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# GEOCHEMISTRY OF PELAGIC SEDIMENTS AND NODULES IN THE ABYSSAL CLARION FRACTURE ZONE, WESTERN MEXICO

**Mayumy A. CABRERA-RAMÍREZ[1*], Arturo CARRANZA-EDWARDS[2], John S. ARMSTRONG-ALTRIN[2] & Leticia ROSALES-HOZ[2]**

[1]*Facultad de Ingeniería, Departamento de Geología, Universidad Nacional Autónoma de México, Circuito Exterior s/n, 04510, México D.F., México *e-mail:mayumycr@unam.mx; mayari77@yahoo.com.mx*

[2]*Instituto de Ciencias del Mar y Limnología, Unidad Académica de Procesos Oceánicos y Costeros, Universidad Nacional Autónoma de México, Circuito Exterior s/n, 04510, México D.F., México*

*e-mail: dr.arturo.carranza@gmail.com; john_arms@yahoo.com*

**Abstract:** An oceanographic cruise on board the R/V El Puma (from the National Autonomous University of Mexico) was performed around the volcanic rocks of Clarion Island (CIR) in the western region of the Exclusive Economic Zone (EEZ) of Mexico. Surface sediments, nodules and representative rock samples from the CIR were collected. Texture is mainly constituted by silt and clay that suggest the influence of pelagic muds carried from the mainland to the deep sea by sea currents. The sandy fraction (less abundant) of the sediments is characterized by micronodules, pumice and remains of siliceous organisms. The most abundant muddy sediment fraction contains smectite, which played a role in the incorporation and release of metals and REE into the polymetallic nodules. The Mn, Ni, Co and REE concentrations in the studied sediments and nodules were slightly enriched when compared to UCC, NASC and CIR rocks.

**Keywords:** pelagic sediments, Clarion island, polymetallic nodules, Mexico.

## 1. INTRODUCTION

Polymetallic nodules have been considered as a potential strategic resource since the early 70's (Rona 2008). Consequent exploitation and rapid technological advancement to mine these resources requires establishing the geological environment baseline in order to prevent environmental damage. Thus it becomes necessary to study the geological parameters of the substrates where the nodules occur for a proper management of these. In studies of sediments associated with the nodules it has been observed that there is a close relationship among different sedimentological parameters (e.g., grain size and sorting of pelagic sediments; smooth or rough nodules surfaces, *etc*.) with the nodules mineralogy and geochemistry (Von Stackelberg & Beiersdorf 1991, Dubinin et al., 2008, McMurtry, 2010; Cabrera et al., 2013). This relationship is helpful to study the origin of deep sea nodules, whether they are diagenetic, hydrogenic or mixed (Calvert & Price 1977, Reyss & Lalou, 1981, Grupe et al., 2001). In some cases, the deep sea nodules were affected by biogenic influence, because they were found in sediments that have abundant bacterial communities (Li et al., 1996; Hu et al., 2000; Wu et al., 2013), fossilized organisms enriched in Mn, Ni and Cu (Nayak et al., 2013).

The genetic differences in nodules related to the type of sediment in which they are deposited have been studied in all oceans of the world (e.g., Banakar et al., 1989, González et al., 2010). Morgan (2000) reported that the area of the fracture zone Clarion-Clipperton is one of the richest zones for the formation of polymetallic nodules (Knoop et al., 1998, Cronan 2000, Duliu et al., 2008) in a region that is characterized by the accumulation of siliceous pelagic muds.

There are several geochemical studies on the distribution of major and trace element concentrations in both polymetallic nodules and their associated sediments where significant compositional variations were observed (Rankin & Glasby 1979, Dymond et al., 1984, Glasby et al., 1987, Kasten et al., 1998, Duliu et al., 2008). These studies suggest that the distribution of major (Si, Al, Fe, Mn, Mg, Ca, Na, Ti and P) and trace elements (Ni, Cu, Co, Zn, Pb) including REE may be associated with metal supply sources to the depositional environment (Halbach et al., 1980, Jahuari 1990), which contribute to the formation of different types of nodules.

The study of the distribution of REE in nodules and associated sediments based on indicators such as Ce and Eu anomalies may also provide information on their origin. For example, hydrothermal deposits of Fe-Mn are characterized by negative Ce and positive Eu anomalies (Mills & Eldefield 1995, Hein et al., 1997). In contrast, positive Ce anomalies are common in hydrogenetic deposits (Hein et al., 1997). Rare earth elements concentrated in Fe oxides are considered as hydrogenetic, while enrichment of Mn oxides (Kunzendorf et al., 1993) is considered as diagenetic.

Within the EEZ of Mexico in the Pacific Ocean, there are only a few studies were published related to the origin and distribution of polymetallic nodules and sediments (Rosales & Carranza 2001, Carranza & Rosales 2003, Cabrera et al., 2013). The objective of this paper is to establish the relationship among textural, mineralogical and geochemical parameters in sediments and nodules collected near the Clarion Island and to understand the processes of nodule formation.

## 2. GEOLOGICAL SETTING

Samples of abyssal nodules and sediments were collected during the oceanographic cruise MIMAR VI on board of the R/V EL PUMA. Samples were located between 15° 00' 00" and 22° 00' 00" north latitude and between 110° 00' 00" and 119° 00' 00" west longitude (Fig. 1). The water depth varied between 3500 and 4050 m. The polymetallic nodules and surface sediment samples were collected using a box corer in 12 oceanographic stations. Twenty four samples were geochemically analyzed for geochemistry i.e., 12 nodules and 12 surface sediment samples.

The physiography of the area is dominated by seamounts and the abyssal plains are characterized by pelagic sediments associated with nodules (Jung et al., 1998). The study area is bounded by the Pacific Plate, the Riviera Plate and the East Pacific Rise.

## 3. SAMPLING AND METHODS

On board of the R/V El Puma the samples were collected during Mimar VI oceanographic cruise in February 2009. Sediment samples and nodules were collected from the first cm of the box corer and were preserved in plastic bags. Similarly, buried nodules were extracted in the laboratory when the sediments from the corer were sampled. Rock samples collected from the Clarion Island were safely preserved in plastic bags; all samples were kept in refrigeration at 4ºC until analysis.

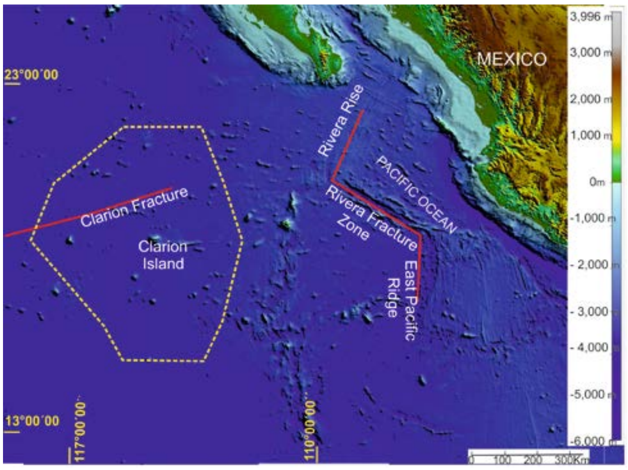


Figure 1. Map showing study area (dashed yellow polygon) (modified after Ryan et al. 2009).

Textural analysis of the sediment particles smaller than 2000µ (sand, silt and clay sizes) were performed using a laser analyzer Beckman Coulter L5230. Mineralogical studies were carried out in the sandy fraction of the sediment that was previously separated by wet sieving. For this compositional determination transmitted light optical microscopy was used to complement the analysis of fine particles using an electron microprobe with an equipment Jeol JXA-8900 at the Institute of Geology, UNAM.

The clay fraction was analyzed by X-ray diffraction with a Shimadzu XRD-6000 diffractometer equipped with Ni filter, copper anode, 40 kV/30 mA and monochromatic with a Cu anode, 40 mA kV/30, and Ka monochromatic radiation. Major element concentrations both in nodules and surface sediment samples, were obtained by XRF with an X ray sequential spectrometer (Siemens SRS 3000). Trace elements including REE were analyzed by ICP-MS. In order to interpret a possible source for the chemical composition of the studied sediments and nodules the geochemistry of rocks collected from the Clarion Island were compared. The geochemistry data of this study were normalized using upper continental crust (UCC) (Taylor & McLennan, 1985) and the North American Shale Composite (NASC) (Gromet et al., 1984) average values.

