

CHEMISTRY AND POSSIBLE RESOURCE POTENTIAL OF COBALT RICH FERROMANGANESE CRUSTS FROM AFANASIY-NIKITIN SEAMOUNT IN THE INDIAN OCEAN

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ABSTRACT

Samples of ferromanganese encrustations (Fe-Mn Crusts) dredged from the upper flank of the Afanasiy-Nikitin seamount, above the Carbonate Compensation Depth (CCD) in the Northern Central Indian Ocean (NCIO) were analysed for Al, Fe, Mn, Ca, Ba, Cu, Ni, Co, Zn and V and found to be rich in Co (upto 0.88 %). Mineralogically, the studied Fe-Mn crust samples contain poorly crystalline δ -MnO₂, and minor amount of Carbonate Fluorapatite (CFA) and feldspars. The low Mn/Fe ratios (< 2), δ -MnO₂ dominant mineralogy and the interelement associations show that these crusts are formed by slow hydrogenetic precipitation of colloidal Fe-Mn oxyhydroxides. Fe, Mn, Co, Zn and V exhibit mutually strong positive association ($r > 0.7$) indicating their incorporation into the Fe-Mn crust during the hydrogenetic precipitation. The Al on the other hand, appears to be independent and diluent for hydrogenetic component. Therefore, the Al in the Fe-Mn crusts might be due to the presence of fine lithogenous detritus intermixed with hydrogenetic component. Another detrital indicator element 'Ti', instead of showing the affinity to Al exhibits affinity towards hydrogenetic oxide elements suggesting a possible incorporation into Fe-Mn crust analogous to other transition metals.

The Afanasiy-Nikitin seamount has an area of approximately 50,000 km² above the CCD, of which around 10% of the area (~ 5,000 km²) falling within the intermediate water Oxygen Minimum Zone ($< 2\text{mL/L O}_2$) appears to be a potential site for the formation of cobalt enriched Fe-Mn crusts. Assuming, an average thickness of the crust to be 2 cm, average Co concentration of 0.5%, and all the 5,000 km² potential area being covered with the Fe-Mn crusts, a first approximation resource evaluation could yield 180 million tonnes of Fe-Mn crust containing 0.9 million tonnes of Cobalt metal. Therefore, the Afanasiy-Nikitin seamount may prove to be a promising area for cobalt metal. However, a detailed survey and exploration are necessary to assess the actual resource potential since the present study is based only on one operation.

INTRODUCTION

Marine ferromanganese deposits have been widely reported in the world oceans from the abyssal seabed and seamounts. At abyssal depth, they generally occur as nodules at the sediment water-interface. The ferromanganese deposits capping the seamounts and submarine hills above the CCD enrich Co and occur as slabs known as Cobalt rich Fe-Mn crust (Hein et al. 1987). Cobalt content as high as 2% has been reported in some of the Pacific ocean seamount Fe-Mn crusts (Manheim, 1986). The Fe-Mn crusts distributed on slopes of seamount, ridges, plateaus and submarine hills above CCD are mainly of hydrogenetic origin and form by slow precipitation of inorganic colloidal particles consisting of hydrated metal oxides from near-bottom seawater. The Fe-Mn crusts have been shown to record contemporary oceanographic conditions during their growth period (Segl et al. 1984; Banakar and Borole, 1991; Banakar et al. 1997; De Carlo, 1991; Eisenhauer et al. 1992; Hein et al. 1992a; 1992b). The occurrence of hydrothermal crusts has also been reported from several seamounts and can be differentiated chemically from the hydrogenous crusts by their distinctly different composition (Hein et al. 1992a; Usui et al. 1993).

Fe-Mn crusts from the Pacific are the ones most extensively studied (Scott et al. 1972; Glasby, 1973; Friedrich and Wiechowski, 1980; Aplin and Cronan, 1985; Puteanus and Halbach, 1988). On the other hand, little work has been carried out on Indian Ocean Fe-Mn crusts. An accumulation rate of 2-4 mm/my was obtained for two Fe-Mn crusts of hydrogenetic origin collected from a water depth well below the CCD in the Central Indian Basin (Banakar and Borole, 1991). Based on the extrapolated U-Th isotope dates, these authors concluded that the Fe-Mn crust growth in the Central Indian Ocean began around 13 Ma corresponding to the establishment of modern Antarctic Bottom Water circulation. A Fe-Mn crust from the Afanasiy-Nikitin seamount was shown to record the oceanographic conditions prevailed during its growth period which began to accrete in the Late-Miocene (Banakar et al. 1997). Apart from these few studies, there have been no reports related to the economic potential of the Fe-Mn crusts from the Equatorial or Central Indian ocean. In the present study we report the inter- and intra-crust compositional variations in the samples collected from the upper flank of the seamount and assess their probable economic importance. As the present study is based on single location samples, may not indicate a precise evaluation, but certainly provides some information on the possibility of cobalt resource potential on the Afanasiy-Nikitin seamount.

