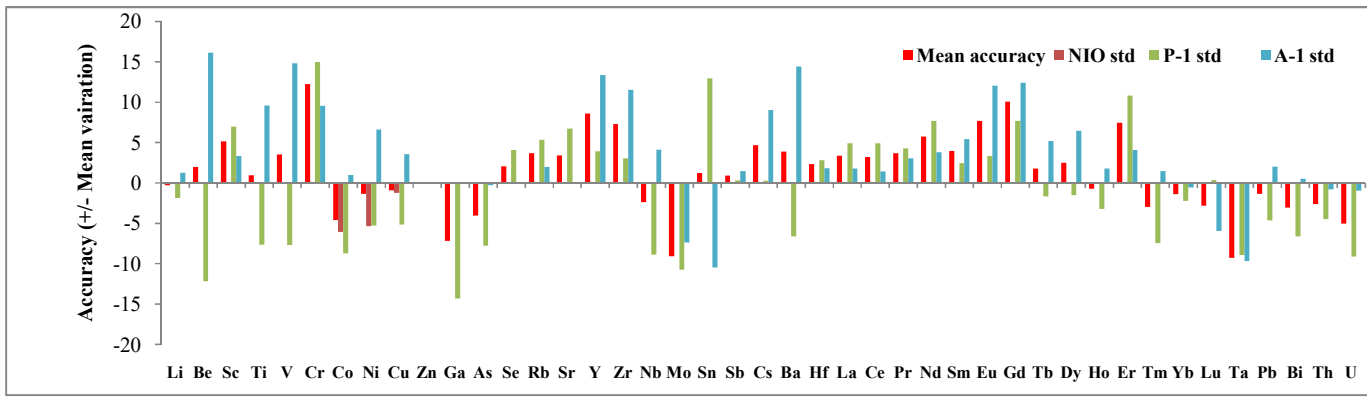
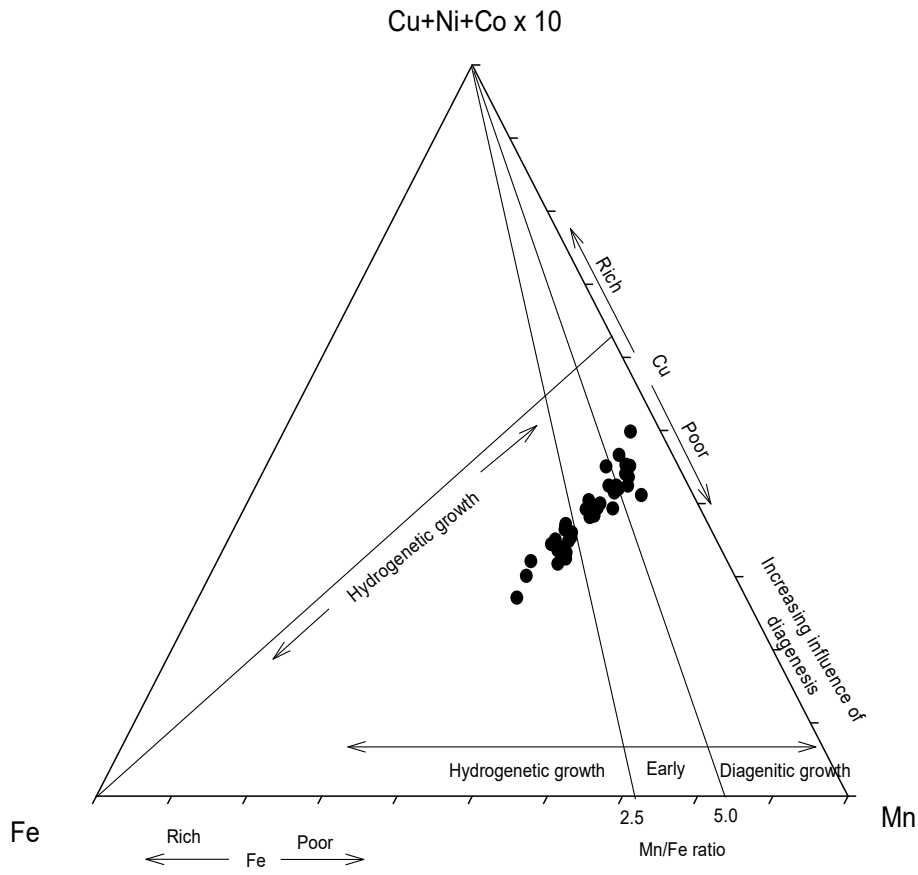
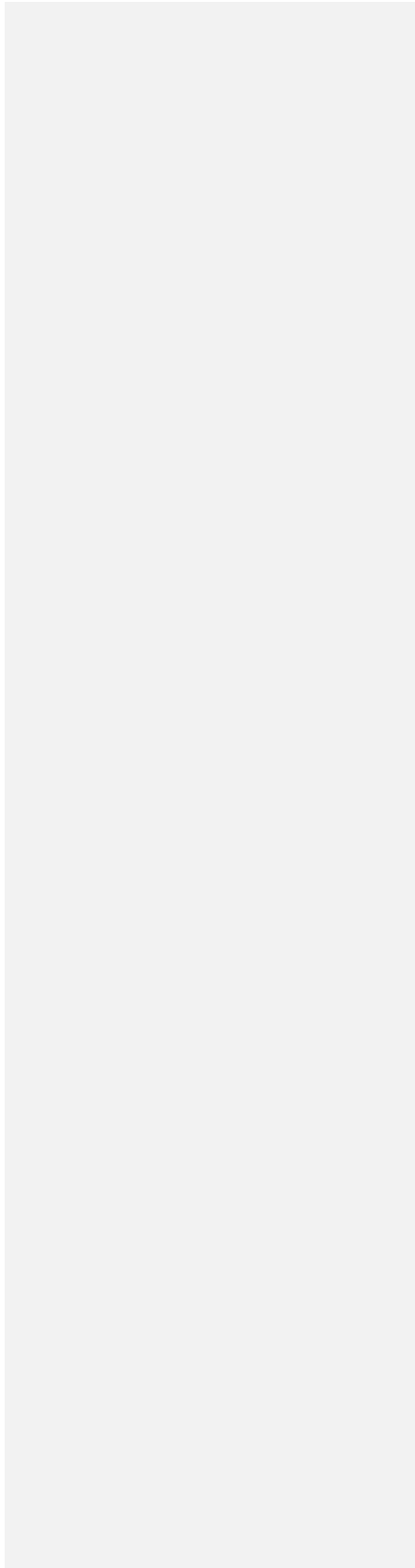