## 4. RESULTS

### 4.1 Texture

The studied sediments are mostly siliceous at the south of study area whereas in the north study area the sediments are mostly terrigenous. The collected nodules present three types of surface textures: smooth on both sides (SS), rough on both sides (RR), and smooth top and rough bottom (SR) and the line of contact between the two are in sediment-water interface. Altogether four different types of internal structures can be identified: laminated, dendritic, massive and botryoidal and distinguished the following type of nuclei: clay sediment, organic remains, pumice, micronodules and nodule fragments.

Pelagic sediments found as a substrate for polymetallic nodules are abundant in silt fraction with average values vary between 54.89% and 67.96%, while the clay fraction of the sediment varies between 30.49% and 45.91%. The sand fraction being the minor textural component (Tab. 1) thus the sediments in the study area were classified texturally as clayey silt sediments. Carranza (2001) found a clear relationship between the particle size and sorting (terrigenous and biogenous) in pelagic muds of continental origin, this probably means that the sediment texture suggests that the northern portion of the studied region is affected by mud pelagic sediments partially derived from NW continental Mexico.

Table1. Textural parameters of sediment samples.

| Sediment sample | Mzφ | σφ | Ski | Kg | Sand % | Silt % | Clay % |
|---|---|---|---|---|---|---|---|
| 1 | 7.71 | 1.64 | -0.03 | 0.95 | 0.07 | 56.04 | 43.89 |
| 2 | 7.59 | 1.69 | -0.03 | 0.96 | 0.11 | 58.61 | 41.28 |
| 3 | 7.50 | 1.76 | -0.07 | 0.94 | 0.14 | 59.39 | 40.47 |
| 4 | 7.47 | 1.75 | -0.03 | 0.94 | 0.13 | 60.83 | 39.05 |
| 5 | 7.46 | 1.73 | 0.01 | 0.95 | 0.34 | 61.71 | 37.95 |
| 6 | 7.85 | 1.56 | 0.01 | 0.96 | 0.00 | 54.09 | 45.91 |
| 7 | 7.10 | 1.88 | 0.01 | 0.90 | 1.26 | 66.05 | 32.70 |
| 8 | 7.02 | 1.85 | 0.03 | 0.89 | 1.15 | 67.96 | 30.90 |
| 9 | 7.03 | 1.97 | -0.06 | 0.85 | 3.10 | 63.28 | 33.62 |
| 10 | 6.94 | 1.90 | -0.03 | 0.86 | 1.48 | 67.93 | 30.59 |
| 11 | 6.98 | 1.93 | -0.01 | 0.87 | 2.87 | 65.34 | 31.80 |
| 12 | 6.92 | 1.91 | 0.02 | 0.85 | 2.15 | 67.36 | 30.49 |
| Ave | 7.30 | 1.80 | -0.01 | 0.91 | 1.07 | 62.38 | 36.55 |
| Stand Dev | 0.33 | 0.13 | 0.03 | 0.04 | 1.13 | 4.72 | 5.54 |

### 4.2 Petrography

The petrographic characterization of surface sediment samples showed that three components were abundant: micronodules, biogenic, and pumice fragments (Fig. 2). The sediments are less abundant in volcanic glass, quartz, plagioclase and barite. The biogenic materials found in the associated sediments (Fig. 2) and polymetallic nodules are usually diatoms, and sponge spicules. In this study biogenic corresponds with radiolarians (Fig. 3) that were mainly distributed in the southern region of the study area while the polymetallic nodules were associated with clay aggregates and pumice fragments. The sediments are abundant in smectite and illite, and less abundant in kaolinite.

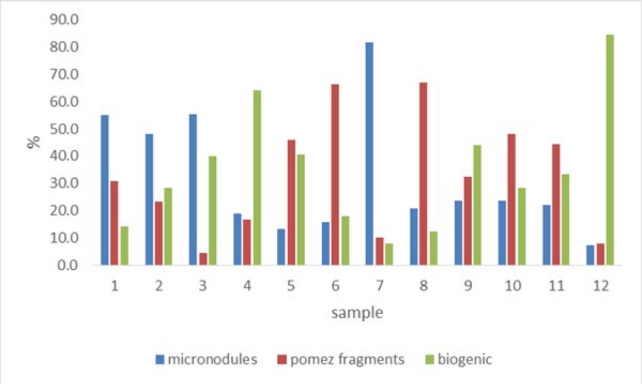


Figure 2. Mineralogical components of the sandy fraction in the surface sediment.

### 4.3 Geochemistry

The average concentration of the major (Na, Al, K, Ca, Ti, Fe and Mn), trace and rare earth elements of the nodules and pelagic sediments (Table 2) is compared with UCC (Taylor & McLennan, 1985), NASC (Gromet et al., 1984) and Clarion Island rocks CIR (this study).

This comparison reveals that the Na, Al, K, Ca, Ti and Fe concentrations in nodules (Fig. 4) and in pelagic sediments (Fig. 5) are comparable to the upper continental crust (UCC) with average values of 0.21 for Na, 0.38 for Al, 0.61 for Ca, 0.29 for K and 0.80 for Ti, and in pelagic sediments 1.30 for Na, 1.30 for Al, 0.88 for K, 0.48 for Ca and 1.19 for Ti. However, the Mn concentrations in the pelagic sediments are higher than in the UCC with an enrichment factor of 22.50. For the nodules, the enrichment factor is 383.72 (Table 3). In contrast, the Fe enrichment factor in nodules is 2.4 and in sediments it is 2.0. The higher abundance of Mn in the sediments compared with that of Fe could probably be explained by the abundance of smectite (Von Stackelberg, 1997).

The content of Sc, V, Cr, Sr, Rb, Sr, Zr, Nb, Cs, Hf, Th and U, in both sediments and nodules, show values near the UCC, while REE (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) have an enrichment average value of 3.4 in sediments and 6.5 for nodules. The concentrations of Ni and Co are significantly higher in nodules than in the UCC with an enrichment factor of 479.4 and 133.7 respectively.

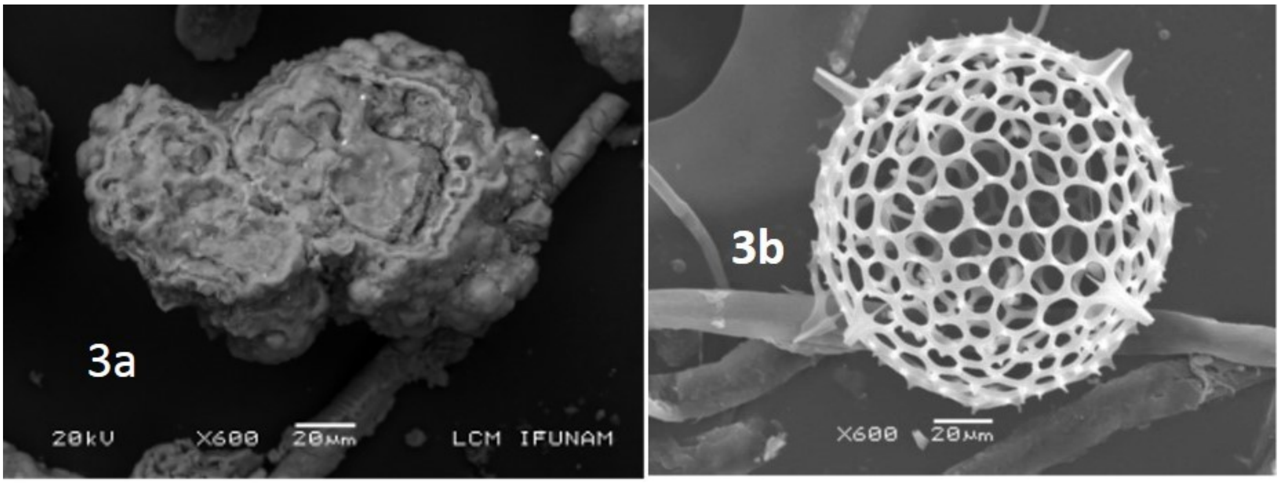

Figure 3. Main components of the sand fraction of the sediment. (a) micronodule, (b) radiolarian.