MATERIAL AND METHODS

The Afanasiy-Nikitin seamount is located around 3° S latitude and 83° E longitude in the NCIO and extends ~300 km in NS and ~200 km in EW directions (Fig. 1). Its summit is located at 1550 m water depth (Rudenko, 1994). Dredging operation along a precise track from 1700 to 1600 m on the uppermost flank of the seamount has yielded only Fe-Mn crusts of

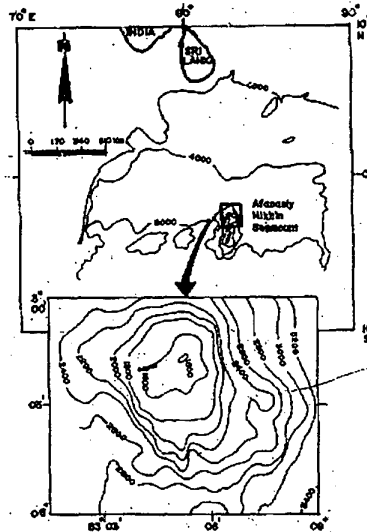


Fig. 1. Schematic map showing the location of the Afanasiy-Nikitin seamount. The dredge track is represented by a thick line on the magnified portion of the seamount bathymetry (adopted from Rudenko, 1994).

varying morphology. Megascopically, the dredged specimens are composed of Fe-Mn oxide material and non-oxide substrates. The Fe-Mn oxide layers exhibit variation in colour, thickness and texture. Samples ANC-1, 2 and 5 are composed of ~ 3 cm thick Fe-Mn oxide material with coarse grained surface texture, impregnated with Carbonate-fluorapatite layer and concretionary in appearance. The cavities are often filled with carbonate material. Samples ANC-3, 6, 7 and 9 are massive slab of 2-3 cm thick Fe-Mn oxide with smooth surface texture, with little non-oxide material. The samples ANC-4 and 8 are massive slab of 4-5 cm thick Fe-Mn oxide containing a distinct intermediate layer of (1-1.5 cm thick) carbonate Fluorapatite. The surface texture is rough and botryoidal. Three distinct colour zones could be distinguished in thick oxide layered specimens. In general the outer layer is smooth, dark brown, and 1 cm thick. The intermediate layer is coarse and light brown in colour. Also in this zone growth of apatite and detrital material intermixing was noticed (also see Banakar et al. 1997). The innermost layer is dark and granular in nature. Several subsamples chipped-off from these specimen were used in the present study.

The subsamples were dried at room temperature and ground to ~230 mesh in an agate mortar. The aliquots were leached in 6N HCl and the leachate was diluted to 100 ml in 18 mohm/cm quality deionised water. The solutions were analysed on a Perkin-Elmer[®] ICP-AES. Plasma-400, calibrated using a near crust composition multi-element calibration standard prepared from single element stock solutions of Aldrich[®] chemicals. Duplicate analysis of USGS A-1 nodule standard were used for the accuracy estimation of the analytical results. The analytical errors were within $\pm 5\%$ for Mn, Fe, Co, Cu, V, Zn, Al, Ni, Ba, Sr, Ca, Al, Ni, Ba and Sr; and $\pm 11\%$ for Ti. The mineralogical analysis was carried out on two samples (ANC-2 and ANC-9) on a Phillips[®] X-ray diffractometer.

RESULTS AND DISCUSSION

Mineralogically the samples contain poorly crystalline material mainly composed of d-MnO₂ identified with the broad hump like peaks around 2.4 Å^o and 1.4 Å^o. The other identifiable minor minerals are Carbonate Fluorapatite (CFA, 2.71 Å^o, 2.61 Å^o, and 2.55 Å^o) and Feldspars (3.2 Å^o).

Major and minor element concentration and Mn/Fe ratios in the samples analysed are presented in Table. 1 and show significant variation between the samples. The concentration ranges are: 6.75% to 17.74% for Fe; 7.41% to 23.27% for Mn; 0.03% to 0.12% for Cu; 0.24% to 0.58% for Ni; 0.15% to 0.88% for Co; and 0.03% to 0.1% for Zn.