Figure 3





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Figure 4

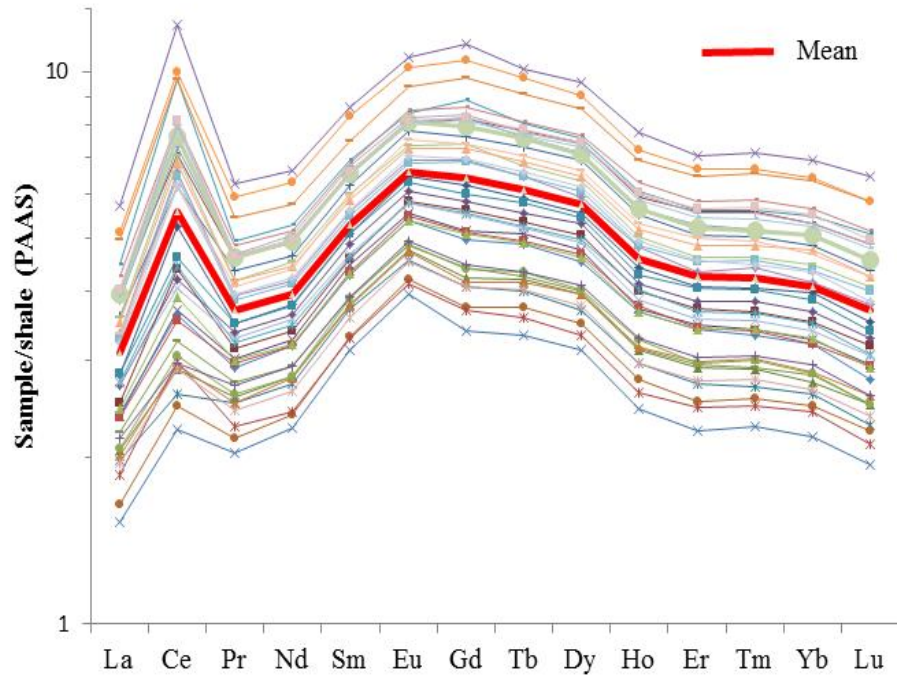
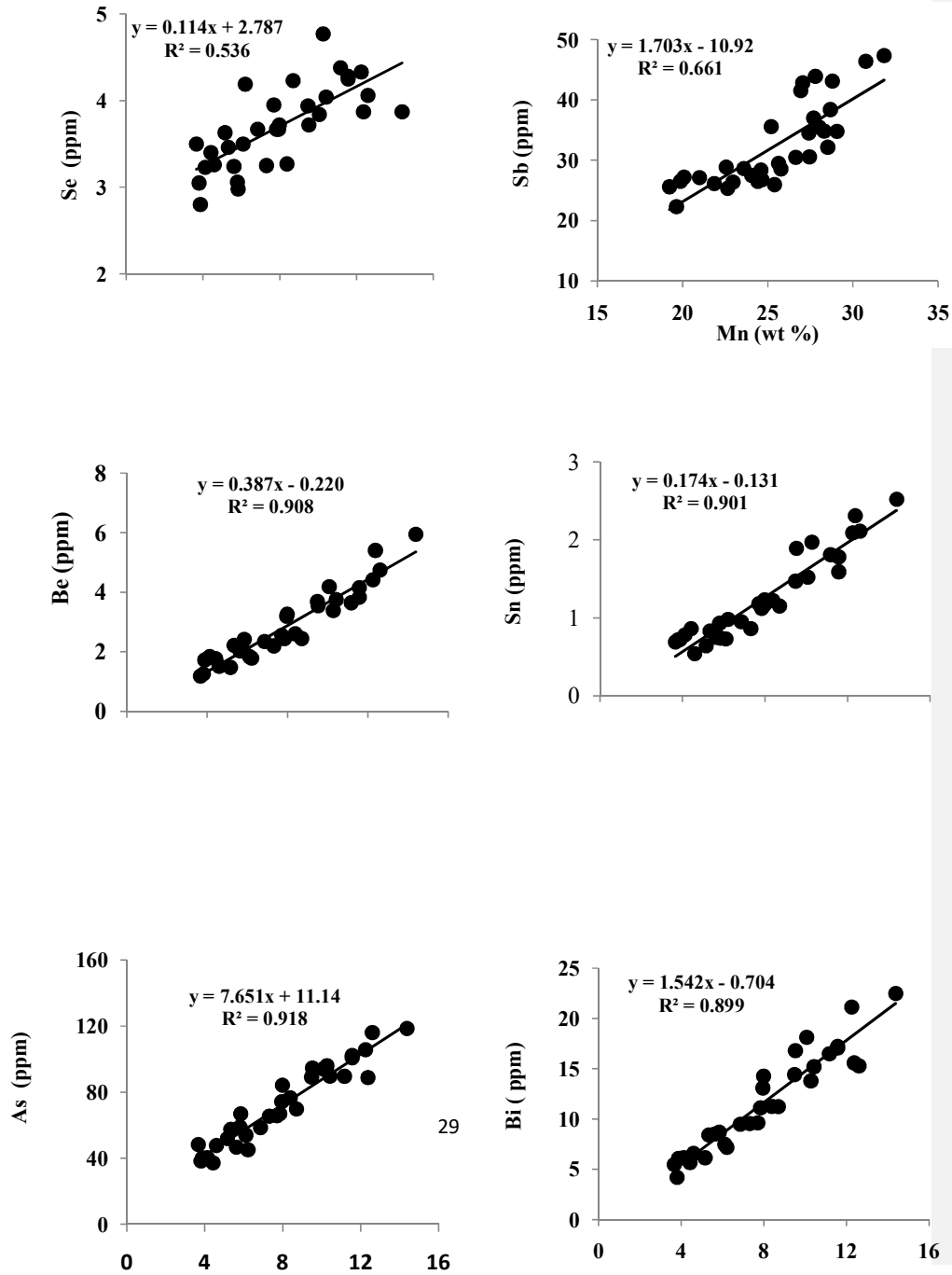