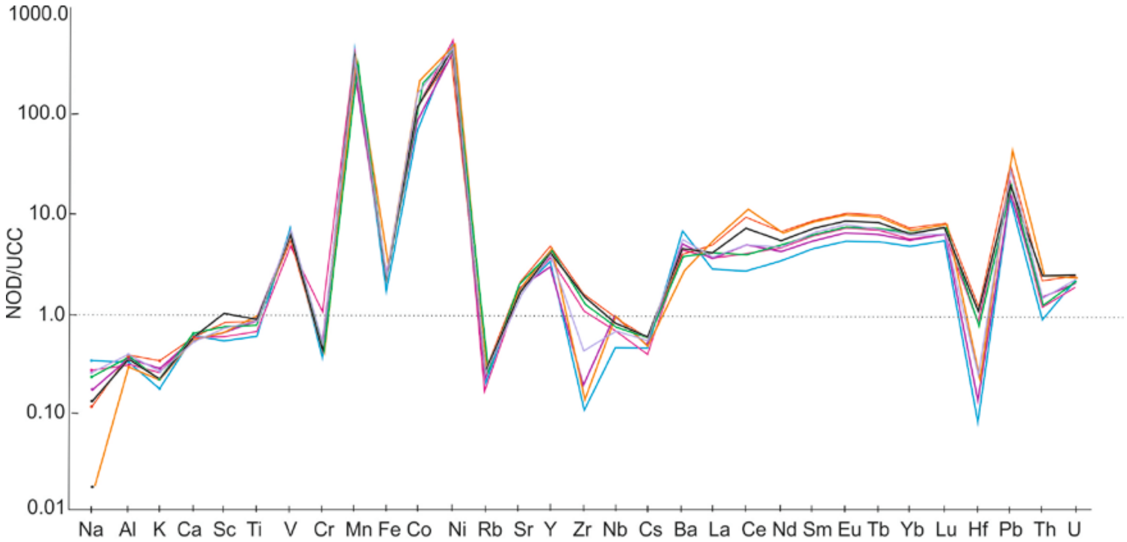

Figure 4. Major and trace element concentration in nodules near Clarion Island, normalized to upper continental crust (UCC).

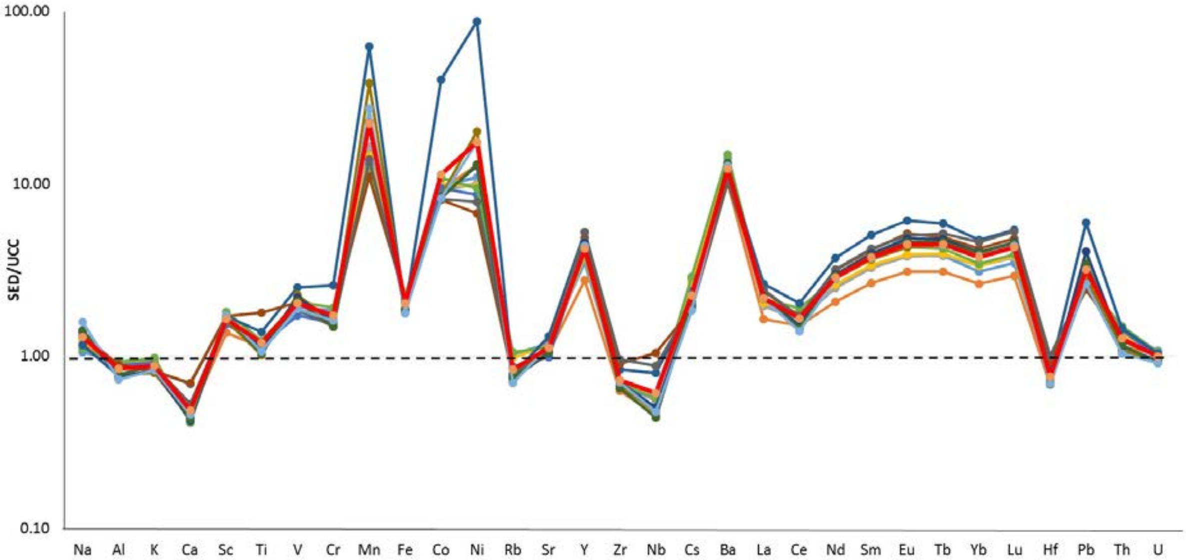

Figure 5. Major and trace element concentration in surface sediments near Clarion Island, normalized to upper continental crust (UCC; Taylor & McLennan, 1985).

Table 2. Contents of major components and trace elements in nodules (NOD) and sediments (SED), as well as the reference values of North American Shale Composite (NASC) Gromet et al.,1984), upper continental crust (UCC) (Taylor & McLennan 1985) and Clarion Island rocks (CI: this study). AVE (average).