The chemical composition of Fe-Mn nodules and crusts vary between Fe and Mn end members. Using this property and including a third parameter (combined Cu, Co and Ni concentration), Bonatti et al. (1972) and Halbach et al. (1981) proposed a triangular diagram to classify the marine Fe-Mn deposits. In all the studied samples, the Mn/Fe ratios are <2 (Table 1), all the samples fall in the hydrogenetic area in the triangular diagram (Fig. 2) and the d-MnO₂ is the main mineral phase. Thus all the studied samples are of hydrogenetic origin with significant enrichment of Co (up to 0.9%).

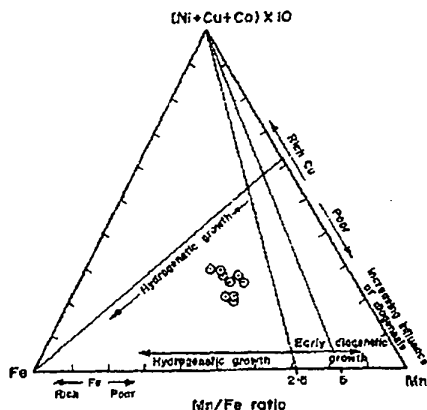


Fig. 2. Plot of the composition of the studied ferro-manganese crust samples in the triangular diagram of Bonatti et al. (1972) (Modified after Halbach et al., 1981).

Several transition metals incorporate in the Fe-Mn crusts as a result of adsorptive scavenging by precipitating Fe-Mn oxyhydroxide colloidal particles in the ambient sea water. Amongst several metals, bivalent Co oxidises to Co^{3+} on the surfaces of Mn-oxide colloidal particles and get enriched over the other minor metals in the crust (Aplin and Cronan, 1985), moreover, oxidised Co is more stable and insoluble in sea water (Halbach et al. 1983). Therefore, the seamounts bathing in waters of intense OMZ are capped by Fe-Mn crusts containing very high Mn (up to 40%) and Co (up to 2%) (Hein et al. 1987).

Though the Afanasiy-Nikitin seamount does not experience intense OMZ, an intermediate water OMZ ($O_2 < 2 \text{ mL/L}$) is expected due to high productivity in the equatorial zone. The Mn released to the water by oxidising organic matter might get enriched in this OMZ and reprecipitate as colloidal Mn-oxide to form the Fe-Mn crusts. Therefore, the Fe-Mn crusts on this seamount might have accreted in response to a weak OMZ enriching moderately high cobalt. The Al/Ti ratio in the samples are lower (< 3) than the crustal average (~ 16 , Taylor and McLennan, 1985) indicating considerable enrichment of Ti over Al. If the Al and Ti were strictly the structurally bound elements in detrital component of the Fe-Mn crust, then one would expect a nearly similar ratio as that of crustal ratio. Therefore, a significant enrichment of Ti over the Al might indicate the precipitation of Ti as Fe-Ti hydrate alongwith Mn-oxide (Koschinsky and Halbach, 1995). As the location of the Afanasiy-Nikitin seamount is far removed from the land mass, the detrital input to the area is only very fine, clay size particles, either as eolian dust or as suspended load reaching beyond the distal Bengal Fan. Most of the eolian dust comprising aluminosilicate was removed as residue while leaching. Where as, significant portion of the clay fraction might have been leached by 6N HCl, as evident by the presence of immobile Al and Ti in the leach solution. We assume that, the crustal ratio or pelagic clay ratio of Al/Ti (15-17) also should be obtained for the present Fe-Mn crust samples, if all the Ti is from crustal source; because, there is a significant enrichment of Ti over Al, we suggest an additional source of Ti, probably from the dissolved Ti pool in ambient water.

The Ca/Al ratio in the studied Fe-Mn crusts is much higher (2 to 15) than the crustal average of ~ 0.4 . The observed high calcium (~ 11 to 15%) in the samples ANC-1, 2, 5 and 8 may be attributed to the intermixing of coarse grained clastic materials such as the calcite and CFA with that of Fe-Mn oxide material. The samples (ANC-3, 6, 7 and 9) having low Ca ($< 5\%$) exhibit higher Mn and Fe concentration with enrichment of Co (up to 0.9%) indicating the carbonate fraction (as either CFA or calcite) dilute the oxide material and cobalt enrichment.