Figure 5



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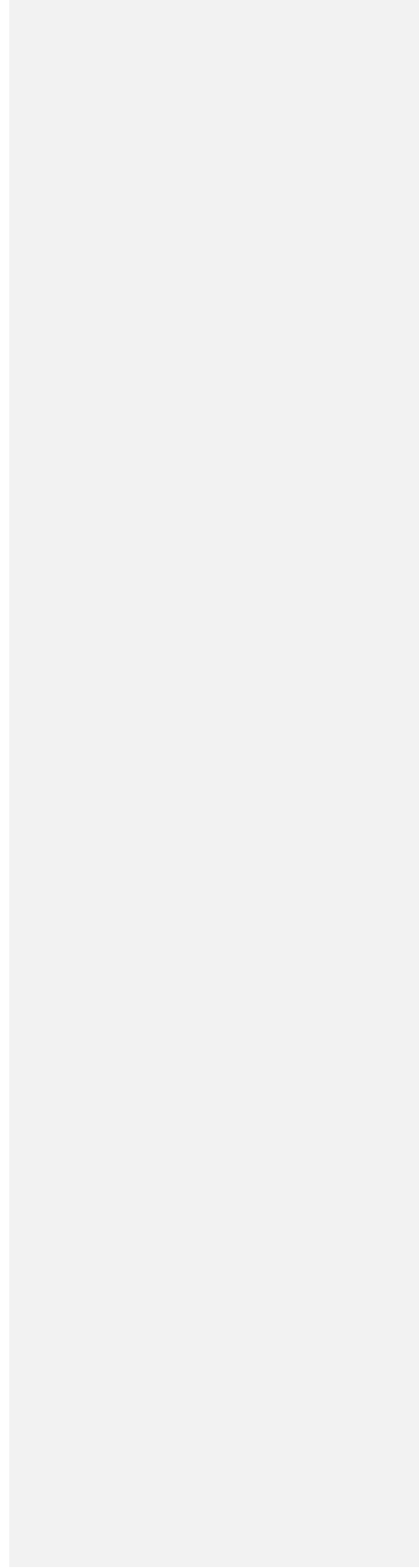


Figure 6