| | **Na** | **Mg** | **Al** | **P** | **K** | **Ca** | **Sc** | **Ti** | **V** | **Cr** | **Mn** | **Fe** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **NASC** | 7479.00 | 17189.00 | 89471.00 | 541.00 | 31546.00 | 24303.00 | 14.90 | 4676.00 | – | 124.50 | 4646.00 | 39565.00 |
| **UCC** | 28200.00 | – | 84700.00 | – | 27400.00 | 25000.00 | 10.00 | 3600.00 | 60.00 | 35.00 | 600.00 | 35000.00 |
| **CLARION ISLAND (CI)** | 30331.81 | 21395.19 | 87939.77 | 4577.85 | 19190.92 | 41511.43 | 17.11 | 13676.07 | 141.38 | 59.41 | 1464.90 | 84125.46 |
| NOD-1 | 3709.86 | 20325.39 | 30280.70 | 2164.70 | 7887.25 | 16154.95 | 8.18 | 2877.60 | 410.62 | 14.38 | 234771.10 | 92326.42 |
| NOD-2 | 7642.31 | 20747.58 | 34251.07 | 1918.71 | 8551.44 | 15011.24 | 8.06 | 2158.20 | 385.25 | 16.31 | 242439.31 | 81205.29 |
| NOD-3 | 3932.45 | 19842.89 | 36262.73 | 2312.30 | 9713.77 | 15940.50 | 10.53 | 3237.29 | 364.95 | 16.00 | 206576.88 | 93445.53 |
| NOD-4 | 6232.56 | 19360.39 | 31233.59 | 2066.31 | 6973.99 | 16440.88 | 5.90 | 2457.95 | 385.46 | 14.26 | 241819.65 | 83513.45 |
| NOD-5 | 3635.66 | 18757.26 | 35574.53 | 2263.10 | 9547.72 | 15797.54 | 8.69 | 3237.29 | 334.22 | 12.73 | 198443.93 | 93445.53 |
| NOD-6 | 593.58 | 22315.71 | 30968.90 | 2312.30 | 7306.08 | 15869.02 | 6.66 | 3776.84 | 388.15 | 12.54 | 220751.45 | 102748.12 |
| NOD-7 | 6677.75 | 22195.09 | 34621.64 | 1672.72 | 9215.63 | 13009.74 | 7.26 | 2937.55 | 300.03 | 39.30 | 188374.57 | 74840.36 |
| NOD-8 | 5564.79 | 17189.13 | 32504.11 | 2164.70 | 8302.37 | 14582.34 | 6.96 | 3357.19 | 397.26 | 17.31 | 194261.27 | 85262.05 |
| NOD-9 | 7048.73 | 21712.58 | 30704.21 | 2066.31 | 6143.75 | 16083.47 | 7.50 | 2757.70 | 422.51 | 12.18 | 258008.09 | 80645.73 |
| NOD-10 | 7642.31 | 21833.21 | 32609.99 | 1967.91 | 7223.06 | 13438.63 | 6.27 | 2997.50 | 426.26 | 14.19 | 250184.97 | 73931.08 |
| NOD-11 | 8458.48 | 22014.15 | 29751.32 | 1918.71 | 7804.23 | 15869.02 | 6.32 | 2757.70 | 382.38 | 12.56 | 258705.20 | 77148.52 |
| NOD-12 | 9794.03 | 18154.13 | 29433.69 | 2066.31 | 5230.49 | 14868.27 | 5.56 | 2158.20 | 452.86 | 13.56 | 268464.74 | 60851.51 |
| AVE NOD | 5911.04 | 20370.63 | 32349.71 | 2074.51 | 7824.98 | 15255.47 | 7.32 | 2892.58 | 387.50 | 16.28 | 230233.43 | 83280.30 |
| SED-1 | 29894.05 | 20729.49 | 78862.17 | 1485.77 | 26210.57 | 10393.49 | 16.47 | 4304.40 | 116.11 | 64.68 | 8984.97 | 78862.17 |
| SED-2 | 33025.17 | 19288.01 | 75415.89 | 1697.32 | 24774.26 | 11480.02 | 13.75 | 4064.60 | 111.61 | 59.64 | 13733.06 | 75415.89 |
| SED-3 | 37803.47 | 18280.79 | 74182.43 | 1795.72 | 24923.71 | 10936.76 | 15.95 | 3926.72 | 108.18 | 54.89 | 9860.23 | 74182.43 |
| SED-4 | 34561.05 | 19318.17 | 75680.58 | 1707.16 | 25521.48 | 10672.27 | 17.47 | 4046.62 | 121.61 | 60.97 | 8721.62 | 75680.58 |
| SED-5 | 36497.60 | 19553.39 | 75230.61 | 2179.46 | 25388.64 | 11715.91 | 15.37 | 4190.50 | 103.73 | 54.95 | 7761.16 | 75230.61 |
| SED-6 | 31229.60 | 20819.96 | 78301.03 | 1638.29 | 26924.58 | 10322.01 | 18.16 | 4424.30 | 124.50 | 67.34 | 7397.11 | 78301.03 |
| SED-7 | 32654.18 | 21833.21 | 65013.52 | 2828.87 | 22482.81 | 17348.70 | 17.13 | 4999.82 | 151.09 | 90.06 | 37705.90 | 65013.52 |
| SED-8 | 36831.49 | 18021.44 | 75950.57 | 2764.92 | 22291.86 | 17455.92 | 17.03 | 6444.61 | 123.12 | 60.28 | 6607.05 | 75950.57 |
| SED-9 | 39702.92 | 16483.47 | 72001.37 | 2272.94 | 24201.40 | 13252.78 | 16.33 | 4118.56 | 112.06 | 52.17 | 8311.10 | 72001.37 |
| SED-10 | 39517.42 | 17261.50 | 66104.04 | 2140.10 | 21909.95 | 10951.05 | 16.13 | 3662.94 | 137.30 | 54.04 | 23043.35 | 66104.04 |
| SED-11 | 39925.51 | 19378.48 | 63605.36 | 2130.26 | 22657.16 | 10600.79 | 16.36 | 4046.62 | 131.47 | 56.57 | 13004.97 | 63605.36 |
| SED-12 | 39376.45 | 18895.98 | 66109.34 | 2199.14 | 24085.17 | 10772.35 | 16.99 | 3746.87 | 125.26 | 51.78 | 13740.81 | 66109.34 |
| SED-13 | 44570.25 | 19076.92 | 61868.98 | 2110.58 | 22856.42 | 11437.13 | 17.28 | 3836.79 | 113.29 | 56.35 | 16513.76 | 61868.98 |
| AVE SED | 36583.78 | 19149.29 | 71409.68 | 2073.12 | 24171.39 | 12103.02 | 16.49 | 4293.34 | 121.49 | 60.29 | 13491.16 | 71409.68 |
| CI-1 | 29493.38 | 19770.51 | 89486.89 | 7197.63 | 19186.77 | 38135.69 | 15.37 | 16522.19 | 114.87 | 4.20 | 1603.35 | 92941.93 |
| CI-2 | 21272.34 | 31278.18 | 86421.76 | 3975.18 | 12835.46 | 61481.73 | 23.82 | 18086.89 | 218.19 | 138.43 | 1154.10 | 84114.97 |
| CI-3 | 25598.03 | 27020.10 | 86924.67 | 2951.87 | 10054.17 | 58172.11 | 21.98 | 19130.02 | 251.13 | 58.73 | 1378.73 | 98222.72 |
| CI-4 | 29396.93 | 20681.24 | 79989.76 | 7979.88 | 14545.75 | 48800.81 | 20.31 | 17984.97 | 153.00 | 16.00 | 1611.10 | 102293.48 |
| CI-5 | 46224.85 | 1574.16 | 90498.01 | 900.32 | 37808.98 | 5239.64 | 6.99 | 2853.62 | 20.30 | 5.54 | 1851.21 | 57787.95 |
| CI-6 | 22541.11 | 40361.28 | 85675.33 | 2833.79 | 11947.11 | 62854.19 | 24.52 | 17091.72 | 230.75 | 159.80 | 1239.31 | 83037.83 |
| CI-7 | 42945.33 | 2756.29 | 94653.66 | 8127.47 | 36131.90 | 12537.96 | 7.46 | 3363.19 | 6.17 | 2.51 | 1657.57 | 56493.98 |
| CI-8 | 25182.53 | 27719.73 | 89868.04 | 2656.68 | 11017.24 | 44869.30 | 16.40 | 14375.99 | 136.62 | 90.06 | 1223.82 | 98110.81 |
| AVE CI | 30331.81 | 21395.19 | 87939.77 | 4577.85 | 19190.92 | 41511.43 | 17.11 | 13676.07 | 141.38 | 59.41 | 1464.90 | 84125.46 |