The interelement relationships in the samples are given in Table 2. The Co, Zn and V exhibit a strong sympathetic association with both Mn and Fe ($r > 0.7$) suggesting that these transition metals occur as Mn-Fe oxide forming group. The Ti association with Mn and Fe is moderately sympathetic ($r > 0.5$), supporting our suggestion of decoupling Ti from detrital source and coupling it with Mn-Fe oxide precipitation. The elements Al and Ba remain independent without exhibiting significant relationship with any of the metals analysed. However, antithetic relationship of Al and Ba with most of the oxide group elements might indicate their diluting effect on the oxide fraction in the Fe-Mn crust. Similarly the Ca which is bound to carbonate or carbonate-apatite exhibits considerable negative association with oxide group elements as expected. The intriguing negative relationship of Ni and Cu with Mn, Fe, Co, Zn and V, and their mutual strong positive relationship ($r > 0.8$) might be due to preferentially increased up-take of Co by the precipitating Mn-Fe oxyhydroxide. These relationships are brought out clearly in the scatter plots (Fig. 3). The chemical variation and interelemental associations though not aid to assess the actual fractionation of elements between various carrier phases, they certainly help in understanding the basic process involved and source of metals for the accretion of studied seamount Fe-Mn crust samples.

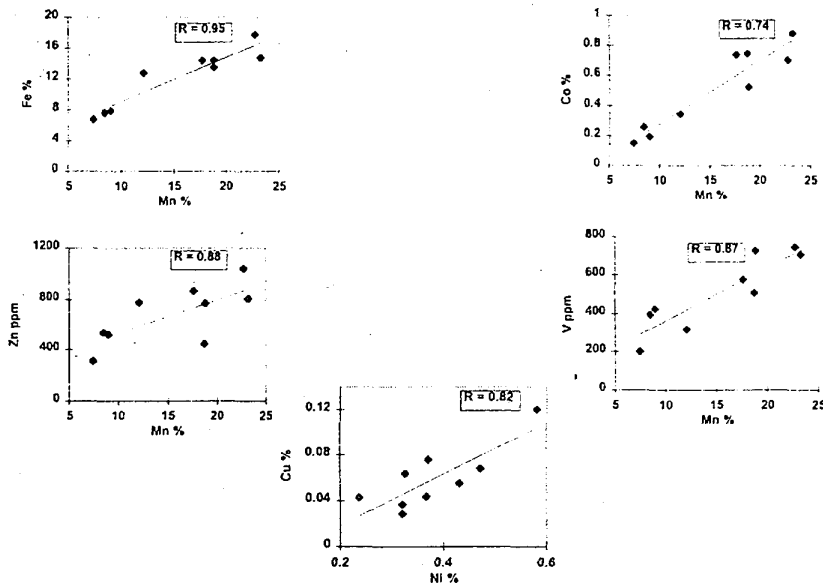


Fig. 3. The X-Y scatter plots exhibiting significant linear relationships for various elements analysed.

Table 1. Results of elemental chemical analysis carried out on the dredged samples from the Afanasiy-Nikitin seamount.

Sample	Al %	Fe %	Mn %	Ca %	Ti %	Co %	Ni %	Cu *	V *	Ba *	Sr *	Zn *	Mn/Fe
ANC-1	0.85	7.86	8.99	14.32	0.52	0.19	0.24	423	423	1052	1578	521	1.14
ANC-2	0.62	7.53	8.47	14.82	0.27	0.26	0.32	285	391	1374	1512	539	1.13
ANC-3	0.68	13.51	17.78	1.89	0.99	0.74	0.47	682	509	1215	1149	447	1.39
ANC-4	0.29	12.80	12.08	3.82	0.36	0.34	0.58	1198	314	1489	542	773	0.94
ANC-5	0.31	6.75	7.41	11.18	0.29	0.15	0.37	754	198	3593	1054	314	1.10
ANC-6	1.31	14.39	17.65	4.45	0.79	0.74	0.32	366	578	1002	1341	861	1.23
ANC-7	0.53	17.74	22.75	2.66	0.82	0.70	0.37	437	745	1117	1612	1040	1.28
ANC-8	0.61	14.37	18.83	11.59	0.78	0.52	0.33	637	724	1600	1951	768	1.31
ANC-9	0.39	14.84	23.27	3.29	0.88	0.88	0.43	544	706	1403	1709	802	1.57
Average	0.62	12.20	15.36	7.57	0.63	0.50	0.38	592	510	1538	1383	674	1.23

* Values are in ppm.

Table 2. Correlation matrix for all the samples analysed.