| | Co | Ni | As | Rb | Sr | Y | Zr | Nb | Sb | Cs | Ba | La | Ce |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **NASC** | 25.70 | 58.00 | 28.40 | 125.00 | 142.00 | – | 200.00 | – | 2.09 | 5.16 | 636.00 | 31.10 | 66.70 |
| **UCC** | 10.00 | 20.00 | – | 110.00 | 350.00 | 22.00 | 240.00 | 25.00 | – | 3.70 | 700.00 | 30.00 | 64.00 |
| **CLARION ISLAND (CI)** | 36.46 | 42.70 | – | 41.26 | 424.17 | 53.13 | 389.54 | 73.45 | 0.19 | 0.20 | 715.88 | 47.95 | 91.28 |
| NOD-1 | 1395.68 | 8206.82 | 105.33 | 23.87 | 745.97 | 110.26 | 378.52 | 21.76 | 38.28 | 1.81 | 2259.92 | 164.38 | 620.43 |
| NOD-2 | 876.59 | 8776.71 | 83.00 | 28.53 | 612.68 | 85.72 | 78.00 | 12.94 | 37.81 | 2.29 | 2652.29 | 113.70 | 341.81 |
| NOD-3 | 1130.13 | 8001.43 | 92.39 | 26.90 | 684.25 | 104.55 | 334.14 | 19.96 | 35.31 | 2.23 | 3324.50 | 132.33 | 471.47 |
| NOD-4 | 1457.97 | 10344.78 | 86.51 | 24.34 | 630.37 | 91.85 | 45.67 | 14.21 | 43.99 | 1.93 | 2372.85 | 120.13 | 401.25 |
| NOD-5 | 1651.71 | 8085.48 | 87.21 | 20.32 | 648.78 | 98.45 | 159.16 | 26.46 | 36.58 | 1.74 | 2419.42 | 183.26 | 623.17 |
| NOD-6 | 2245.69 | 10838.36 | 107.09 | 20.17 | 702.11 | 106.44 | 33.70 | 27.84 | 40.70 | 1.70 | 2105.67 | 182.40 | 747.72 |
| NOD-7 | 2082.94 | 9702.87 | 67.79 | 30.35 | 581.53 | 81.08 | 43.73 | 17.10 | 30.86 | 2.28 | 5500.07 | 92.01 | 244.42 |
| NOD-8 | 915.27 | 9745.44 | 88.54 | 23.83 | 668.33 | 95.30 | 50.53 | 25.69 | 36.52 | 1.75 | 3291.99 | 112.07 | 342.89 |
| NOD-9 | 774.11 | 11146.52 | 92.09 | 20.16 | 686.40 | 97.67 | 301.04 | 17.68 | 45.59 | 1.54 | 2735.78 | 123.94 | 268.13 |
| NOD-10 | 1590.85 | 8989.87 | 74.88 | 22.56 | 537.66 | 77.54 | 98.04 | 16.91 | 42.12 | 1.82 | 3999.48 | 111.67 | 291.66 |
| NOD-11 | 1218.37 | 11112.91 | 77.55 | 19.62 | 596.14 | 84.24 | 284.85 | 18.44 | 42.00 | 1.53 | 3251.70 | 117.60 | 280.04 |
| NOD-12 | 706.86 | 10109.58 | 67.29 | 22.76 | 614.55 | 74.87 | 26.91 | 11.44 | 43.17 | 1.69 | 4727.11 | 85.04 | 174.63 |
| AVE NOD | 1337.18 | 9588.40 | 85.80 | 23.62 | 642.40 | 92.33 | 152.86 | 19.20 | 39.41 | 1.86 | 3220.06 | 128.21 | 400.63 |
| SED-1 | 97.51 | 218.42 | 16.25 | 112.83 | 415.43 | 77.18 | 164.65 | 13.92 | 3.79 | 10.43 | 9879.58 | 60.37 | 113.18 |
| SED-2 | 92.45 | 256.77 | 18.15 | 95.09 | 370.56 | 60.72 | 150.76 | 11.40 | 4.12 | 9.01 | 7176.45 | 49.54 | 96.30 |
| SED-3 | 91.23 | 202.79 | 16.36 | 95.01 | 373.29 | 82.33 | 166.49 | 13.84 | 4.11 | 8.95 | 7897.60 | 58.73 | 104.16 |
| SED-4 | 99.83 | 195.16 | 16.60 | 107.69 | 405.70 | 84.32 | 167.26 | 14.31 | 3.96 | 9.94 | 9157.55 | 61.16 | 114.83 |
| SED-5 | 94.40 | 172.64 | 13.81 | 96.04 | 345.33 | 94.57 | 156.13 | 14.55 | 3.30 | 8.85 | 8190.72 | 66.07 | 111.30 |
| SED-6 | 107.96 | 189.12 | 16.00 | 115.82 | 396.20 | 85.80 | 166.17 | 14.30 | 3.51 | 10.71 | 10368.09 | 64.80 | 121.24 |
| SED-7 | 402.09 | 1757.25 | 24.87 | 86.35 | 455.62 | 115.80 | 200.52 | 20.03 | 9.43 | 7.50 | 8637.52 | 79.26 | 129.36 |
| SED-8 | 80.85 | 135.30 | 14.80 | 83.70 | 410.61 | 107.00 | 216.35 | 26.04 | 3.31 | 6.97 | 7121.79 | 72.00 | 109.24 |
| SED-9 | 81.98 | 157.21 | 17.19 | 86.93 | 379.41 | 115.99 | 231.20 | 22.03 | 3.80 | 7.31 | 7303.77 | 73.42 | 108.36 |
| SED-10 | 84.86 | 404.70 | 21.57 | 78.57 | 402.33 | 97.25 | 161.17 | 11.89 | 6.24 | 7.00 | 9183.47 | 66.68 | 93.96 |
| SED-11 | 83.90 | 253.80 | 20.21 | 81.76 | 366.06 | 99.74 | 168.72 | 12.62 | 4.43 | 7.25 | 8566.11 | 66.91 | 96.42 |
| SED-12 | 82.48 | 259.38 | 20.11 | 83.08 | 368.93 | 94.48 | 156.64 | 11.00 | 4.26 | 7.64 | 9226.06 | 66.69 | 92.85 |
| SED-13 | 82.30 | 348.81 | 20.73 | 77.10 | 402.94 | 96.24 | 168.67 | 11.93 | 5.39 | 6.81 | 8955.50 | 65.47 | 89.29 |
| AVE SED | 113.99 | 350.10 | 18.20 | 92.31 | 391.72 | 93.19 | 174.98 | 15.22 | 4.59 | 8.34 | 8589.55 | 65.47 | 106.19 |
| CI-1 | 31.10 | 2.88 | – | 44.66 | 447.75 | 48.92 | 421.73 | 74.56 | 0.15 | 0.16 | 581.46 | 56.11 | 113.34 |
| CI-2 | 53.38 | 93.57 | – | 29.00 | 610.16 | 32.83 | 271.34 | 55.35 | 0.36 | 0.14 | 491.25 | 40.48 | 81.02 |
| CI-3 | 47.46 | 44.12 | – | 23.38 | 485.05 | 45.80 | 222.32 | 39.35 | 0.07 | 0.16 | 319.17 | 30.67 | 62.06 |
| CI-4 | 42.18 | 11.56 | – | 33.80 | 480.49 | 56.13 | 290.97 | 60.87 | 0.09 | 0.19 | 491.20 | 47.23 | 93.70 |
| CI-5 | 10.22 | 1.74 | – | 81.11 | 170.02 | 100.17 | 741.92 | 148.40 | 0.17 | 0.43 | 1451.94 | 93.74 | 149.23 |
| CI-6 | 52.67 | 101.00 | – | 29.28 | 642.50 | 29.41 | 275.89 | 48.40 | 0.11 | 0.18 | 424.66 | 33.84 | 71.30 |
| CI-7 | 5.38 | 0.85 | – | 64.11 | 184.81 | 43.34 | 661.70 | 119.06 | 0.41 | 0.24 | 1636.47 | 44.36 | 90.21 |
| CI-8 | 49.33 | 85.86 | – | 24.71 | 372.60 | 68.48 | 230.43 | 41.61 | 0.18 | 0.12 | 330.85 | 37.13 | 69.38 |
| AVE CI | 36.46 | 42.70 | – | 41.26 | 424.17 | 53.13 | 389.54 | 73.45 | 0.19 | 0.20 | 715.88 | 47.95 | 91.28 |

| | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Hf | Ta | Pb | Th | U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **NASC** | – | 27.40 | 5.59 | 1.18 | – | 0.85 | – | – | – | – | 3.06 | 0.46 | 6.30 | 1.12 | – | 12.30 | 2.66 |
| **UCC** | – | 26.00 | 4.50 | 0.88 | – | 0.64 | – | – | – | – | 2.20 | 0.32 | 5.80 | – | 15.00 | 10.50 | 2.50 |
| **CLARION ISLAND (CI)** | 12.19 | 49.06 | 11.18 | 3.47 | 10.77 | 1.60 | 9.40 | 1.75 | 4.65 | – | 4.03 | 0.58 | 9.23 | 4.12 | 7.62 | 6.06 | 1.09 |
| NOD-1 | 44.26 | 179.05 | 40.67 | 9.53 | 42.04 | 6.52 | 34.39 | 6.54 | 17.157 | 2.51 | 16.03 | 2.68 | 6.44 | 0.50 | 515.96 | 25.78 | 6.16 |
| NOD-2 | 30.46 | 124.84 | 28.35 | 6.71 | 29.35 | 4.62 | 24.83 | 4.76 | 12.788 | 1.89 | 12.37 | 2.05 | 1.12 | 0.22 | 253.03 | 16.61 | 4.62 |
| NOD-3 | 34.71 | 143.10 | 32.26 | 7.60 | 34.45 | 5.32 | 28.92 | 5.63 | 15.099 | 2.24 | 14.49 | 2.44 | 6.21 | 0.53 | 354.83 | 23.38 | 5.37 |
| NOD-4 | 31.94 | 132.02 | 29.74 | 7.08 | 31.27 | 4.88 | 26.12 | 5.12 | 13.650 | 2.01 | 13.05 | 2.18 | 0.76 | 0.21 | 362.12 | 16.62 | 5.32 |
| NOD-5 | 46.87 | 188.79 | 41.60 | 9.67 | 42.48 | 6.46 | 33.26 | 6.19 | 15.917 | 2.30 | 14.71 | 2.47 | 1.47 | 0.30 | 505.34 | 23.82 | 5.32 |
| NOD-6 | 47.91 | 193.35 | 43.20 | 10.09 | 44.03 | 6.74 | 34.89 | 6.50 | 16.886 | 2.47 | 15.73 | 2.60 | 0.66 | 0.16 | 685.14 | 27.12 | 5.97 |
| NOD-7 | 26.00 | 108.40 | 24.91 | 5.85 | 25.79 | 4.04 | 21.72 | 4.24 | 11.291 | 1.70 | 10.84 | 1.80 | 0.69 | 0.32 | 352.83 | 13.00 | 4.14 |
| NOD-8 | 28.87 | 119.40 | 26.88 | 6.39 | 28.53 | 4.54 | 25.13 | 5.02 | 13.674 | 2.06 | 13.43 | 2.25 | 0.82 | 0.56 | 261.68 | 16.77 | 5.79 |
| NOD-9 | 31.72 | 131.87 | 29.53 | 7.10 | 30.66 | 4.89 | 26.74 | 5.29 | 14.327 | 2.15 | 14.04 | 2.36 | 4.61 | 0.40 | 262.00 | 13.62 | 5.43 |
| NOD-10 | 31.00 | 128.13 | 29.65 | 7.00 | 29.99 | 4.77 | 25.44 | 4.86 | 12.832 | 1.91 | 12.28 | 2.00 | 1.33 | 0.27 | 402.19 | 13.94 | 5.15 |
| NOD-11 | 30.65 | 127.10 | 28.74 | 6.79 | 29.56 | 4.71 | 25.61 | 5.00 | 13.447 | 1.99 | 13.06 | 2.17 | 5.14 | 0.43 | 350.68 | 13.29 | 5.04 |
| NOD-12 | 22.07 | 91.84 | 20.63 | 4.87 | 21.64 | 3.45 | 19.23 | 3.87 | 10.488 | 1.59 | 10.38 | 1.72 | 0.50 | 0.13 | 222.46 | 9.85 | 5.04 |
| AVE NOD | 33.87 | 138.99 | 31.35 | 7.39 | 32.48 | 5.08 | 27.19 | 5.25 | 13.96 | 2.07 | 13.37 | 2.23 | 2.48 | 0.34 | 377.36 | 17.82 | 5.04 |
| SED-1 | 16.53 | 66.70 | 15.12 | 3.39 | 15.55 | 2.44 | 13.37 | 2.67 | 7.39 | 1.06 | 6.79 | 1.12 | 4.27 | 0.98 | 40.61 | 14.59 | 5.04 |
| SED-2 | 13.22 | 53.89 | 12.00 | 2.73 | 12.56 | 1.98 | 10.95 | 2.17 | 6.02 | 0.89 | 5.78 | 0.93 | 3.98 | 0.84 | 42.33 | 12.01 | 5.04 |
| SED-3 | 15.85 | 64.92 | 14.58 | 3.34 | 15.39 | 2.48 | 13.89 | 2.81 | 7.83 | 1.14 | 7.35 | 1.21 | 4.35 | 1.00 | 53.49 | 13.08 | 5.04 |
| SED-4 | 16.66 | 67.72 | 15.18 | 3.44 | 16.11 | 2.52 | 14.17 | 2.85 | 7.83 | 1.14 | 7.35 | 1.22 | 4.30 | 1.01 | 42.49 | 14.22 | 5.04 |
| SED-5 | 18.70 | 76.84 | 17.66 | 4.04 | 18.79 | 2.98 | 16.67 | 3.35 | 9.25 | 1.33 | 8.55 | 1.42 | 4.32 | 1.09 | 39.86 | 14.97 | 5.04 |
| SED-6 | 17.99 | 73.13 | 16.60 | 3.78 | 17.30 | 2.71 | 14.98 | 2.96 | 8.16 | 1.18 | 7.58 | 1.25 | 4.35 | 1.05 | 40.39 | 15.72 | 5.04 |
| SED-7 | 23.29 | 96.73 | 22.84 | 5.41 | 23.83 | 3.78 | 20.92 | 4.16 | 11.34 | 1.63 | 10.44 | 1.73 | 4.71 | 1.27 | 89.16 | 15.21 | 5.04 |
| SED-8 | 19.92 | 81.95 | 18.53 | 4.54 | 19.95 | 3.14 | 17.87 | 3.63 | 10.07 | 1.45 | 9.30 | 1.55 | 5.47 | 1.67 | 36.44 | 12.96 | 5.04 |
| SED-9 | 20.05 | 83.26 | 18.91 | 4.42 | 20.32 | 3.31 | 18.76 | 3.89 | 10.80 | 1.57 | 10.16 | 1.70 | 5.84 | 1.46 | 41.10 | 13.27 | 5.04 |
| SED-10 | 17.67 | 73.32 | 16.36 | 3.79 | 17.76 | 2.82 | 16.05 | 3.33 | 9.18 | 1.33 | 8.57 | 1.43 | 4.04 | 0.86 | 43.62 | 11.45 | 5.04 |
| SED-11 | 18.90 | 77.88 | 17.80 | 4.24 | 19.28 | 3.06 | 17.24 | 3.50 | 9.62 | 1.39 | 8.88 | 1.47 | 4.06 | 0.89 | 60.85 | 12.01 | 5.04 |
| SED-12 | 18.41 | 75.78 | 17.28 | 4.05 | 18.55 | 2.95 | 16.69 | 3.39 | 9.39 | 1.34 | 8.73 | 1.46 | 3.98 | 0.83 | 51.70 | 12.19 | 5.04 |
| SED-13 | 17.85 | 73.47 | 16.67 | 3.94 | 17.54 | 2.83 | 16.03 | 3.27 | 9.14 | 1.32 | 8.43 | 1.41 | 4.01 | 0.80 | 39.32 | 10.89 | 5.04 |
| AVE SED | 18.08 | 74.27 | 16.89 | 3.93 | 17.92 | 2.85 | 15.97 | 3.23 | 8.93 | 1.29 | 8.30 | 1.38 | 4.44 | 1.06 | 47.80 | 13.28 | 5.04 |
| CI-1 | 14.89 | 60.51 | 13.65 | 4.16 | 12.55 | 1.79 | 9.94 | 1.76 | 4.40 | – | 3.46 | 0.48 | 9.47 | 4.38 | 7.30 | 6.77 | 5.04 |
| CI-2 | 10.39 | 41.29 | 8.81 | 2.63 | 7.97 | 1.16 | 6.40 | 1.17 | 3.02 | – | 2.48 | 0.35 | 6.44 | 3.27 | 13.42 | 4.55 | 5.04 |
| CI-3 | 8.46 | 36.26 | 9.01 | 2.79 | 9.31 | 1.40 | 8.23 | 1.56 | 4.07 | – | 3.42 | 0.49 | 5.48 | 2.37 | 2.52 | 2.78 | 5.04 |
| CI-4 | 13.29 | 56.43 | 13.47 | 3.91 | 13.08 | 1.86 | 10.62 | 1.93 | 4.96 | – | 3.99 | 0.55 | 7.83 | 3.59 | 4.22 | 4.77 | 5.04 |
| CI-5 | 19.45 | 72.07 | 15.41 | 4.58 | 14.78 | 2.26 | 14.51 | 2.76 | 7.89 | – | 7.56 | 1.13 | 17.17 | 7.44 | 9.46 | 11.67 | 5.04 |
| CI-6 | 8.88 | 35.78 | 7.77 | 2.38 | 7.08 | 1.04 | 5.76 | 1.05 | 2.70 | – | 2.24 | 0.32 | 5.79 | 2.90 | 3.50 | 4.04 | 5.04 |
| CI-7 | 11.89 | 45.21 | 10.05 | 3.69 | 9.04 | 1.43 | 8.51 | 1.60 | 4.36 | – | 4.21 | 0.63 | 15.77 | 6.59 | 14.38 | 10.57 | 5.04 |
| CI-8 | 10.30 | 44.88 | 11.28 | 3.63 | 12.36 | 1.84 | 11.24 | 2.17 | 5.81 | – | 4.90 | 0.70 | 5.91 | 2.40 | 6.18 | 3.35 | 5.04 |
| AVE CI | 12.19 | 49.06 | 11.18 | 3.47 | 10.77 | 1.60 | 9.40 | 1.75 | 4.65 | – | 4.03 | 0.58 | 9.23 | 4.12 | 7.62 | 6.06 | 5.04 |

On the other hand, the relationships of major element (Na, Al, K, Ca, Ti and Fe) in nodules (Fig. 6) and sediments (Fig. 7) are close to NASC concentration; similar results were also found by Duliu et al., 2008, with an exception of Mn that has an average ratio of 49.56 in the nodules. However, for Co and Ni the average ratios of nodules referred to NASC are 52.03 and 165.32, respectively.