	Al	Fe	Mn	Ti	Ca	Ba	Sr	Cu	Ni	Co	Zn	V
Al	1.000											
Fe	0.059	1.000										
Mn	0.047	0.946	1.000									
Ti	0.323	0.506	0.606	1.000								
Ca	0.043	-0.543	-0.488	-0.640	1.000							
Ba	-0.519	-0.408	-0.368	-0.503	0.276	1.000						
Sr	0.265	0.304	0.509	0.425	0.306	-0.287	1.000					
Cu	-0.596	-0.017	-0.183	-0.213	-0.318	0.346	-0.730	1.000				
Ni	-0.553	0.139	0.019	0.052	-0.672	0.077	-0.699	0.815	1.000			
Co	0.236	0.649	0.736	0.901	-0.788	-0.493	0.293	-0.175	0.244	1.000		
Zn	0.164	0.966	0.880	0.446	-0.503	-0.577	0.274	-0.103	0.098	0.603	1.000	
V	0.245	0.774	0.868	0.816	-0.385	-0.582	0.724	-0.398	-0.163	0.793	0.743	1.000

RESOURCE POTENTIAL

The cobalt enrichment in the studied crust samples is upto 4 times higher compared to the deepsea ferromanganese oxides and crusts (Cronan, 1977, Glasby et al., 1986 and Valsangkar and Khadge, 1989). The high cobalt content in these Mn-Fe crusts may suggest their potential as future cobalt resource. There have been no reports of economically viable land deposits of cobalt in India. Therefore, seamount cobalt rich Mn-Fe crusts may prove to be important. We estimate the probable cobalt resource on Afanasiy-Nikitin seamount based on several assumptions as:

- a) the formation of cobalt rich crust is nearly uniform over the seamount with an average cobalt content of 0.5%;
- b) a minimum of 10% area of the seamount lying above the CCD is covered with Fe-Mn crusts;
- c) a minimum average crust thickness of 2 cm over the 10% area;
- d) the geometry of the seamount is near to a cone; and,
- e) the inter-crust chemical variation is within the presently reported ranges.

These assumptions were of necessity because the present study is based only on one sampling operation. Therefore, the following resource estimate is with high degree of uncertainty.

Thus obtained total quantity of cobalt rich Mn-Fe crusts is around 180 million tonnes holding about 0.9 million tonnes of cobalt metal within, and spread over an area of about 5,000 km² on the Afanasiy-Nikitin seamount. These guesimates need confirmation by additional sampling and detailed exploration.

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REFERENCES

- APLIN, A.C. and CRONAN, D.S. (1985). Ferromanganese oxide deposits from Central Pacific Ocean. I: Encrustations from the Line Island Archipelago. *Geochim. Cosmochim. Acta.*, v. 49, pp.427-436.
- BANAKAR, V.K. and BOROLE, D.V. (1991). Depth profiles of ²³⁰Th_{excess}, transition metals and mineralogy of ferromanganese crusts of the Central Indian Basin and implications for palaeoceanographic influence on crust genesis. *Chem. Geol. (Isot. Geosci. Sect.)*, v.94, pp.33-44.
- BANAKAR, V.K., PATTAN, J.N. and MUDHOLKAR, A.V. (1997). Palaeoceanographic conditions during the formation of a ferromanganese crust from the Afanasiy-Nikitin seamount, North Central Indian Ocean: geochemical evidence, *Marine Geology*, v.136, pp.299-315.
- BONATTI, E., KRAEMER, T. and RYDELL, H. (1972). Classification and genesis of submarine iron-manganese deposits. In: D.R. Horn (editor), *Ferromanganese Deposits on the Ocean Floor*. Nat. Sci. Found., Washington, D.C., pp.149-166.
- CRONAN, D.S. (1977). Deep-Sea nodules. In: Glasby (Editor), *Marine Manganese Deposits*. Elsevier, Amsterdam, pp. 11-44.
- DE CARLO, E.H. (1991). Palaeoceanographic implications of rare earth element variability within a Fe-Mn crust from the Central Pacific ocean. *Mar. Geol.*, v.98, pp.449-467.

- EISENHAEUER, A., GOEN, K., PERNICKA, E. and MANGINI, A. (1992). Climatic influence on the growth rates of the Mn-crusts during the late Quaternary. *Earth Planet. Sci. Lett.*, v.109, pp.25-36.
- FRIEDRICH, G. and WEICHOWSKI, A.S. (1980). Mineralogy and chemistry of a ferromanganese crust from a deep sea hill, central Pacific. *Mar. Geol.*, v.37, pp.71-90.
- GLASBY, G.P. (1973). Manganese deposits from the SW Pacific. Hawaii Inst. Geophys., Honolulu, Hawaii, Rep. HIG-72-23, pp.59-82.
- GLASBY, G.P., N.F. EXON and M.A. MEYLAN. 1986. Manganese nodules in the S W Pacific. In *Sedimentation and mineral deposits in the southwestern Pacific Ocean*, D.S. Cronan, ed. Florida, Academic, pp. 237-262.
- HALBACH, P., SCHERHAG, C., HEBISCH, O. and MARCHIG, V. (1981). Geochemical and Mineralogical control of different genetic types of deep-sea nodules from Pacific Ocean. *Mineral. Deposita.*, v.16, pp.59-84.
- HALBACH, P., SEGL, M., PUTEANUS, D. and MANGINI, A. (1983). Relationship between Co-fluxes and growth rates in ferro-manganese deposits from the central Pacific seamount areas. *Nature.*, v.304, pp.716-719.
- HALBACH and MANHEIM. (1984). Potential of cobalt and other metals in ferromanganese crusts on seamounts of the Central Pacific Basin. *Marine Mining.*, v.4, pp.319-336.
- HEIN, J.R., MORGENSON, L.A., CLAGUE, D.A. and KOSKI, R.A. SCHULZ. (1987). Cobalt rich ferromanganese crusts from the exclusive economic zone of the United States and nodules from the oceanic Pacific. In David W. Scholl, Arthur Grantz and John G. Vedder (Editors), *Circum-Pacific Council for Energy and Mineral Resources, Earth Science Series, Volume 6*. Houston, Texas, U.S.A., pp. 753-771.
- HEIN, J.R., SCHULZ, M.S. and GEIN, L.M. (1992a). Central Pacific cobalt rich ferromanganese crusts: historical perspective and regional variability. In B.H. Keating and B.R. Bolton (Editors), *Geology and Offshore Mineral Resources of the Central Pacific Basin*, Circum-Pac. Counc. Energy Miner. Resour. (Earth. Sci. Ser., 15) Springer, New York., pp. 261-283.
- HEIN, J.R., BOHRSON, W.A., SCHULZ, M.S., NOBLE, M. and CLAGUE, D.A. (1992b). Variation in the fine scale composition of a central Pacific ferromanganese crust. *Paleoceanography.*, v.7, pp.63-77.
- KOSCHINSKY, A. and HALBACH, P. (1995). Sequential leaching of marine ferromanganese precipitates: Genetic implications. *Geochimica et Cosmochimica Acta*, v.59, pp.5113-5132.
- MANHEIM, F.T. (1986). Marine cobalt resources. *Science.*, v.232, pp. 600-608.
- PUTEANUS, D. and HALBACH, P. (1988). Correlation of Co-concentration and growth rates-a method for age determination of ferromanganese crusts. *Chem. Geol.*, v.69, pp.79-85.
- RUDENKO, M.V. (1994). Morphostructure of the Afanasiy-Nikitin seamount. *Oceanology.* v.35, pp.525-530.
- SCOTT, R.B., RONA, P.A., BUTTLER, M.W., SCOTT, M.R., KENNET, J.P., NALWALK, A.J., WARME, J.E. and MCCREVEY, J.A. (1972). Mn crusts from the Atlantis fracture zone. *Eos (Trans. Am. Geophys. Union)*, v.53(4), pp.529 (abstract).
- SEGL, M., MANGINI, A., BONANI, G., HOFMAN, H.J., NESSI, M., SUTER, M., WOLFI, W., FRIEDRICH, G., PLUGER, W.L., WIECHOWSKI, A. and BEER, J. (1984). ¹⁰Be dating of a manganese crust from central north Pacific and implication for ocean palaeo-circulation. *Nature*, v.309, pp.540-543.
- TAYLOR and MCLENAN (1985). *The continental crust: Composition and Evolution*, Blackwell Scientific, Oxford, pp. 15-16.
- USUI, A., NASHIMURA, A. and IIZASA, K. (1993). Submersible observations of manganese nodules and crust deposits on the Tenpo seamount, northwestern Pacific. *Mar. Geores. Geotech.*, v.11, pp.262-291.
- VALSANGKAR, A.B. and KHADGF, N.H. (1989). Size Analyses and Geochemistry of Ferromanganese Nodules from the Central Indian Ocean Basin. *Marine Mining.*, v.8, pp.325-347.