Table 3. Element enrichment in ferromanganese nodules relative to UCC (Taylor & McLennan, 1985) and NASC (Gromet et al., 1984).

| Element (ppm) | Upper Continental Crust (UCC) | North American Shale Composite (NASC) | Nodules (this study) | Sediments (this study) | Enrichment Factor of Nodules relative to UCC | Enrichment Factor of Sediments relative to UCC | Enrichment Factor of Nodules relative to NASC | Enrichment Factor of Sediments relative to NASC |
|---|---|---|---|---|---|---|---|---|
| Mn | 600.0 | 4646.00 | 230233.4 | 13491.2 | 383.7 | 22.5 | 49.6 | 2.9 |
| Fe | 35000.0 | 39565.00 | 83280.3 | 71409.7 | 2.4 | 2.0 | 2.1 | 1.8 |
| Co | 10.0 | 25.70 | 1337.2 | 114.0 | 133.7 | 11.4 | 52.0 | 4.4 |
| Ni | 20.0 | 58.00 | 9588.4 | 350.1 | 479.4 | 17.5 | 165.3 | 6.0 |
| La | 30.0 | 31.10 | 128.2 | 65.5 | 4.3 | 2.2 | 4.1 | 2.1 |
| Ce | 64.0 | 66.70 | 400.6 | 106.2 | 6.3 | 1.7 | 6.0 | 1.6 |
| Nd | 26.0 | 27.40 | 139.0 | 74.3 | 5.3 | 2.9 | 5.1 | 2.7 |
| Sm | 4.5 | 5.59 | 31.3 | 16.9 | 7.0 | 3.8 | 5.6 | 3.0 |
| Eu | 0.9 | 1.18 | 7.4 | 3.9 | 8.4 | 4.5 | 6.3 | 3.3 |
| Tb | 0.6 | 0.85 | 5.1 | 2.8 | 7.9 | 4.4 | 6.0 | 3.3 |
| Yb | 2.2 | 3.06 | 13.4 | 8.3 | 6.1 | 3.8 | 4.4 | 2.7 |
| Lu | 0.3 | 0.46 | 2.2 | 1.4 | 7.0 | 4.3 | 4.8 | 3.0 |

The enrichment of Mn, Ni and Co in pelagic sediments and polymetallic nodules around Clarion Island is probably related to the tectonic activity of the study area, where the sediments are largely influenced by the East Pacific Ridge divergent margin leading to the generation of hydrothermal plumes that contribute as metal sources for polymetallic nodules in the study area (Zhang et al., 2012).

The REE contents in sediments and nodules (Table 3) are close to the average UCC and NASC values, with an exception of Eu, which is enriched in the nodules/UCC ratio.

Furthermore, the nodules (Fig. 8) and pelagic sediments (Fig. 9) are compared with the average composition of volcanic rocks of Clarion Island (CIR), analyzed in this study, it is observed that the concentration of major element (Si, Al, Mg, Ca, Na, K, P, Ti and Fe) in nodules and pelagic sediments are closer to the average composition of Clarion island rocks. Mn is enriched, with an average ratio of 9.21for nodules and 157.17 for surface sediments. In the case of trace elements (Be, Sc, V, Cr, Zn, Rb, Sr, Y, Zr and Nb) and rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) the concentration is similar to the average pattern of CIR. However, in nodules, the Ni, Co, Mo, Sb and Cs contents are slightly higher than in the CIR.

The average concentration of rare earth elements (including Sc and Y) in the nodules of this sector of the Pacific Ocean has been reported as 1096.96 ppm (Zhang et al., 2012), in this study it varies from 551.89 ppm with a maximum value of 1467.61 ppm in nodules collected from the Eastern study area. The surface sediments have an average of 454.36 ppm with a maximum value of 567.65 ppm. The Ce content is 400.63 ppm for nodules and 106.19 ppm for sediments, representing 42.54% of the total rare earth elements content in the nodules. There is an enrichment in the heavy rare earth elements (Eu, Tb, Yb, Lu, Y) in sediments related to nodules, however, in light rare earth elements (La, Ce, Nd, Sm), particularly Ce is showing a negative anomaly for sediments and positive to slightly negative anomaly for nodules.

## 5. DISCUSSION

It has been observed that there is a direct relationship between nodule abundance and availability of nuclei (Mukhopadhyay & Ghosh 2010). Although the nodules are associated with basalt, pumice, glass, limestone fragments and shark teeth. The core sediments of this study consist of nodules associated with fragments of pumice, clays or abundant micronodules aggregates (<5mm), the latter can be provided by the proximity to fracture zones, seamounts and the East Pacific Rise that is a source of sufficient metals (Dekov et al., 2003) and enriched the growth and development of macro-nodules (> 5mm). The macro-nodule abundance is favored by the presence and coalescence of micro-nodules so the mineralogical and geochemical relationship between nodules and sediments are genetic influenced by the geotectonic environment related to hydrothermal vents from oceanic rifts. This higher abundance of nodules is identified in the southern region of the study area, where the substrate is predominantly silty-clay with siliceous sediments. This has also been reported as one of the most favorable substrates for the growth of the polymetallic nodules (Ghosh & Mukhopadhyay 1995, Mukhopadhyay et al., 2007).

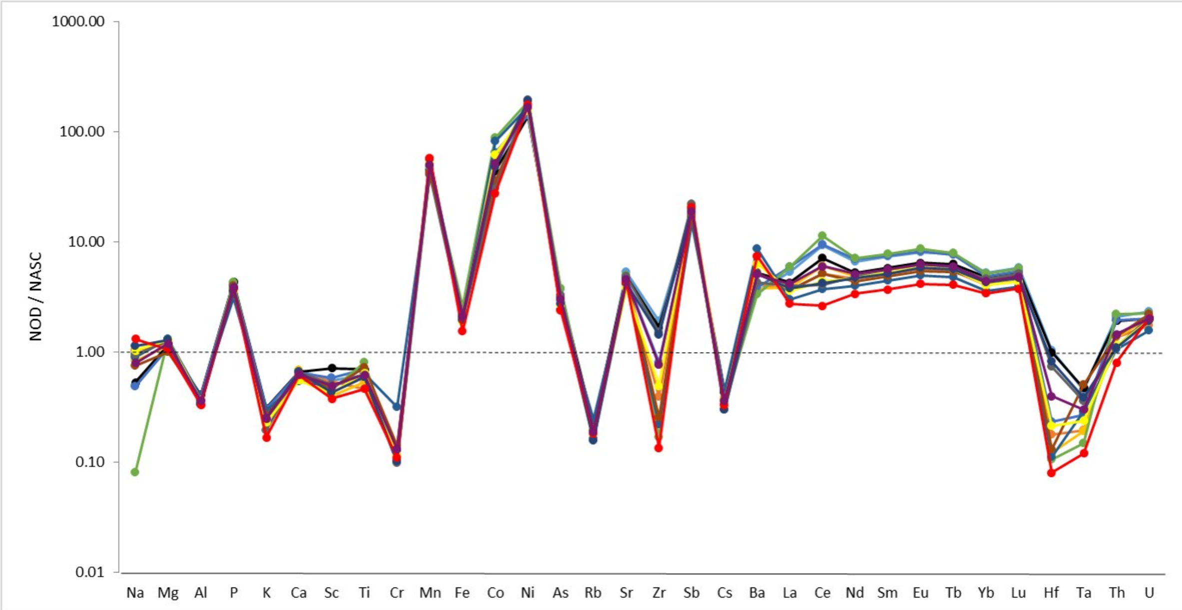


Figure 6. Major and trace element concentration in nodules near Clarion Island, normalized to NASC (Gromet et al., 1984).

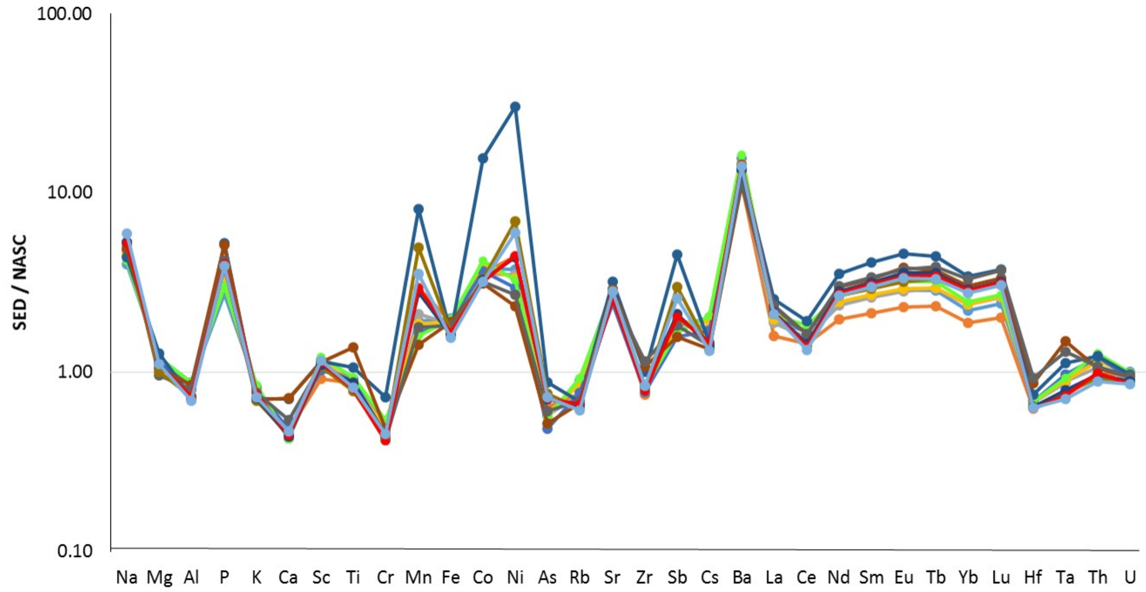


Figure 7. Major and trace element concentration in surface sediments near Clarion Island, normalized to NASC (Gromet et al., 1984).

The abundance of smectite among other clay minerals within the surface sediments can be related to an authigenic source (Hein et al., 1997, Canet et al., 2008). The high abundance of Mn content related to a low Fe content in sediments may indicate the provenance of igneous rocks associated with the East Pacific Rise and transported to the west by the North Pacific Equatorial current that flow between 10° N and 20°N. This current moves across the study area (Marchig & Gundlach 1982, Duliu et al., 2008. Also insoluble Fe precipitates allowing its precipitation near hydrothermal sources, while Mn can arrive in the study area from even more distance sources, as suggested by Dekov et al., (2003).

A further evidence of hydrothermal provenance for the surface sediments is identified by the negative Ce anomalies, which are associated with that hydrothermal activity, and there is also a negative relationship observed between Ce anomalies with submarine volcanism at the spreading centers of the sea floor (Toyoda et al., 1990). In seawater, cerium exists in the form of $Ce^{4+}$, which is easy to hydrolyze and coprecipitate with manganese. Therefore, marine manganese nodule has positive Ce anomaly. This Ce anomaly of manganese nodules and sediments was considered an important redox indicator (Calvert et al., 1987; Kunzendorf & Gwozdz, 1989; Rezaee et al., 2009) and is probably that positive Ce anomalies

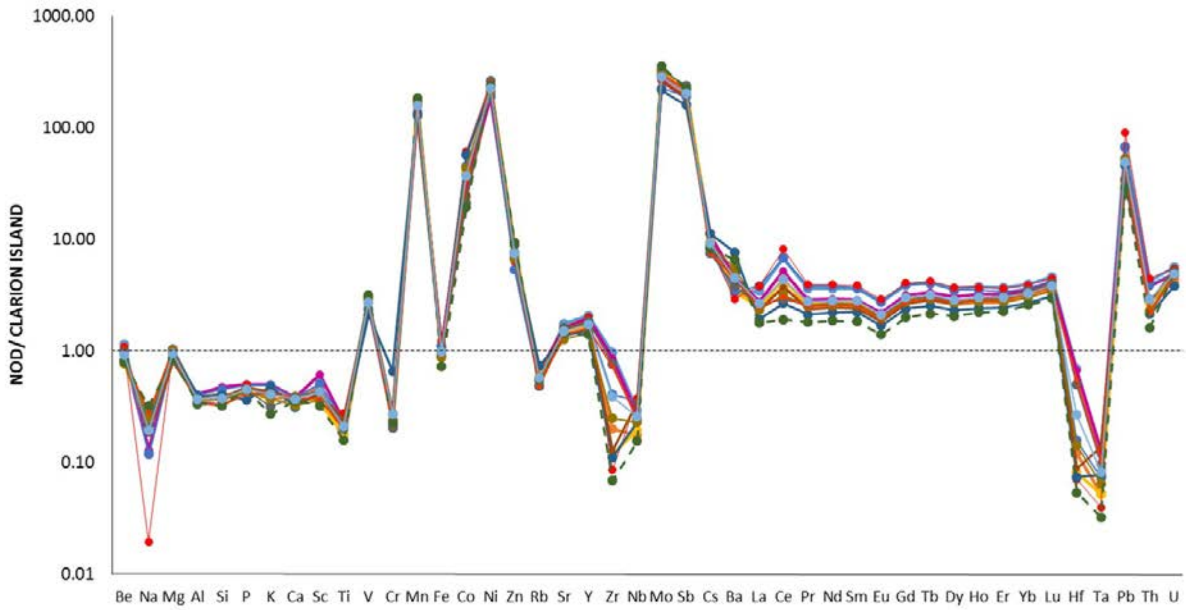

Figure 8. Major and trace element concentration in nodules near Clarion Island, normalized by CIR rocks (this study).

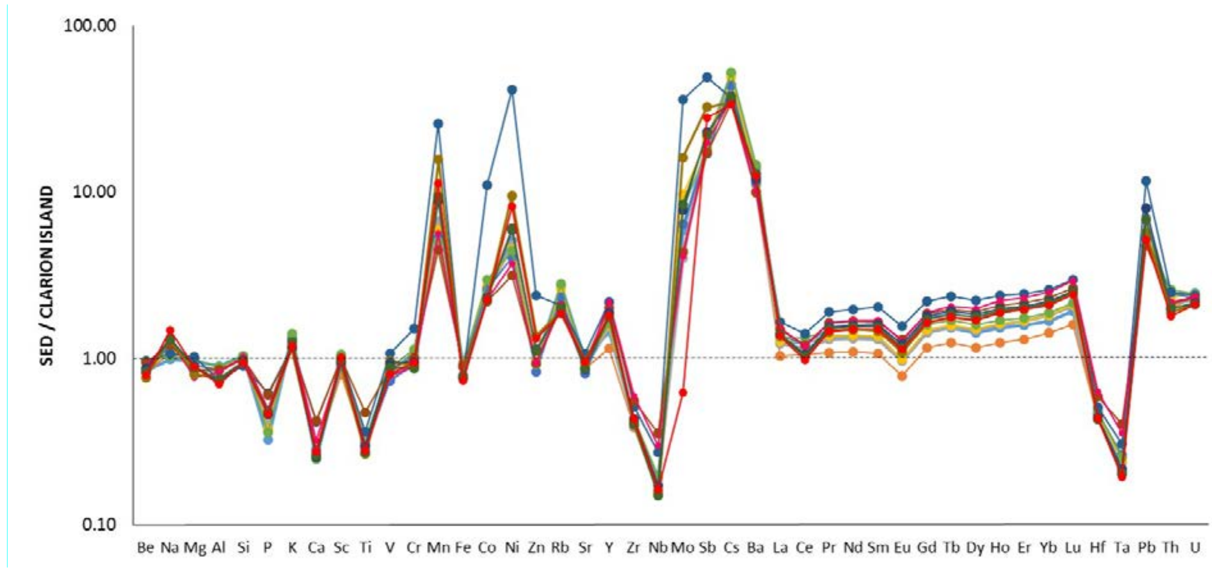

Figure 9. Major and trace element concentration in surface sediments near the Clarion Island, normalized to CIR (this study).

in sediments from this study confirm that these sediments represent an oxidized environment. Ce/La have been used as an indicator of the relationship between the hydrogenic (>2.0) and hydrothermal (<2.0) impact upon sediments, the Ce/La in this study are lower than 2.0 indicating an hydrothermal origin.

A comparative analysis of major, trace, and REE concentrations of sediments shows a closer relationship with the geochemistry data of the CIR rocks, which reveals the igneous origin of the metals supplied to nodules and its associated sediments. Furthermore Nowell et al., (1998) have been used the ratio La/Sm as an indicator of the geochemistry of seamounts considering the ratio La/Sm less than 1.0, in this case the value is < 1.0 and it seems to be related with Clarion Island. Is evident that the metal supply in sediments of this Pacific area has a mixed genesis among hydrogenic and hydrothermal as another pacific zones (Von Stackelber 1997, Usui & Someya 1997, Prakash et al., 2012).

## 6. CONCLUSIONS

The textural parameters (Mzφ and σIφ) and mineralogy reveal that the northern part of the study area is associated with terrigenous sediments, whereas the southern part is influenced by the authigenic micro-nodules.

The main components of the sand fraction are characterized by high contents of micro-nodules, pumice and biogenic siliceous sediments. The fine fraction (silts and clays) has abundant proportions of smectite that influence the adsorption of metals in sediments and involved also as a source of trace metals in nodules.

Manganese is more enriched in nodules relative to sediments, while iron is enriched slightly both in sediments and nodules. The trace elements such as Cu, Ni, Co and Zn are enriched in sediments and nodules while the major elements Na, Al, K, Ca, and Ti are depleted regardless being compared to UCC, NASC or CIR (Clarion Island rocks) that belong to an emerged seamount. Rare earth element concentrations are generally enriched when compared to UCC, NASC or CIR. The latest may be useful for regional comparative purposes of the CCZ nodules and sediments. The Ce negative anomalies support the hydrothermal influence in nodules and in surface sediments.

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